APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2001; **15**: 809–819
DOI: 10.1002/aoc.235

Solid-state NMR and FT IR studies of the preparation of Si–B–C–N ceramics from boron-modified polysilazanes

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Multinuclear (^{29}Si,^{13}C,^{11}B,^{15}N,^{1}H) solid-state NMR and FT IR spectroscopy is employed to investigate the thermolysis of boron-modified polyhydridovinylsilazane, $[B(C_2H_4{-\!\!-}SiHNH)_3]_n$, from which a high-temperature stable Si–B–C–N ceramic can be formed. The study is focused primarily on the characterization of the amorphous intermediates on the atomic scale, where such spectroscopic techniques have demonstrated their particular suitability. In addition, data are provided for the transformation from the amorphous to the crystalline ceramic. It is shown that the transformation of the polymeric precursor to the (amorphous) pre-ceramic network is completed at around 500 °C. At this temperature the BN domains and Si–C–N units of mixed composition are formed. Above this temperature a continuous transformation to the ceramic takes place. At 1050 °C the amorphous ceramic consists of three main components: (i) amorphous (graphite-like) carbon; (ii) planar BN domains; and (iii) an Si–C–N matrix (SiC_xN_{4-x} units with $x = 0, 1, 2$). In addition, a considerable amount of hydrogen is present even at this temperature. The NMR studies have further shown that above 1700 °C the amorphous ceramic demixes, along with the formation of crystalline silicon nitride and silicon carbide. Likewise, structural changes for BN domains have been registered that are attributed to the formation of turbostratic BN(C) interface layers. In summary, the present study has demonstrated that the combination of multinuclear solid-state NMR and FT IR spectroscopy is a powerful method to probe the thermolytic preparation of ternary and quaternary ceramic materials. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: solid state NMR; FT IR; Si–B–C–N ceramics; polysilazane; precursor thermolysis

Received 10 March 2000; accepted 19 September 2000

INTRODUCTION

Non-oxide ceramics, such as silicon nitride- or silicon nitride/silicon carbide-based composites, exhibit exceptional material properties. They are known for their creep and corrosion resistance, high tensile strength and hardness and are suitable for high-temperature applications. Such ceramics most commonly are prepared by sintering silicon nitride and silicon carbide powders in the presence of suitable additives,[1,2] where the latter, however, limit the applicability of these materials at elevated temperatures.[3] Here, another preparation route for ceramics appears to be very promising, in that it does not require sintering aids.[4–8] The method is based on the thermolysis of suitable pre-ceramic (polymeric) precursors and offers several advantages. Apart from the renunciation of sinter additives, the ceramics derived exhibit a much better homogeneity on the molecular level. In addition, with this latter preparation route a better

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Contract/grant sponsor: Deutsche Forschungsgemeinschaft.
Contract/grant sponsor: Fonds des Chemischen Industrie.

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. Crystallization occurs upon further heating, giving rise to thermodynamically stable phases beyond 1400 °C.[7] Previous studies have shown that the macroscopic properties of such ternary Si–C–N ceramics are closely related to both the actual composition and structure on the molecular level. The polymer-to-ceramic conversion route thus offers a further advantage, since the molecular structure and composition can be controlled by the choice of the pre-ceramic polymers.

Recently, it has been demonstrated that Si–B–C–N ceramics, derived from boron-modified polymers, possess exceptional high-temperature stability.[7–11] Unlike the situation in Si–C–N ceramics, so far only little is known about the structural evolution during the preparation of such quaternary Si–B–C–N ceramic systems. As mentioned earlier, the thermolysis comprises various amorphous intermediate stages, which rules out the application of conventional X-ray techniques to obtain structural information of such systems. In this connection, solid-state NMR spectroscopy has proven to be a very powerful technique, being applicable to amorphous systems.[12–14] NMR spectroscopy can thus be used to probe the local environment (short-range order up to a few ångströms) around various NMR-active nuclei, which is accessible by studying the molecular interactions between a specific nucleus and the nuclei in the next (molecular) neighborhood. Numerous examples for such applications have been reported in literature.[12–15]

In the present contribution, solid-state NMR techniques have been applied to determine the structural changes during the preparation of quaternary Si–B–C–N ceramics by the thermolysis of hydroborated polyhydridovinylsilazane. NMR spectroscopy in such ceramic systems is of particular attraction, since all nuclei that build up the final ceramic and ceramic precursors, i.e. ^{13}C, ^{29}Si, ^{1}H, ^{11}B, ^{15}N, are NMR-active and — apart from ^{15}N — can be studied without any kind of isotope enrichment of the samples.[16–25] To our knowledge this is the first comprehensive solid-state NMR study on the thermolysis of polymeric precursors that form Si–B–C–N ceramics. On the basis of our structural assignment, which is further supported by complementary FT IR experiments, ceramization or reaction schemes are proposed that occur during the thermolysis process.

