Solid-State NMR Studies of the Preparation of Si−Al−C−N Ceramics from Aluminum-Modified Polysilazanes and Polysilylcarbodiimides

Frank Berger,[†] Markus Weinmann,[‡] Fritz Aldinger,[‡] and Klaus Müller*,[†]

Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55,
D-70569 Stuttgart, Germany, and Max-Planck-Institut für Metallforschung and Institut für
Nichtmetallische Anorganische Materialien, Universität Stuttgart, Pulvermetallurgisches
Laboratorium, Heisenbergstr. 5, D-70569 Stuttgart, Germany

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Multinuclear (^{13}C, ^{29}Si, ^{27}Al, ^{1}H) solid-state NMR spectroscopy and EPR and FT IR experiments are employed to investigate the thermolysis of aluminum-modified poly(hydridovinylsilazane), $[Al(C_2H_4-SiHNH)_3]_n$, from which Si−Al−C−N ceramics can be formed. In addition, a comparative study is provided for different aluminum-modified polysilazanes and polysilylcarbodiimides in the amorphous state at 1400 °C. The investigation primarily aims at the structural characterization of the amorphous intermediates, where such spectroscopic techniques have demonstrated their particular suitability. It is shown that the transformation of the polymeric precursor to the (amorphous) preceramic network is completed at around 500 °C. At this temperature AlN domains, as well as Si−C−N clusters of mixed composition, are formed. Above this temperature a continuous transformation to the ceramic material takes place. In addition, above 700 °C a considerable amount of free carbon-centered radicals is detectable. Eventually, three main components are found for the amorphous ceramic at 1050 °C which remain up to 1400 °C: (i) amorphous (graphite-like) carbon, (ii) AlN domains (with tetrahedral, pentagonal, and octahedral coordinated aluminum atoms), and (iii) a Si−C−N matrix (SiC_xN_{4-x} units with $x = 0, 1, 2, 4$). It is worthwhile to note that even at such high thermolysis temperatures a considerable amount of hydrogen can be detected as well. Comparative solid-state NMR experiments also have been performed on the amorphous ceramics fired at 1400 °C, derived from polysilazanes and polysilylcarbodiimides that differ in their basic structure as well as Si/N and Al/N ratios. For all samples the same basic components could be assigned. The actual composition of the amorphous ceramic, however, differs which can be related to the basic structure of the precursor polymer. In summary, the present spectroscopic study demonstrates that the introduction of aluminum atoms in the ternary Si−C−N matrix shows new aspects in the field of precursor ceramics.

Introduction

Non-oxide ceramics, such as silicon nitride or silicon nitride/silicon carbide based composites, exhibit exceptional thermomechanical properties. They are known for their creep and corrosion resistance, high tensile strength and hardness, and suitability for high-temperature applications. These ceramics can be prepared by sintering silicon nitride and silicon carbide powders in the presence of suitable additives, such as Al_2O_3 and Y_2O_3,[1,2] where the latter, however, limit the applicability of these materials at elevated temperatures.[3] Recently, an alternative preparation route for ceramics has been proposed that appears to be very promising, as it does not require sintering aids.[4−8] The method is based on the thermolysis of suitable polymeric precursors and offers several advantages. Apart from the renunciation of sinter additives, the derived ceramics exhibit a much better homogeneity on the molecular level. In addition, a better flexibility in the design of ceramic tools can be achieved.

It is known that the polymer-to-ceramic conversion proceeds via amorphous intermediates, until at about 1000 °C an amorphous ceramic is formed. Upon further heating crystallization occurs, giving rise to thermodynamically stable phases beyond 1400 °C.[7] Previous studies have shown that the macroscopic properties of ternary Si−C−N ceramics are closely related to both the actual composition and structural formation on the

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* To whom correspondence should be addressed. Phone: ++ 49 (711) 685 4470. Fax: ++ 49 (711) 685 4467. E-mail: k.mueller@ipc.uni-stuttgart.de.

[†] Institut für Physikalische Chemie.

[‡] Max-Planck-Institut für Metallforschung and Institut für Nichtmetallische Anorganische Materialien.

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molecular level. The polymer-to-ceramic conversion route thus offers a further advantage, because the molecular structure and composition can be controlled by the choice of the preceramic polymers.

In this context it has been demonstrated that quaternary Si−B−C−N ceramics, derived from boron-modified polysilazanes, possess exceptional high-temperature stability, which by far overrides that reported for Si−C−N ceramics.[8−11] The thermal stability was explained with a special morphology of the materials which evolves during a post-thermolysis heat treatment and consists of nanocrystalline SiC and Si_3N_4 and an amorphous BNC_x phase. It was proven by spectroscopic methods and analytical TEM that the BNC_x phase is composed of graphitic carbon and h-BN. Because of their almost identical lattice parameters, graphite-like structures were considered to be dissolved in h-BN, leading to a decrease of its activity. It was supposed that for this reason the thermodynamically expected decomposition of Si−N units due to a carbothermal reduction is retarded.

It is therefore of general interest to synthesize Si−Al−C−N ceramics in order to investigate the influence of the substitution of boron with its higher homologue aluminum on the thermal properties of the derived materials. In contrast to h-BN, AlN forms a Wurzite type lattice, which, because of very different lattice parameters, cannot dissolve graphite. Consequently, very different thermal stability and phase evolution are expected.

However, unlike the situation in Si−C−N and Si−B−C−N ceramics, so far only little is known about the structural evolution during the preparation of such quaternary Si−Al−C−N systems.[12−14] As mentioned earlier, the preparation of such ceramics involves amorphous intermediates, which rules out the application of conventional techniques for structure determination. Here, solid-state NMR spectroscopy has proven to be a powerful technique that is also applicable for the characterization of even amorphous systems.[15−17] NMR spectroscopy can thus be used to probe the local environment (short-range order up to a few Å) around selected nuclei, whose magnetic properties are affected by the local electronic environment as well as molecular interactions with nuclei in the next neighborhood. NMR spectroscopy is of particular attraction for the aforementioned ternary and quaternary ceramic systems, as these materials (including the precursor polymers) contain various NMR-active nuclei, such as ^{13}C, ^{29}Si, ^{1}H, or ^{27}Al, which can be studied without any further isotopic enrichment.[17−28]

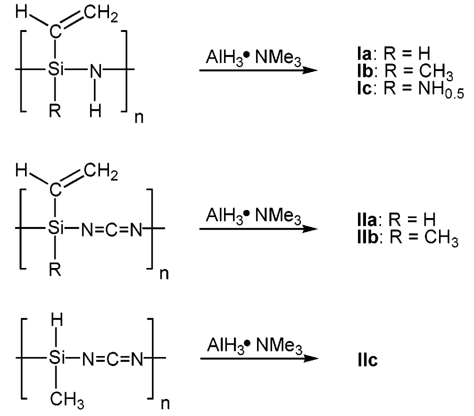

Figure 1. Molecular structures of polysilazanes and polysilylcarbodiimides that were reacted with $AlH_3{\cdot}NMe_3$.

In the present contribution solid-state NMR techniques are applied to determine structural changes during the preparation of quaternary Si−Al−C−N ceramics by thermolysis of hydroaluminated poly(hydridovinylsilazane) with Si/N and Al/N ratios of 1:1 and 1:3, respectively. In addition, solid-state NMR techniques are used to examine the amorphous state of different hydroaluminated polysilazanes and polysilylcarbodiimides fired at 1400 °C (Si/N and Al/N ratios of 1:2 and 1:6, respectively) and variable Si/C ratios. The basic structures of the various polymeric precursors studied here are given in Figure 1. The NMR studies are completed by EPR and FT IR experiments which provide additional structural information for these systems.