EXPERIMENTAL

Materials

Synthesis

Boron-modified polyhydridovinylsilazane, $[B(C_2H_4—SiHNH)_3]_n$, was synthesized by the reaction of dichlorovinylsilane with ammonia and subsequent hydroboration with borane dimethyl sulfide, $BH_3{\cdot}S(CH_3)_2$, as described elsewhere.[10] ^{15}N NMR measurements were done on ^{15}N-enriched samples, which were prepared according to the above procedure by using ^{15}N-enriched ammonia (Campro Scientific, Berlin; 99 at. % ^{15}N).

Thermolysis

Samples were prepared by the thermolysis of 2 to 4 g of the polymeric precursor in a quartz tube under a steady flow (50 ml min^{-1}) of purified argon in a programmable tube furnace (Gero HTRV 40–250). Starting at ambient temperature, the following heating program was used: (i) an initial 1 K min^{-1} ramp to the desired thermolysis temperature; (ii) a 2 h hold at the thermolysis temperature; (iii) sample cooling with a rate of 2 K min^{-1}, during which the sample was allowed to cool to room temperature.

NMR measurements

All NMR experiments were carried out on Bruker CXP 300 and MSL 300 spectrometers 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. ^{29}Si, ^{13}C, ^{11}B and ^{15}N NMR experiments were done at 59.60 MHz, 75.47 MHz, 96.26 MHz and 30.42 MHz respectively.

^{29}Si, ^{13}C, and ^{15}N 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 (^{13}C, ^{29}Si) and 5.5 μs (^{15}N). Recycle delays up to 30 min (^{13}C), 3 min (^{29}Si, amorphous ceramic), 20 min (^{29}Si, crystalline ceramic) and 1 min (^{15}N) were used during single pulse excitation experiments. During the CP experiments, spin lock fields of 62.5 kHz (^{13}C, ^{29}Si), 45.5 kHz (^{15}N) and contact times of 3 ms (^{13}C, ^{29}Si), 5 ms (^{15}N) were employed at recycle delays between 6 and 8 s. ^{29}Si and ^{13}C chemical shifts were determined relative to external standards Q_8M_8, the trimethylsilylester of octameric silicate, and adamantane. These values were then expressed relative to the reference compound tetramethylsilane (TMS) ($\delta = 0$ ppm). ^{15}N chemical

Table 1 Theoretical ^{29}Si chemical shift values obtained from quantum chemical calculations[a]

Compound	Structural component	δ (^{29}Si)[b] (ppm)
$(CH_3)(H)\mathit{Si}[NH(SiH_3)]_2$	$\mathit{Si}HC(sp^3)N_2$	−8
$(CH_3)_2(H)\mathit{Si}[NH(SiH_3)]$	$\mathit{Si}HC_2(sp^3)N$	−4
$(CH_3)_3\mathit{Si}[N(SiH_3)_2]$ or $(CH_3)_3\mathit{Si}[NH(SiH_3)]$	$\mathit{Si}C_3(sp^3)N$	+10, + 7
$(CH_3)_2\mathit{Si}[N(SiH_3)_2]_2$ or $(CH_3)_2\mathit{Si}[NH(SiH_3)]_2$	$\mathit{Si}C_2(sp^3)N_2$	−4, − 1
$(CH_3)\mathit{Si}[N(SiH_3)_2]_3$	$\mathit{Si}C(sp^3)N_3$	−21
$\mathit{Si}[N(SiH_3)_2]_4$	$\mathit{Si}N_4$	−33

[a] Ref. 31.
[b] Relative to TMS ($\delta = 0$ ppm).

shifts are given relative to CH_3NO_2 ($\delta = 0$ ppm) after external calibration with $^{15}NH_4{}^{15}NO_3$ ($NH_4{}^+$: −358.4 ppm). Inversion recovery CP (IRCP) measurements[26,27] were done using a modified IRCP sequence with simultaneous phase inversion, as described in Ref 28.