Experimental Section

Materials. *Synthesis.* The aluminum-modified poly(vinylsilazanes), $\{Al[C_2H_4{-}Si(R)NH]_3\}_n$ [**Ia**, R = H; **Ib**, R = CH_3; **Ic**, R = $NH_{0.5}$] were prepared according to a procedure described for boron-modified poly(vinylsilazanes).[10] Precursor synthesis was performed by ammonolysis of chlorovinylsilanes $(H_2C{=}CH)Si(R)Cl_2$ (R = H, CH_3, Cl) in tetrahydrofurane, followed by treatment with trimethylamine alane, $AlH_3{\cdot}NMe_3$, in toluene solution. Aluminum-modified polysilylcarbodiimides $\{Al[(R^1)Si(R^2)NCN]_3\}_n$ [**IIa**, $R^1 = C_2H_4$, $R^2 = H$; **IIb**, $R^1 = C_2H_4$, $R^2 = CH_3$; **IIc**, $R^1 = CH_3$, $R^2 = H$] were prepared by the reaction of methyldichlorosilane or vinyl-substituted chlorosilanes $(H_2C{=}CH)Si(R^2)Cl_2$ (R^2 = H, CH_3) with cyanamide in the presence of pyridine in tetrahydrofurane and subsequent treatment with $AlH_3{\cdot}NMe_3$ in toluene solution.

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Table 1. Experimentally Determined Relative Areas and Peak-to-Peak Distances from the EPR Investigations of Sample Poly(hydridovinylsilazane) Ia

temperature (°C)	relative area	peak-to-peak distance (G)
700	127	9.09
800	144	7.03
1050	1000	0.88
1400	45	1.08

Thermolysis. The samples for NMR, EPR, and FT IR experiments − all measurements were performed at room temperature − were prepared by thermolysis of 1−2 g of the polymeric precursor in a quartz or aluminum oxide tube under a steady flow (50 mL/min) of purified argon in a programmable tube furnace (Gero HTRV 40-250). Starting at room temperature, the following heating program was used: (i) an initial 1 K/min ramp to the desired thermolysis temperature, (ii) a 2 h hold at the thermolysis temperature, and (iii) sample cooling with a rate of 2 K/min, during which the sample was allowed to cool to room temperature.

NMR Measurements. NMR experiments on the samples were carried out on a Bruker MSL 300 spectrometer operating at a static magnetic field of 7.05 T (^{1}H frequency 300.13 MHz) using a 4-mm magic angle spinning (MAS) probe. ^{13}C, ^{27}Al, and ^{29}Si NMR experiments were done at 75.47, 78.2, and 59.6 MHz, respectively. High-speed ^{1}H MAS experiments were carried out on a Bruker DSX 400 spectrometer (magnetic field strength 9.4 T, ^{1}H NMR frequency 399.94 MHz) using a 2.5-mm MAS probe (sample rotation frequency 34.5 kHz).

^{13}C and ^{29}Si NMR spectra were recorded under MAS conditions (sample rotation frequency 5 kHz) with either single-pulse or cross-polarization (CP) excitation, using $\pi/2$ pulse widths of 4.0 μs. Recycle delays up to 2 min were used during single-pulse excitation experiments. During the CP experiments spin lock fields of 62.5 kHz and contact times of 3 ms were employed at recycle delays of 6 s. ^{29}Si and ^{13}C chemical shifts were determined relative to external standards Q_8M_8, the trimethylsilylester of octameric silicate, and adamantane, respectively. These values were then expressed relative to TMS ($\delta = 0$ ppm). Inversion recovery cross-polarization (IRCP) measurements[29,30] were done using a modified IRCP sequence with simultaneous phase inversion, as described in ref 31.

^{1}H MAS NMR spectra were recorded at sample spinning rates of 12 kHz and 34.5 kHz and single-pulse excitation ($\pi/2$ pulse width 4.0 μs and 1.6 μs) with a recycle delay up to 10 s. ^{1}H chemical shifts were directly referenced to TMS as external standard. ^{27}Al MAS NMR spectra were recorded at a sample spinning rate of 12 kHz and single-pulse excitation using $\pi/5$ pulses (pulse length 1.2 μs) with a recycle delay of 1 s. ^{27}Al chemical shifts were directly referenced to $Al(H_2O)_6^{3+}$ ($\delta = 0$ ppm) as external standard.

EPR Measurements. EPR experiments were performed on a Bruker EMX spectrometer operating at 9.5 GHz (X-band). All measurements were done at room temperature. The experimental peak-to-peak distances and relative signal intensities, shown in Table 1, were derived with the aid of the Grams/32 software package (Galactic, Salem, NH). All peak intensities are given relative to the intensity of the sample referring to an annealing temperature of 1050 °C, which was set to 1000 (estimated error 7%).

FT IR Measurements. FT IR spectra were recorded at room temperature with a Bruker IFS 66 FT IR spectrometer using KBr pellets. All experiments were performed under a slight nitrogen flow.

Results and Discussion

In the following we report on multinuclear solid-state NMR investigations, as well as complementary EPR and FT IR studies, of the thermolysis intermediates between room temperature and 1400 °C from aluminum-modified poly(hydridosilazane), with idealized structure $[Al(C_2H_4\text{-}SiHNH)_3]_n$ (**Ia**). In addition, solid-state NMR results are provided for the amorphous ceramics (at 1400 °C) from two aluminum-modified poly(vinylsilazanes) (**Ib** and **Ic**) and three aluminum-modified polysilylcarbodiimides (**IIa** to **IIc**), with the structures of the precursor polymers as given in Figure 1. Their Si/N ratios are 1:1 (polysilazanes **Ia**, **Ib**), 1:1.5 (polysilazanes **Ic**), and 1:2 (polysilylcarbodiimides), whereas the actual Si/C ratio varies with the sample. All spectroscopic studies were performed at room temperature. The samples referring to the intermediate stages of the thermolysis were subjected to a particular temperature program to ensure transfer of the actual intermediate structure to room temperature (see Experimental Section). This method for studying intermediate structures during precursor thermolysis at room temperature is well established. For instance, it has been shown previously by thermogravimetry and simultaneous mass spectroscopy of the volatile thermolysis products that the structural changes observed in the ^{29}Si NMR spectra of the corresponding intermediates—again obtained via a similar heating and quenching procedure as in the present work—can be directly related to the formation and release of the (in-situ) detected gaseous products.[32]

For ceramic precursors examined here a series of NMR active nuclei—^{13}C, ^{29}Si, ^{27}Al, and ^{1}H—is accessible that was used to probe the local order during the thermolysis process. In the present work two methods have been employed for assigning the individual NMR signals: (i) chemical shift values from suitable reference compounds, and (ii) ^{13}C spectral editing techniques, i.e., IRCP measurements, from which various CH_x ($x = 0$ to 3) segments[29−31] can be distinguished.

Representative multinuclear solid-state NMR, EPR, and FT IR spectra of Al-modified poly(hydridovinylsilazane) (**Ia**) are given in Figures 2−9. They cover the temperature range from 25 to 1400 °C. In addition, selected NMR spectra of ceramics derived from Al-modified polysilazanes **Ib** and **Ic** and polysilylcarbodiimides **IIa** to **IIc** are given in Figures 10−13.

From ^{1}H NMR measurements it was concluded that even after heating the polymers to 1400 °C a substantial amount of hydrogen could be detected (compare Figure 6). This finite proton content is a prerequisite for performing ^{13}C and ^{29}Si NMR experiments using the cross-polarization (CP) technique, which results in a considerable reduction of the data acquisition times as compared to single-pulse excitation.

Thermolysis of Al-Modified Poly(hydridovinylsilazane) Ia. Experimental ^{13}C NMR spectra are given in Figure 2. The spectrum of the polymeric precursor (bottom) exhibits a set of signals in the aliphatic region at 11, 21, and 31 ppm along with two overlapping signals at 133 and 141 ppm. The signal at 31 ppm in the aliphatic region can be attributed to the ***C***H unit, whereas ***C***H_2 and ***C***H_3 groups are responsible for the resonances at 21 and 11 ppm, respectively. The formation of these structural components can be explained

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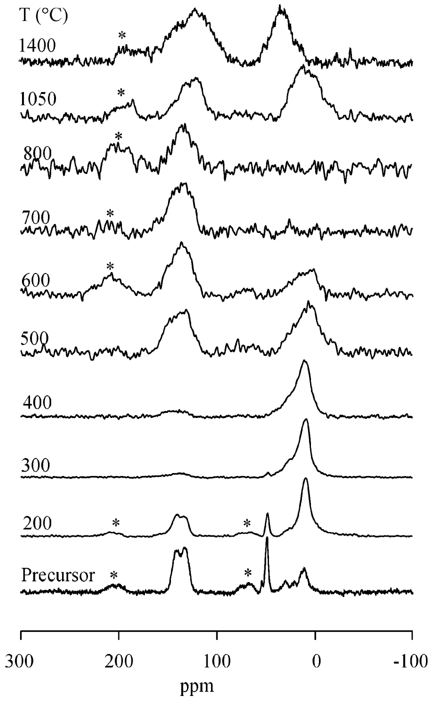
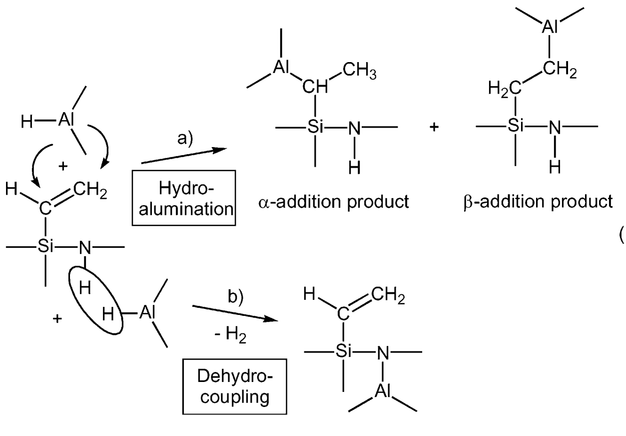


Figure 2. Experimental ^{13}C NMR spectra of aluminum-modified poly(vinylsilazane) **Ia** at various stages of the thermolysis process. Asterisks indicate spinning sidebands. All spectra, except at 1400 °C, were recorded with cross-polarization.

by the addition of aluminum to both the α- and β-vinyl carbons of the polymeric precursor,[33,34] as shown in eq 1a.



(1)

The ^{13}C NMR signals at 133 and 141 ppm refer to remaining olefinic groups that did not react during the hydroalumination step. This is a consequence of the strong affinity of aluminum to nitrogen which results in a dehydrocoupling reaction between AlH$_3$ and the NH groups in the polysilazane chains, as shown in eq 1b. In addition, a resonance signal is visible at 49 ppm. It can be attributed to the methyl groups of trimethylamine, which most probably is coordinated to alkylaluminum units that form upon hydroalumination (eq 1a).

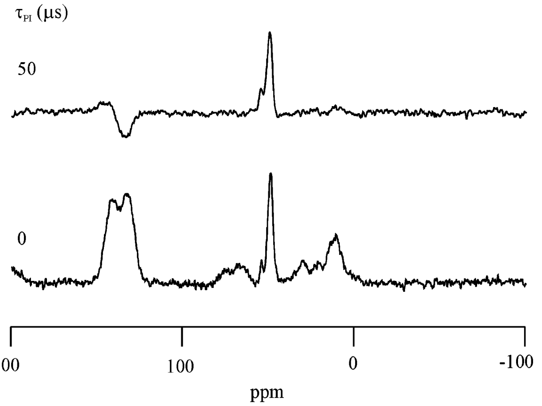


Figure 3. Experimental ^{13}C IRCP spectra of aluminum-modified poly(vinylsilazane) **Ia** from the polymeric precursor. The experimental conditions are given in the Experimental Section with $\tau_{\mathrm{CP}} = 1500\ \mu$s and τ_{PI} as given in the figure.

The above assignment is supported by spectral editing experiments,[29−31] namely IRCP experiments (see Figure 3), which clearly prove that the overlapping signals at 133 and 141 ppm are a superposition of $=\boldsymbol{C}\mathrm{H}_2$ and $=\boldsymbol{C}\mathrm{H}$ signals. If the IRCP experiment is performed with values of $\tau_{\mathrm{CP}} = 1500\ \mu$s and $\tau_{\mathrm{PI}} = 50\ \mu$s (see Figure 3), signals of negative intensity can be attributed to $=\boldsymbol{C}\mathrm{H}_2$ groups, whereas the signal for the $=\boldsymbol{C}\mathrm{H}$ group vanishes. Theoretically, the $=\boldsymbol{C}\mathrm{H}_2$ signal intensity is expected to be −33% of its original value from the CP experiment.[31,35] On this basis, the signals at 141 and 133 ppm in fact can be attributed to $=\boldsymbol{C}\mathrm{H}$ and $=\boldsymbol{C}\mathrm{H}_2$ groups, respectively. The second ^{13}C NMR signal due to aliphatic CH$_2$ groups at 21 ppm is inverted as well. However, this spectral component hardly can be identified in the IRCP spectrum because the relative peak intensity of this structural unit is also very weak in the normal CP/MAS spectrum. It should be noted that a quantitative discussion of the IRCP experiments requires the analysis of the complete build-up curves.[29−31,36] Nevertheless, a qualitative discussion of the spectral assignment is possible on the basis of the selected IRCP spectrum, as done in the present case.

In contrast, for the reaction of poly(vinylsilazane) with trialkylamine boranes, BH$_3$·NR$_3$ (R = Me, Et), a selective hydroboration of the vinyl units was reported.[37] The differences in the selectivity of the reaction of L·BH$_3$ and L·AlH$_3$ with poly(hydridovinylsilazanes)[37] can be traced back to the different reactivity of AlH$_3$ and BH$_3$ toward C=C groups and N−H functions which can be explained by their different Lewis base acidity.[38] Because aluminum organyles possess a distinguished Lewis acidity, reactions of alanes with vinylated silazanes are therefore not restricted to addition to the olefinic groups. Rather, dehydrocoupling with formation of Al−N units is favored.

Upon heating to 200 °C, the intensity of the olefinic carbon atoms reduces significantly, whereas that of aliphatic carbons increases. This result points to a thermally induced polymerization of the silicon-bonded vinyl groups and their transformation into aliphatic hydrocarbons. A quite similar behavior has been registered for the polymer-to-ceramic transformation of poly-

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(methylvinylsilazane).[24] At the same time, the signal due to trimethylamine at 49 ppm is still visible, however, with reduced intensity. Obviously, trimethylamine is partially disintegrated via the formation and release of methane.

Further heating to 300 °C results in the disappearance of the signals at 133 and 141 ppm, whereas those in the high field region, generated by CH_3, CH_2, and CH groups, further increase in intensity. This suggests that the transformation of $HC{=}CH_2$ units to saturated alkyl groups is completed at this temperature. Above 400 °C, the signals broaden considerably and the signal/noise ratio is reduced. In addition, a broad spectral component of low intensity at around 138 ppm is visible, the intensity of which increases further upon heating to 500 °C, and which—according to previous studies[25,27,37]—can be assigned to amorphous (graphite-like) carbon. Obviously, the sample heated to 500 °C reflects the completion of thermally induced cross-linking and the onset of full transformation of the preceramic network into the amorphous ceramic.