^{1}H MAS NMR spectra were recorded at a sample spinning rate of 12 kHz and single pulse excitation ($\pi/2$ pulse width: 4.0 µs) with a recycle delay of 2 s. The ^{1}H chemical shifts were directly referenced to TMS as external standard.

^{11}B NMR (central transition spectra) and ^{11}B satellite transition (SATRAS) spectra[29,30] were recorded with single pulse excitation using $\pi/3$ (pulse length: 2.4 µs) and $\pi/12$ (pulse length: 0.6 µs) pulses respectively, as well as recycle delays of 2 s and a sample rotation frequency of 12 kHz. The spectra were calibrated relative to an aqueous solution of H_3BO_3 ($\delta = 19.6$ ppm) as external standard and are given relative to $BF_3{\cdot}OEt_2$ ($\delta = 0$ ppm).

FT IR measurements

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

^{29}Si NMR chemical shift calculations

Theoretical ^{29}Si NMR chemical shifts were obtained with the program package DeMon using a density functional theory approach.[31,32] To do so, appropriate model compounds were chosen, followed by geometry optimization using the MOPAC program package (PM3 basis set).[33] DeMon simulations were done on the basis of such optimized molecular structures, employing the IGLO II basis set. Representative results for various model compounds are given in Table 1. Further details can be found elsewhere.[34]

^{11}B NMR spectra simulations

The theoretical ^{11}B NMR spectra (central transition only) under MAS conditions were simulated with a FORTRAN program based on published analytical equations that exist for the ultra-fast spinning case.[35,36] The effect of spinning sidebands due to the finite spinning speeds is thus neglected in the theoretical ^{11}B NMR spectra.

RESULTS AND DISCUSSION

In the following we report on multinuclear solid-state NMR and complementary FT IR studies of the thermolysis intermediates from boron-modified polyhydridovinylsilazane, $[B(C_2H_4{-}SiHNH)_3]_n$. All spectroscopic studies were performed at room temperature. The samples referring to the intermediate stages of the thermolysis were subjected to a particular temperature programme to ensure transfer of the actual intermediate structure to room temperature (see Experimental section). Previous calorimetric, thermogravimetric and X-ray studies have shown that the thermolysis is accompanied by an amorphous-to-crystalline transition at about 1750 °C.[10] In the present study we will primarily discuss the temperature range from room temperature to 1050 °C, which covers the amorphous intermediate stages. In addition, ^{29}Si and ^{11}B NMR data will be presented for the transition to the crystalline state.

Solid-state NMR spectroscopy has proven to be of particular use for the determination of the short-range order in amorphous phases.[12–15] The structural information most frequently is derived from the chemical shifts and quadrupolar coupling

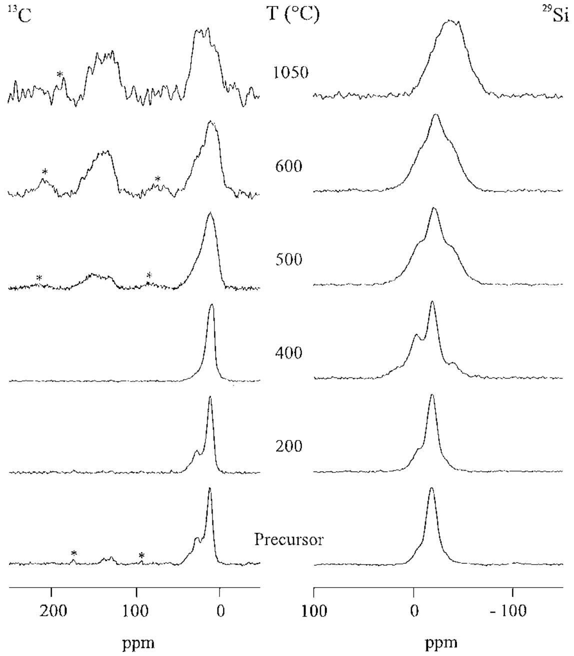
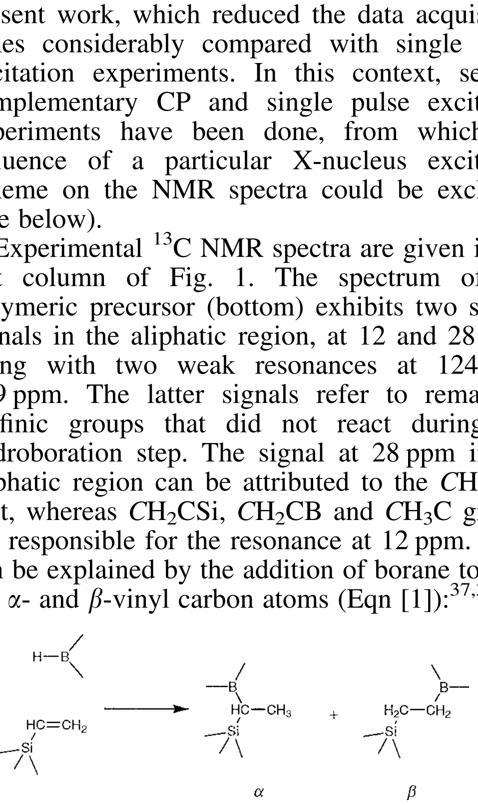