At higher thermolysis temperatures of 700 and 800 °C the signals in the aliphatic region are found to vanish completely. This observation is most probably a consequence of the generation of a considerable amount of paramagnetic centers in the environment of sp^3 carbon atoms, as also discussed earlier for Si−B−C−N systems.[39] We take up this point at the end of this discussion. In the amorphous ceramic at 1050 and 1400 °C carbon is found to exist again in two main fractions, namely as graphite-like domains, given by the broad resonance centered at about 138 ppm, as well as $\boldsymbol{C}H_xSi_{4-x}$ units ($x = 0$, 1, or 2) within a Si−C−N matrix, reflected by the broad high field component below 50 ppm.[37] This result is similar to that obtained for the corresponding boron-modified polysilazane, in which the amorphous ceramic at 1050 °C exhibited the same main components. In summary, thermolysis of Al-modified polysilazanes can be divided into two steps: (i) cross-linking by thermally induced olefin polymerization which proceeds up to 300 °C, and (ii) dehydrogenation of aliphatic hydrocarbons into graphite-like and SiC motifs.

The ^{29}Si NMR spectrum of the polymeric precursor, shown in Figure 4, exhibits a broad signal centered at −28 ppm. It can be attributed to the $\boldsymbol{Si}HC(sp^2)N_2$ group, because the chemical shift corresponds to that of the starting compound $[(H_2C{=}CH)SiH{-}NH]_n$. The signal possesses a weak shoulder around −18 ppm which is a typical value for $\boldsymbol{Si}HC(sp^3)N_2$ units,[37,40] as they are generated in the hydroalumination of poly(vinylsilazane). This observation confirms the proposed possible reaction pathways (1a) and (1b), and the suggested polymer structures made on the basis of ^{13}C NMR spectroscopy.

Heating to 200 °C inverts the relative signal intensities of the ^{29}Si NMR resonances. The resonance at −18 ppm increases in intensity, whereas the relative intensity of the high field signal decreases. This effect is a consequence of the polymerization of the olefinic groups as stated above. Upon heating to 300 °C the resonance of the $\boldsymbol{Si}HC(sp^2)N_2$ units almost disappears, whereas a new spectral component is found at ∼0 ppm, which can be attributed to $\boldsymbol{Si}C_2N_2$ groups.[37] This can be explained by a rearrangement in the coordination sphere of the silicon atoms. That is, new Si−C bonds form at the expense of Si−H structures, whereby hydrogen is released from the sample. The additional low-field spectral component in the positive ppm range stems from $\boldsymbol{Si}C_3N$ units, which exist between 300 and 400 °C as a result of reaction scheme (2).

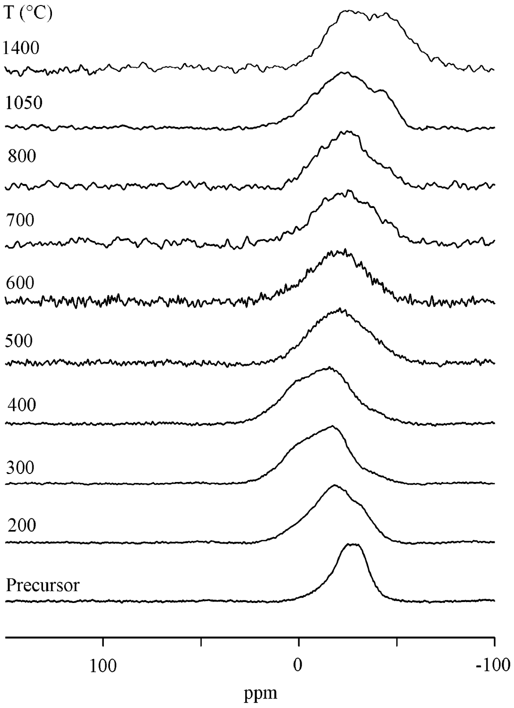
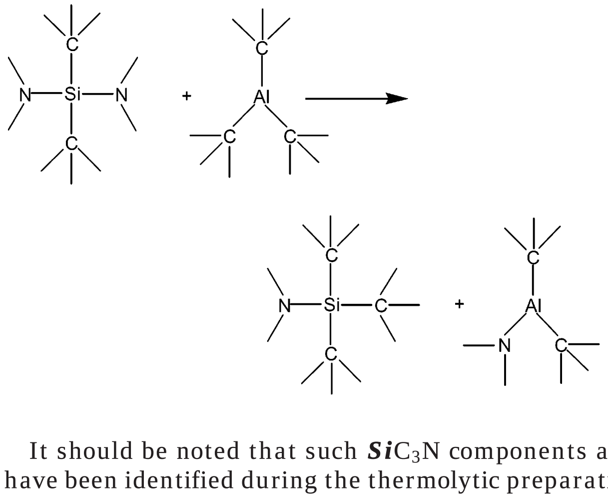


Figure 4. Experimental ^{29}Si NMR spectra of aluminum-modified poly(vinylsilazane) **Ia** at various stages of the thermolysis process. All spectra, except at 1050 and 1400 °C, were recorded with cross-polarization.



(2)

It should be noted that such $\boldsymbol{Si}C_3N$ components also have been identified during the thermolytic preparation of Si−B−C−N ceramics.[41,42]

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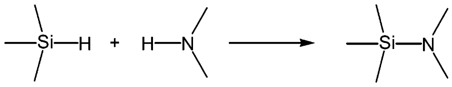
Further heating does not cause significant changes in the appearance of the spectrum, which still suggests the presence of $\boldsymbol{Si}\mathrm{HC(sp^3)N_2}$ units besides $\boldsymbol{Si}\mathrm{C_2N_2}$ and $\mathrm{SiC_3N}$ structures. Heating the sample to 500 °C causes a shift of the signal maximum toward higher field, resulting in a more symmetric line shape. The observed signal (maximum at −23 ppm) is typical for a superposition of resonances of mixed Si environments, i.e., $\boldsymbol{Si}\mathrm{C_2N_2}$ and $\boldsymbol{Si}\mathrm{CN_3}$. The latter is formed during dehydrocoupling reactions involving Si−H and H−N groups.


(3)

This conclusion is in agreement with the findings for the corresponding boron-modified poly(hydridosilazane),[37] in which $\boldsymbol{Si}\mathrm{C(sp^3)N_3}$ groups were also formed in this temperature range. The observed, significantly broadened ^{29}Si NMR spectra, which are visible over the whole temperature range, are a consequence of the heterogeneity in the local chemical environment of the individual silicon nuclei. Between 600 and 800 °C the ^{29}Si NMR spectra remain basically unchanged. After heating to 1050 °C a new spectral component arises at −43 ppm, due to the formation of $\boldsymbol{Si}\mathrm{N_4}$ units.[37,43,44] The presence of $\boldsymbol{Si}\mathrm{N_4}$ motifs indicates the onset of demixing and subsequent phase separation which is accompanied by the formation of $\mathrm{SiC_4}$ units: $4\ \mathrm{SiC}_x\mathrm{N}_{4-x} \rightarrow x\mathrm{SiC_4} + (4-x)\mathrm{SiN_4}$. The segregation of further phases such as graphite-like structures or AlN is not directly affected by this demixing. The experimental ^{29}Si NMR spectrum at this temperature thus can be considered as a superposition of NMR lines due to four main structural components, namely $\mathrm{SiC}_x\mathrm{N}_{4-x}$ units with $x = 0, 1, 2,$ or 4, in accordance with the aforementioned ^{13}C NMR data. It is important to note that the present Si−Al−C−N ceramics are completely amorphous over the whole temperature range examined here. From the preliminary X-ray data of the present systems there is no evidence for the crystalline aggregates of SiC or $\mathrm{Si_3N_4}$. In addition, it should be mentioned that for the corresponding boron-modified polysilazane[37] the same Si−C−N matrix has been reported at such elevated temperatures. In general, the formation of carbon-enriched Si−C−N domains, exhibiting a homogeneous element distribution, is considered to be of great importance for the high-temperature stability of ceramic materials.[7]