Figure 1 Experimental ^{13}C (left) and ^{29}Si NMR spectra (right) of hydroborated polyhydridovinylsilazane at various stages of the thermolysis process. The spectra were obtained under MAS conditions and CP, except for the ^{29}Si NMR spectra at 1050 °C, where a single pulse excitation has been applied. Asterisks indicate spinning sidebands. Further details are given in the Experimental section.

constants ($I > \frac{1}{2}$ nuclei) of the individual nuclei, since these magnetic interactions depend directly on the actual molecular environment of the particular nucleus of interest. For the ceramic precursors examined here, a series of nuclei — ^{13}C, ^{29}Si, ^{15}N, ^{1}H and ^{11}B — is accessible that could be used to probe the local order during the thermolysis process. During the experimental analysis of the present work three methods have been employed for the NMR signal assignments: (i) the chemical shift values from suitable reference compounds were taken into account; (ii) ^{13}C and ^{29}Si spectral editing techniques, i.e. IRCP measurements, were applied to distinguish between various CH_x and SiH_x ($x = 0$ to 3) segments;[26–28] (iii) quantum chemical calculations were used for the ^{29}Si chemical shift assignment.[31,32]

Representative multinuclear solid-state NMR and FT IR spectra are given in Figs 1 to 7. They cover the range starting from the precursor polymer at room temperature up to 1050 °C, at which the amorphous ceramic exists. It should be noted that ^{1}H NMR measurements have demonstrated that even for the amorphous ceramic at 1050 °C a substantial amount of hydrogen is present (see below). This finite proton content is a prerequisite for the CP experiments performed during the present work, which reduced the data acquisition times considerably compared with single pulse excitation experiments. In this context, several complementary CP and single pulse excitation experiments have been done, from which the influence of a particular X-nucleus excitation scheme on the NMR spectra could be excluded (see below).

Experimental ^{13}C NMR spectra are given in the left column of Fig. 1. The spectrum of the polymeric precursor (bottom) exhibits two strong signals in the aliphatic region, at 12 and 28 ppm, along with two weak resonances at 124 and 139 ppm. The latter signals refer to remaining olefinic groups that did not react during the hydroboration step. The signal at 28 ppm in the aliphatic region can be attributed to the *C*HCBSi unit, whereas *C*H$_2$CSi, *C*H$_2$CB and *C*H$_3$C groups are responsible for the resonance at 12 ppm. They can be explained by the addition of borane to both the α- and β-vinyl carbon atoms (Eqn [1]):[37,38]



(1)

The above assignment is further supported by spectral editing measurements,[26–28] namely IRCP experiments (see Fig. 2), which clearly prove that

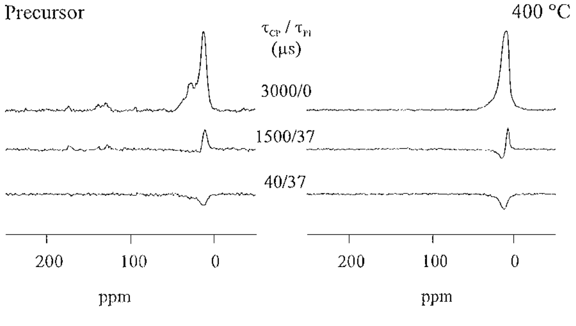
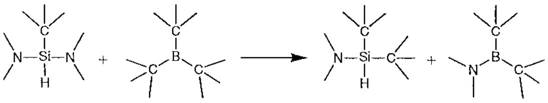