In Figure 5 experimental ^{27}Al NMR spectra are shown. They refer to the excitation of the central $m_I = +1/2 \rightarrow -1/2$ transition. The experimental ^{27}Al NMR spectrum of the polymeric precursor and the thermolysis intermediates below 700 °C are found to be broad and featureless due to the mixed local chemical environment of the aluminum nuclei. According to the chemical shift range that is covered, the aluminum nuclei possess 4-, 5-, and 6-fold coordination. For example, ^{27}Al resonance signals of $\mathrm{AlN_4}$, $\mathrm{AlN_5}$, and $\mathrm{AlN_6}$ were reported to appear at 100, 50, and 0 ppm, respectively.[12,45,46] As mentioned earlier, the strong affinity of aluminum favors dehydrocoupling reactions along with Al−N formation. Nevertheless, at least at low temperatures ($T \leq 200$ °C) a small amount of aluminum atoms bonded to carbon should also exist, as deduced from the ^{13}C NMR spectra (see above). Such structural components should appear as a resonance beyond 150 ppm[46] which, however, cannot be identified unequivocally in the experimental ^{27}Al NMR spectra. This can be related to the fact that Al atoms in $\mathrm{N_2AlR}$, $\mathrm{NAlR_2}$, and $\mathrm{AlR_3}$ units—obtained by at least partial addition of $\mathrm{AlH_3}$ to olefinic groups of the polysilazane—are also coordinated by $\mathrm{NMe_3}$. The expected 4-fold coordinated Al nuclei are expected to resonate in the same chemical shift range as the aforementioned AlN_x segments ($x = 4-6$). Interestingly, the appearance of the ^{27}Al NMR spectra is very similar to, and almost independent of, the actual annealing temperature. The ^{27}Al NMR spectra of the amorphous ceramic at 1050 and 1400 °C exhibit a more pronounced structure. In fact, the signal maximum is found at 100 ppm, which can be assigned to $\mathrm{AlN_4}$ groups, i.e., aluminum in tetrahedral coordination.[12,45,46] In addition, spectral components of smaller amounts are visible in the upfield region which most probably belong to $\mathrm{AlN_5}$ and $\mathrm{AlN_6}$ units, centered at about 50 and 5 ppm.[12,45]

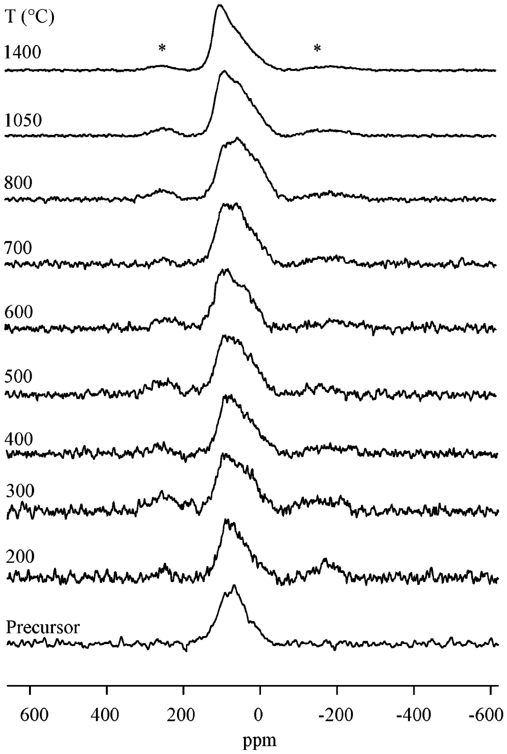


Figure 5. Experimental ^{27}Al NMR spectra of aluminum-modified poly(vinylsilazane) **Ia** at various stages of the thermolysis process. Asterisks indicate spinning sidebands.

Representative experimental ^{1}H NMR spectra of the thermolysis intermediates are given in Figure 6. In general, due to the strong ^{1}H−^{1}H dipolar couplings, only a poor resolution is found for the spectra detected with a sample spinning speed of 12 kHz. For the polymeric precursor at least two spectral components at 2.5 ppm and at 5.1 ppm can be distinguished. The former signal can be attributed to the aliphatic protons[47] and the

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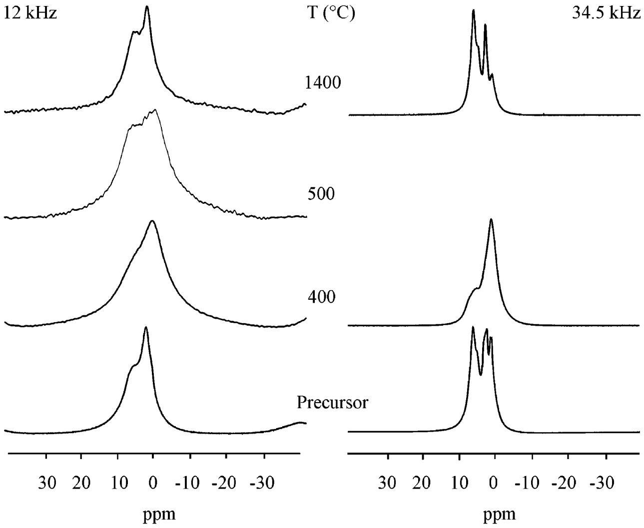

Figure 6. Selected experimental ^{1}H NMR spectra of aluminum-modified poly(vinylsilazane) **Ia** measured with different spinning speeds (left column 12 kHz; right column 34.5 kHz) at four different stages of the thermolysis process.

latter as a superposition from the remaining protons in the olefinic and Si−H groups.[25,47−49] Thermolysis gives rise to a further broadening of the ^{1}H NMR spectra, most probably due to the larger structural inhomogeneity and thus an increasing amorphous character of the sample. After heating to $T \geq 500$ °C two basic spectral components can be distinguished which stem from aliphatic (at about 1 ppm) as well as aromatic protons at 5−6 ppm in the vicinity of graphite-like carbon. Surprisingly, the signals sharpen after thermolysis at 1400 °C which is a consequence of the reduced proton content, i.e., reduction of homogeneous broadening.

A substantial improvement for the resolution of such ^{1}H NMR spectra can be achieved by high-speed MAS experiments at a spinning speed of 34.5 kHz, as also shown in Figure 6. Here, for the polymeric precursor, signals at 0.8, 1.0, 2.5, 5, and 6 ppm can be found. The signals at 0.8 and 1 ppm are attributed to aliphatic protons generated by hydroalumination of the vinyl units and to N−H groups, respectively, which constitute the polymer backbone. The resonance at 2.5 ppm most likely stems from $N-CH_3$ groups[47] in NMe_3, coordinated to Al atoms. The signals at 5.0 and 6.0 ppm originate from Si−H and $H_2C{=}CH$ protons which did not react during the hydroalumination step. For the intermediate thermolysis steps again a broadening of the NMR lines is registered and the spectral resolution decreases. For example, at 400 °C aliphatic protons (at 1 ppm) and protons from Si−H groups (at 5 ppm) can be distinguished. However, for the amorphous ceramic at 1400 °C again a well resolved spectrum is visible with signals at 1, 2.5, and 6 ppm. The latter signal again belongs to aromatic protons, whereas the former signals originate from aliphatic protons and protons in CSi_xH_{4-x} (x = 1−3) units,[49] respectively.