Figure 2 Experimental ^{13}C IRCP spectra of hydroborated polyhydridovinylsilazane before heat treatment (left) and its thermolysis intermediate at 400 °C (right). The experimental conditions are given in the figure (τ_{CP}, τ_{PI}) and in the Experimental section.

the 12 ppm signal is a superposition of CH_3 and CH_2 signals. If the IRCP experiment is done with values of $\tau_{CP} = 40$ μs and $\tau_{PI} = 37$ μs, then signals of negative intensity are expected for CH_2 groups and the CH_3 and CH signals should vanish. Theoretically, the CH_2 signal intensity is expected to be −25% of its original value from the CP experiment.[28] The experimental signal intensity is found to be somewhat smaller, but, as expected, has a negative sign. On the other hand, if τ_{CP} and τ_{PI} are chosen as 1500 μs and 37 μs respectively, then CH groups should have null intensity. At the same time, CH_2 and CH_3 groups should give −33% and 68% respectively of their original intensities in the CP experiment.[28,39] The experimental spectra, given in Fig. 2, indicate that in the precursor polymer the CH_2 and CH_3 signals are too close to be separated by the IRCP experiment. However, if the same experiment is performed with the thermolysis intermediate at 400 °C, as shown in the right column of Fig. 2, then the CH_2 (negative low-field signal) and CH_3 signals (positive high-field signal) are clearly distinguishable.

Upon heating to 400 °C the signal at 28 ppm (CH units) has vanished completely, whereas the signals from CH_3 and CH_2 segments are still present. At 500 °C and above the signals broaden considerably and the signal/noise ratio is drastically reduced. In addition, a broad spectral component is visible at about 130 ppm, which, according to previous studies,[22,24] can be assigned to amorphous (graphite-like) carbon. At higher temperatures the intensity of this latter spectral component increases further, at the expense of the signal intensity of the ‘aliphatic carbon’ region below 50 ppm. In the amorphous ceramic at 1050 °C the carbon is found to exist in two main fractions, namely as graphite-like domains, given by the broad resonance centered at about 130 ppm, as well as $\mathit{C}H_xSi_{4-x}$ units ($x = 0$, 1 or 2) in an Si–C–N matrix, reflected by the broad high-field component below 50 ppm. In summary, the most drastic changes in the ^{13}C NMR spectra are registered around 500 °C, and result from the disintegration of the polymeric precursors and the formation of an amorphous preceramic network.

The ^{29}Si NMR spectrum of the polymeric precursor, shown in Fig. 1 (right column), exhibits a broad line centered at −13 ppm. This resonance can be attributed to the $\mathit{Si}HC(sp^3)N_2$ group, in agreement with experimental values on similar structural units[40] and the theoretical value of −8 ppm derived from quantum chemical calculations (see Table 1). Upon heating to 400 °C additional signals at −37 and −4 ppm show up, of which the latter was already visible as a slight shoulder in the spectrum of the polymeric precursor. The chemical shift value, additional ^{29}Si IRCP measurements (spectra not shown), and theoretical chemical shift calculations (see Table 1) proved that the latter low-field signal reflects an $\mathit{Si}HC_2(sp^3)N$ group. The formation of this structural unit can be traced back to the strong affinity of boron to bind nitrogen. $\mathit{B}NC_2(sp^3)$ and $\mathit{Si}HC_2(sp^3)N$ units are thus formed *via* the reaction scheme in Eqn [2]:


(2)

Consequently, for the Si–B–C–N precursors at temperatures below 500 °C the nitrogen content in the chemical environment of silicon is reduced. This is different from the findings for the corresponding boron-free polysilazanes, where the silicon environment is found to be enriched with nitrogen at such temperatures, most probably due to the lack of competing boron nuclei.[34] Nevertheless, it should be noted that silicon with nitrogen-enriched coordination spheres exists for the present samples. This is reflected by the mentioned high-field signal centered at −37 ppm, which can be attributed to overlapping spectral components from $\mathit{Si}CN_3$ and $\mathit{Si}N_4$ units,[41] which, however, are of much lower intensity.

The spectra of the thermolysis intermediates above 500 °C are characterized by a decrease of the low-field ^{29}Si resonance at −4 ppm ($\mathit{Si}HC_2(sp^3)N$ groups) and an increase in the high-field spectral component at −37 ppm. As will be discussed below, the FT IR spectra in this temperature range display a considerable decrease of the Si—H and N—H stretching band intensities. Both results are explainable by dehydrocoupling reactions between Si—H and N—H groups at such elevated temperatures. They give rise to the formation of nitrogen-enriched silicon coordination spheres (i.e. $\mathit{Si}C_2N_2$, $\mathit{Si}CN_3$, $\mathit{Si}N_4$ units), as given by the high-field components in the experimental ^{29}Si NMR spectra. The broad ^{29}Si resonance in the amorphous ceramic at 1050 °C thus represents a superposition of NMR lines due to three main structural components, namely $\mathit{Si}C_x(sp^3)N_{4-x}$ units with $x = 0$, 1 or 2. In accordance with the previously discussed ^{13}C NMR data, again an Si–C–N matrix is found to contribute to the amorphous ceramic at 1050 °C. It should be noted that the formation of carbon-enriched Si–C–

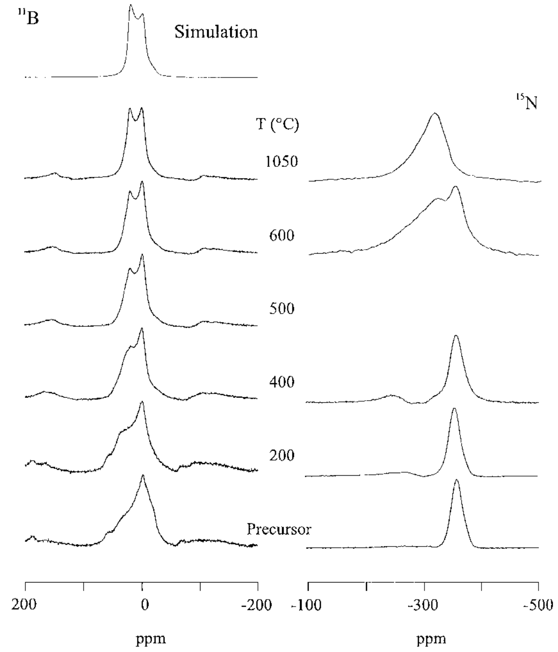


Figure 3 Experimental ^{11}B (left) and ^{15}N NMR spectra (right) of hydroborated polyhydridovinylsilazane at various stages of the thermolysis process. The spectra were obtained under MAS conditions and single pulse excitation (^{11}B) or CP (^{15}N). Further details are given in the Experimental section.

N domains, exhibiting a homogeneous element distribution, is considered to be of great importance for the high-temperature stability of such ceramic materials.[7]

Figure 3 (left) shows the experimental ^{11}B NMR spectra. They refer to the excitation of the central transition ($m_I = -\frac{1}{2}$ to $m_I = +\frac{1}{2}$). Owing to the large quadrupolar moment of the boron nucleus, a second-order broadening is registered in the ^{11}B central transition NMR spectra, which cannot be eliminated by fast rotation at the magic angle.[35,36] The experimental ^{11}B NMR spectra of the polymeric precursor and of the thermolysis intermediates below 500 °C are found to be broad and featureless due to the large heterogeneity in the local chemical environment of the boron nuclei. That is, the boron nuclei exist in both tetrahedral and trigonal coordinations. At the same time, variable amounts of B—N and B—C bonds in their first and second coordination spheres are present in these samples, giving rise to a large distribution of quadrupolar coupling constants, as reflected by the experimental ^{11}B NMR spectra.

Above 500 °C the ^{11}B NMR spectra exhibit quite distinct spectral features. They are typical for trigonally coordinated boron nuclei and are almost identical with the ^{11}B NMR spectrum reported for hexagonal boron nitride. The additional weak signals at both sides of the central resonance refer to spinning sidebands that remain even at spinning rates of 12 kHz. At the top of Fig. 3 (left) a theoretical ^{11}B NMR spectrum is given. The quadrupolar coupling constant of $C_Q = 2.8$ MHz and the asymmetry parameter of $\eta = 0$, used for this simulation, again are very close to the parameters reported for hexagonal boron nitride ($C_Q = 2.9$ MHz, $\eta = 0$).[42]