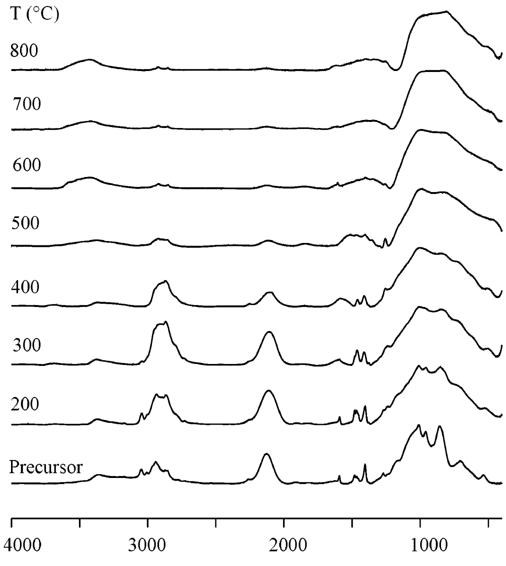

Figure 7. Experimental FT IR spectra of aluminum-modified poly(vinylsilazane) **Ia** at various stages of the thermolysis process.

The results from complementary FT IR measurements are shown in Figure 7. The spectrum of the precursor polymer again confirms the previous ^{13}C NMR result that during the hydroalumination of the vinyl group both α- and β-addition occurs, as given by the symmetric and asymmetric stretching bands of aliphatic units in the range between 2778 and 2942 cm^{-1}.[50,51] Additional vibration bands of the N−H (weak) and Si−H units are observed at 3363 and 2127 cm^{-1}, respectively. C−H stretching bands between 3008 and 3050 cm^{-1} in combination with weak absorption bands at 1593 cm^{-1} confirm the aforementioned presence of residual olefinic units. The signals between 1466 and 1488 cm^{-1} refer to asymmetric double stretching bands of methylene groups.

The intensity increase for the symmetric and asymmetric stretching bands of aliphatic units, observed for the intermediate at 200 °C, can be explained by the aforementioned cross-linking of the olefinic groups which is accompanied by the formation of saturated alkyl chains. For the thermolysis intermediates between 500 and 600 °C the IR vibration bands of the CH_x units (x = 1, 2, 3) have vanished almost completely, which again is an indication of the formation of an amorphous preceramic network at this temperature. Above 600 °C the vibration bands of the N−H and Si−H groups disappear, which is in line with the above-mentioned dehydrocoupling reaction between SiH and NH groups and the formation of Si−N bonds. The FT IR spectrum at 500 °C shows a new very broad band at 806 cm^{-1} ,[52] which can be assigned to the Al−N vibration band in AlN_4 units of the preceramic network. In the samples annealed at 600−800 °C only vibration bands of the AlN units at around 800−1000 cm^{-1} and a very broad absorption at 3400 cm^{-1} are visible. The latter stems

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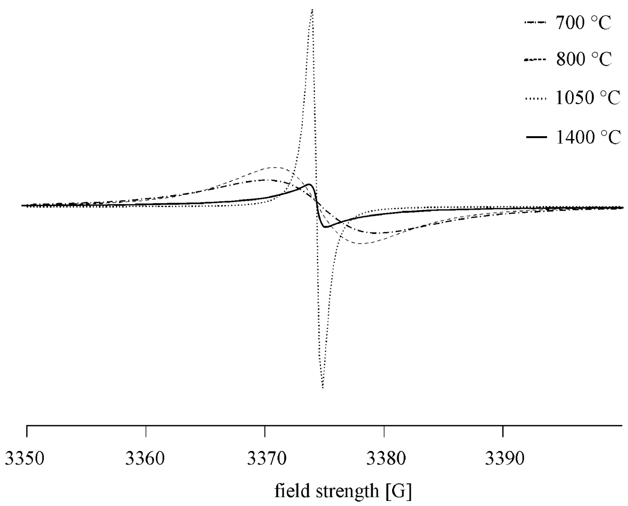

Figure 8. Experimental EPR spectra of aluminum-modified poly(vinylsilazane) **Ia** at various stages of the thermolysis process (700 to 1400 °C).

from either O−H vibration (Si−O−H, Al−O−H) or water which is adsorbed on the surface of the thermolyzed material during the IR sample preparation.

As mentioned earlier, at elevated thermolysis temperatures (700 and 800 °C) the aliphatic components are missing in the ^{13}C NMR spectra. A reduced ^{13}C NMR signal intensity in this temperature range has also been observed in NMR investigations on structurally related compounds.[37,39] One explanation of this phenomenon could be found in the presence of paramagnetic centers.[39] For this reason EPR spectra were recorded for the samples between 700 and 1400 °C, which are shown in Figure 8. On the basis of these spectra a localization of the electron spins on aluminum, nitrogen, and silicon nuclei can be excluded, because otherwise hyperfine lines (coupling with aluminum or nitrogen nuclei) or hyperfine satellites (coupling with silicon nuclei) are expected. The observed EPR signal therefore can be attributed to carbon-centered free radicals with a g-value of 2.006, which agrees with the reported value on Si−B−C−N systems.[39] Table 1 summarizes the derived experimental line widths (i.e., peak-to-peak distances) and relative signal intensities. As can be seen, there is a minimum line width for the intermediate at 1050 °C along with a maximum for the signal intensity. If the line width mainly is governed by an unresolved hyperfine coupling between the electron spins and the nuclear spins from remaining hydrogen, then the initial reduction of the line width temperature could be explained by a loss of hydrogen. In fact, this would be in agreement with the ^{1}H NMR data where a considerable decrease of the signal intensities upon sample heating is registered. Another possible explanation for the observed line width changes could be spin exchange effects on the basis of highly concentrated unpaired electrons. In the present case this second explanation appears to be more likely, as the smallest line width is accompanied by the maximum signal intensity. Thus, the present EPR data provide a consistent picture and can be understood on the basis of spin exchange effects. However, the missing ^{13}C NMR signals cannot be directly related to the absolute amount of radical centers, as derived from our present EPR experiments, because the highest radical concentration is found at 1050 °C where the aliphatic ^{13}C NMR signal reappears again.

At this stage it is worthwhile to note that paramagnetic centers are known to affect spin relaxation and cross-polarization efficiency. Former studies have shown that paramagnetic doping is accompanied by a reduction of both the proton spin−lattice relaxation time T_1 and the proton rotating frame spin−lattice relaxation time (^{1}H $T_{1\rho}$).[53,54] A shorter ^{1}H T_1 is advantageous because shorter recycle delays can be taken during the CP experiment, i.e., the overall acquisition time of the CP experiment is reduced. The cross-polarization efficiency directly depends on ^{1}H $T_{1\rho}$ as well as T_{CH}, the latter of which characterizes the time required for energy exchange between carbon and proton populations. To have an efficient cross-polarization process, T_{CH} should be considerably shorter than ^{1}H $T_{1\rho}$, which reflects the loss of proton polarization. Thus, it can be speculated whether the CP signal intensities in the ^{13}C NMR spectra at 700 °C and above reflect the actual amounts of the various structural components, as the protons in the vicinity of paramagnetic centers might exhibit considerably shorter ^{1}H $T_{1\rho}$ values along with a reduced cross-polarization efficiency to the neighboring carbons. Likewise, the reduced CP efficiency might provide an explanation for the missing ^{13}C NMR signals at 700 and 800 °C, although as mentioned earlier, an even higher radical concentration is found for the sample heated to 1050 °C, where the high-field signal components show up again.

Comparison of the Amorphous Ceramics at 1400 °C. Figures 9−12 show solid-state NMR spectra of the amorphous ceramic fired at 1400 °C from selected polysilazanes (**Ia** to **Ic)** and polysilylcarbodiimides (**IIa** to **IIc**). ^{13}C NMR spectra of the polysilazanes **Ia** to **Ic** are given in Figure 9. The appearance of two sets of resonance signals in the spectra of **Ia** and **Ib** are due to the presence of both aromatic carbon atoms and aliphatic CH_xSi_{4-x} units ($x = 0, 1, 2$).[25,27,37] This indicates that during thermolysis, materials with composition located in the four-phase equilibrium $AlN/Si_3N_4/SiC/C$ are formed. In contrast, thermolysis of nitrogen-rich precursor **Ic** results in a composition which is located in the three-phase equilibrium $AlN/Si_3N_4/C$, which is in accordance with the observation of only one broad resonance signal centered at around 130 ppm. Accordingly, the ^{29}Si NMR spectra of **Ia** and **Ib**, shown in the right column of Figure 9, possess a signal component centered at about −21 ppm due to a superposition of SiC_xN_{4-x} resonances ($x = 1, 2, 4$)[37,43,55,56]—dominated by ***Si***CN_3 and ***Si***C_4 units—along with a signal at about −50 ppm from ***Si***N_4 units. In contrast, the ^{13}C NMR spectrum of sample **Ic** implies that Si−C bonds are completely absent. This latter result for sample **Ic** is in full agreement with the respective ^{29}Si NMR spectrum which exhibits a single resonance centered at around −47 ppm due to ***Si***N_4 units,[44] reflecting the formation of Si_3N_4 units.

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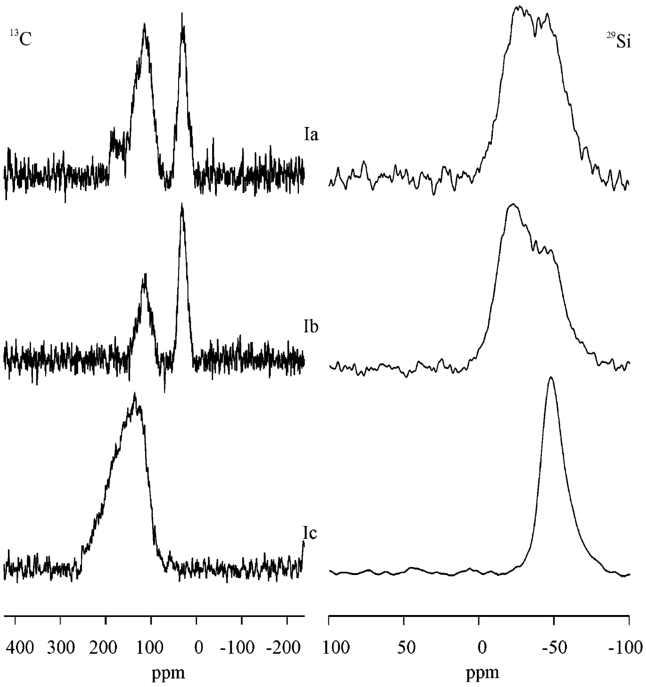

Figure 9. Experimental ^{13}C (left) and ^{29}Si NMR spectra (right) of aluminum-modified poly(vinylsilazane) **Ia**, poly(methylvinylsilazane) **Ib**, and poly(vinylsilsesquiazane) **Ic**, reflecting the amorphous ceramic at 1400 °C. All spectra were recorded with single-pulse excitation.

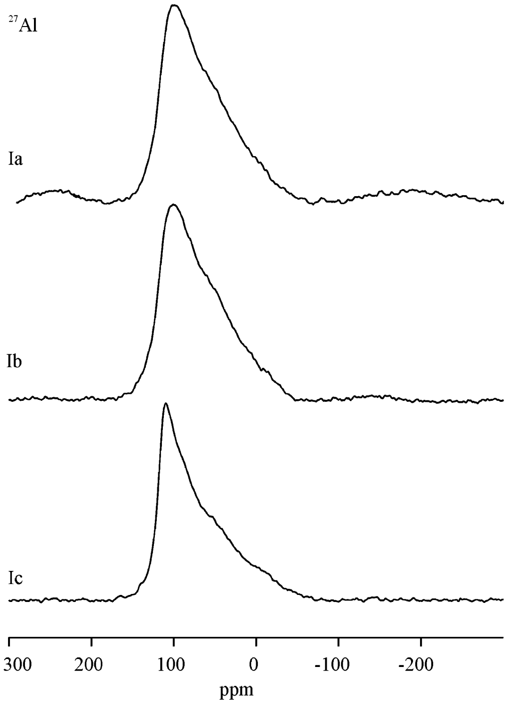

Figure 10. Experimental ^{27}Al NMR spectra of aluminum-modified poly(vinylsilazane) **Ia**, poly(methylvinylsilazane) **Ib**, and poly(vinylsilsesquiazane) **Ic**, reflecting the amorphous ceramic at 1400 °C.

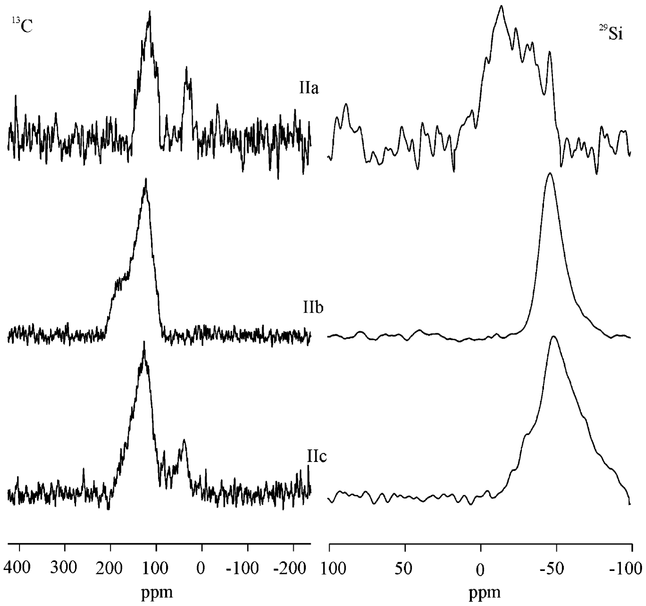

Figure 11. Experimental ^{13}C (left) and ^{29}Si NMR spectra (right) of aluminum-modified poly(vinylsilylcarbodiimide) **IIa**, poly(methylvinylsilylcarbodiimide) **IIb**, and poly(methylsilylcarbodiimide) **IIc**, reflecting the amorphous ceramic at 1400 °C. All spectra were recorded with single-pulse excitation.