The presence of trigonally coordinated boron in the amorphous ceramic, i.e. planar BN$_3$ units, is further supported by the ^{11}B SATRAS NMR spectra,[29,30] presented in Fig. 4. Such SATRAS spectra are dominated by first-order quadrupolar coupling effects, where the spectral widths are directly proportional to the size of the quadrupolar coupling constants.[36] In the case of ^{11}B the quadrupolar coupling constant depends strongly on the actual coordination. That is, trigonally coordinated boron gives rise to large quadrupolar coupling constants, whereas small quadrupolar coupling constants are found for tetrahedral coordination. For comparison, ^{11}B SATRAS spectra are given for hexagonal boron nitride (Fig. 4b) and borax ($Na_2B_4O_{10}\cdot 10H_2O$, Fig. 4c). It should be noted that, for borax, both tetrahedrally and

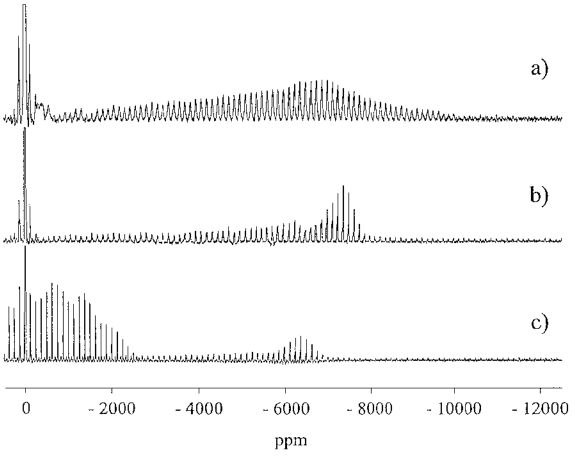


Figure 4 Experimental ^{11}B SATRAS NMR spectra of hydroborated polyhydridovinylsilazane (a), hexagonal boron nitride (b) and borax ($Na_2B_4O_{10}\cdot 10H_2O$) (c). Only the high-field side of the SATRAS spectra, recorded under MAS conditions, are shown. Further details are given in the Experimental section.

trigonally coordinated boron exist. Here, the trigonal coordination can be clearly distinguished, owing to the larger width of the spinning sideband pattern in the corresponding ^{11}B SATRAS subspectrum (about 7000 ppm). At the same time, the subspectrum due to tetrahedrally coordinated boron breaks down at about 2000 ppm. Inspection of Fig. 4 reveals very similar ^{11}B SATRAS spectra for the amorphous ceramic, boron nitride and the subspectrum of borax due to trigonally coordinated boron. This again points to the presence of planar $\mathit{B}N_3$ units, i.e. hexagonal boron nitride domains, in the amorphous ceramic at 1050 °C.

From the above ^{11}B NMR data it is very unlikely that B—C bonds exist at this stage, although a final proof is still to be found. According to the ^{11}B data from solution NMR studies the replacement of a B—N bond by a B—C bond should give rise to a downfield shift of the ^{11}B resonance. The ^{11}B isotropic chemical shifts of BN_3, BN_2C and BC_3 sites thus typically range from 25 to 30 ppm, 30 to 35 ppm and 65 to 85 ppm respectively.[43] At the same time, our ^{11}B isotropic chemical shift value of 30 ppm again fits with the value reported for hexagonal BN, i.e. BN_3 sites.[42] In addition, it is still open as to whether separate amorphous carbon and BN domains exist or whether interdigitated carbon and BN layers build up a ‘homogenous B–C–N phase’. Further work along this line is in progress. Finally, it should be noted that the formation of BN layers is considered to be a prerequisite for the high-temperature stability of Si–B–C–N ceramics, since BN layers serve as diffusion barriers and inhibit the decomposition reaction at higher temperatures.[44]

^{15}N NMR spectra of ^{15}N-enriched samples are given in the right column of Fig. 3. The ^{15}N NMR spectrum for the sample at 500 °C is missing due to the limited amount of ^{15}N-enriched polymer. The polymeric precursor exhibits a single line at -357 ppm arising from the $\mathit{N}HSi_2$ structural unit. Upon heating to 400 °C an additional broad spectral component is visible in the downfield region at about -245 ppm, which is attributed to the formation of $\mathit{N}HB_2$ and $\mathit{N}HBSi$ units. At 600 °C the ^{15}N NMR spectrum is given by a superposition of the former high-field signal that now is shifted slightly to -351 ppm, a signal centered at -320 ppm and a broad downfield shoulder. The former spectral component is the remains of the original polymer network, and the latter components again are characteristic of the amorphous preceramic network.