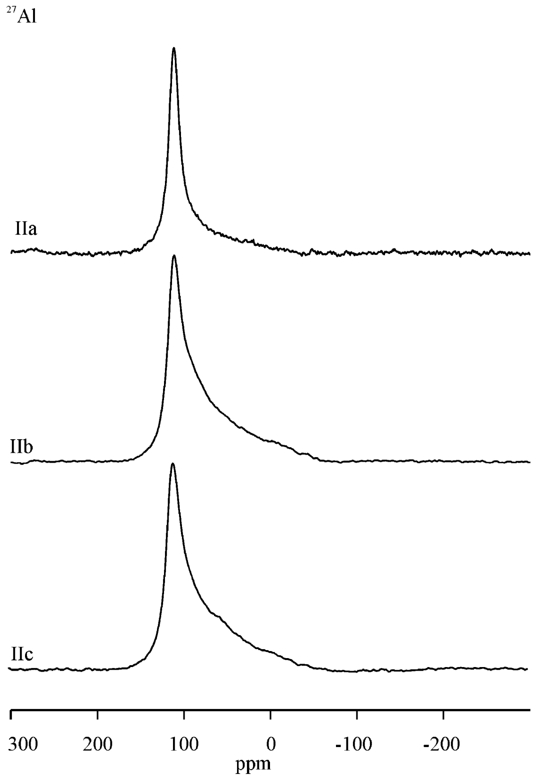

Figure 12. Experimental ^{27}Al NMR spectra of aluminum-modified poly(vinylsilylcarbodiimide) **IIa**, poly(methylvinylsilylcarbodiimide) **IIb**, and poly(methylsilylcarbodiimide) **IIc**, reflecting the amorphous ceramic at 1400 °C.

The ^{27}Al NMR spectra in Figure 10 of the polysilazanes **Ia** to **Ic** appear to be very similar. In either case a maximum occurs at around 100 ppm which can be attributed to tetragonally coordinated aluminum atoms, i.e., the formation of AlN_4 units.[12,45,46] Moreover, additional spectral components in the high field region at about 0 and 50 ppm arising from AlN_5 and AlN_6 units,[12,45,46] i.e., aluminum atoms in pentagonal and octahedral coordination with nitrogen atoms, can be observed. The relative amount of the tetragonal coordination again seems to be highest for sample **Ic**, referring to the system with the lowest carbon content.

A comparison of the derived ^{13}C and ^{29}Si NMR data from polysilylcarbodiimides **IIa** to **IIc** also provide consistent results. Thus, the ^{13}C NMR spectra (see Figure 11) for all samples exhibit a broad spectral component at around 130 ppm due to amorphous (graphite-like) carbon. In addition, for samples **IIa** and **IIc** a second signal at about 40 ppm from CH_xSi_{4-x} units ($x = 0,1,2$) can be found which is not visible in the spectrum of sample **IIb**. The absence of such units is reflected in the ^{29}Si NMR data, as for the latter sample only one peak at -47 ppm due to SiN_4 units is registered. On the other hand, samples **IIa** and **IIc** exhibit additional spectral absorption in the downfield region that is characteristic for the above-mentioned CH_xSi_{4-x} units. Unlike the situation of the polysilazanes, we cannot derive a clear trend for the evolution for the various spectral components as a function of the carbon content in the ^{13}C and ^{29}Si NMR spectra of the polysilylcarbodiimides. The comparison with the polysilazane data reveals a general higher amount of SiN_4 units (at the expense of the amount of the Si−C−N-matrix) for the polysilylcarbodiimides which is a direct consequence of the higher nitrogen content in the basic polymer structure. Here, the Si/N ratio is 1:2, whereas the corresponding polysilazanes possess Si/N ratios of 1:1 (**Ia**, **Ib**) or 1:1.5 (**Ic**). At the same time, on the basis of the ^{13}C NMR experiments, a higher amount of free amorphous carbon can be deduced for the polysilylcarbodiimides.

The experimental ^{27}Al NMR spectra of the polysilylcarbodiimides shown in Figure 12 exhibit a distinct maximum at 110 ppm, arising from AlN_4 units.[12,45,46] Additional high-field components can be seen at around 50 and 0 ppm, which originate from aluminum nuclei that again are pentagonally and hexagonally coordinated with nitrogen atoms. Here again, the higher amount of the AlN_4 structural units in the polysilylcarbodiimides can be related to the aforementioned higher nitrogen content of the ceramic material. However, unlike the situation for the polysilazanes, a clear relationship between the relative amount of the aluminum coordination and the actual carbon or nitrogen content is missing for the polysilylcarbodiimides.

A comparison with the data reported for the corresponding boron-modified polysilazanes as well as boron-free and boron-modified polysilylcarbodiimides[25,57] indicates a close analogy. For these systems in the amorphous ceramic above 1000 °C again a Si−C−N matrix (i.e., SiC_xN_{4-x} units with $x = 0, 1, 2, 4$) is formed along with amorphous carbon and BN domains. Here, the actual amount of the various structural motifs show a strong dependence on the nitrogen content of the precursor polymers. As a result, for the polysilylcarbodiimides a higher amount of SiN_4 components is registered.

Conclusions

Multinuclear solid-state NMR, EPR, and FT IR spectroscopic techniques have been used to follow the thermolysis of aluminum-modified poly(vinylsilazane) between room temperature and 1400 °C to build up a quaternary amorphous ceramic. It has been found that the disintegration of the polymeric precursor is completed at about 500 °C, at which an amorphous preceramic network is formed. Likewise, aluminum is found to exhibit a strong affinity to nitrogen that results in a deduction of nitrogen in the vicinity of silicon atoms below 500 °C. Between 500 and 1050 °C a continuous transformation into the amorphous ceramic is observed. In addition, the EPR data clearly prove the existence of carbon-centered free radicals between 700 and 1400 °C whose amount varies with temperature, and which exist in clusters, as deduced from the derived line width effects due to spin exchange. The amorphous ceramics fired at 1050 and 1400 °C are characterized by the presence of a Si−C−N matrix (i.e., SiC_xN_{4-x} with $x = 0, 1, 2, 4$), amorphous (graphite-like) carbon, and AlN_x domains with aluminum in different coordination sphere ($x = 4, 5, 6$). In this respect, the present system resembles the corresponding boron-modified polysilazane, where in the amorphous ceramic the same structural motifs—with h-BN domains instead of AlN domains—have been reported. It is argued that the formation of carbon-enriched Si−C−N domains, with a homogeneous element distribution, as well as the BN domains (turbostratic BN(C) layers) play a major reason for the high-temperature stability in Si−B−C−N ceramics which frequently do not decompose below 1900 °C. The high-temperature stability of the Si−B−C−N systems is attributed to the fact that the turbostratic BN(C) layers prevent the (decomposition) reaction between Si_3N_4 and graphite to form SiC by (a) acting as a diffusion barrier, (b) increasing the reaction temperature, and (c) stabilizing Si_3N_4.[7,58,59] Despite this close analogy of the derived structural components in the present Si−Al−C−N ceramics, preliminary thermogravimetric measurements have revealed decomposition temperatures below 1600 °C which is a typical value for ternary Si−C−N ceramics.[60] At present, the (molecular) origin of the reduced thermal stability of Si−Al−C−N polymers is not fully understood. However, it is anticipated that the AlN_x units are unable to play the same prominent role as the aforementioned turbostratic BN(C) layers, and cannot prevent the decomposition of the material via the reaction between silicon nitride and graphite-like components.

For comparison, multinuclear solid-state NMR experiments have been performed on the amorphous ceramics fired at 1400 °C derived from polysilazanes and polysilylcarbodiimides that differ in their basic structures. Here again, the same structural components—a Si−C−N matrix, amorphous carbon, and AlN domains—could be assigned. The actual composition of the amorphous ceramic was found to vary considerably with the molecular structure of the precursor polymer. In some cases, distinct trends for the relative amounts of the various structural components could be given.

In summary, the present study has demonstrated that the combination of multinuclear solid-state NMR, EPR, and FT IR techniques is a powerful method for the preparation of precursor-derived ceramics where mainly amorphous intermediates are formed, for which most

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other experimental techniques fail. From this is provided a detailed picture of the structural changes that occur during the precursor thermolysis up to the amorphous ceramic. Further work along this line is in progress.

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