It should be noted that ^{15}N chemical shifts have been reported in the literature for the $\mathit{N}Si_3$ unit[45] (in silicon nitride) and the $\mathit{N}B_3$ unit[46,47] (in boron nitride), and are given as -310 ppm and -285 ppm respectively. Consequently, the new signal at -320 ppm should reflect the $\mathit{N}Si_3$ groups, whereas the broad downfield component can be attributed to the $\mathit{N}B_3$ units. At 1050 °C the high-field component has vanished almost completely. Here, the ^{15}N NMR spectrum is dominated by a signal centered at -315 ppm from $\mathit{N}Si_3$ groups, as well as the above-mentioned downfield shoulder due to the $\mathit{N}B_3$ units. At present, various experimental techniques, e.g. spectral editing techniques, are being examined in order to separate both spectral components in the ^{15}N NMR spectrum of the amorphous ceramic. In this context, experiments on other ^{15}N-enriched samples — comprising boron-free, boron-modified polymeric precursors and higher thermolysis temperatures — are also envisaged. From the above results we can deduce that the ^{15}NMR results are again consistent with both the ^{13}C and ^{29}Si NMR data presented earlier.

During multinuclear solid-state NMR investigations the question frequently arises as to whether CP and single pulse excitation spectra provide identical results. As an example, ^{15}N NMR spectra for the sample heated to 1050 °C that have been recorded with CP and single pulse excitation are given in Fig. 5. Since both ^{15}N NMR spectra are found to be identical, any significant influence by ^{1}H–^{15}N CP can be ruled out in this case. As

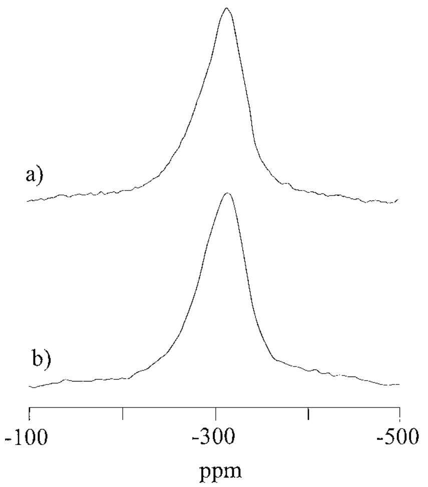


Figure 5 Experimental ^{15}N NMR spectra of hydroborated polyhydridovinylsilazane, heated to 1050 °C, recorded with CP (a) and single pulse excitation (b). Further details are given in the Experimental section.

mentioned earlier, the X-nucleus excitation scheme was also found to have a negligible effect during the ^{13}C and ^{29}Si NMR studies of the present work. The same holds for previous studies on ceramics from polysilylcarbodiimide precursors[22] and polysilazane precursors of other compositions.[34] Obviously, the remaining protons (see next paragraph) — detectable up to at least 1050 °C — are distributed uniformly across the whole sample, allowing for an efficient ^1H–X magnetization transfer (X = ^{13}C, ^{29}Si, ^{15}N).

Representative ^1H NMR spectra are given in Fig. 6. As expected, they exhibit a relatively poor resolution due to the strong ^1H–^1H dipolar couplings. For the precursor sample — in agreement with the above ^{13}C NMR data — the downfield signal at about 7 ppm is assigned to remaining olefinic groups that did not react during the hydroboration step. Furthermore, it can be seen that even at 1050 °C the ^1H NMR absorption covers a broad spectral range, reaching from the aliphatic (~0 ppm) to the aromatic region (~8 ppm). That is, the various structural units in the amorphous ceramic material — assigned from the ^{13}C, ^{29}Si and ^{15}N NMR measurements — are also reflected by the ^1H NMR spectra. In this context, more detailed information is expected from forthcoming ^1H NMR studies under ultra-fast MAS conditions.

The study of the amorphous thermolysis intermediates is completed by FT IR spectroscopy. The FT IR spectrum of the polymeric precursor, given in Fig. 7, again confirms that, during hydroboration of the vinyl group, both α- and β-substitution occurs (see Reaction [1]), as given by the stretching bands at $\nu_{as}(CH_3) = \nu_{as}(CH_2) = 2936\ cm^{-1}$, $\nu_s(CH_3) = \nu_s(CH_2) = 2908\ cm^{-1}$ and $\nu(CH) = 2867\ cm^{-1}$.[48]

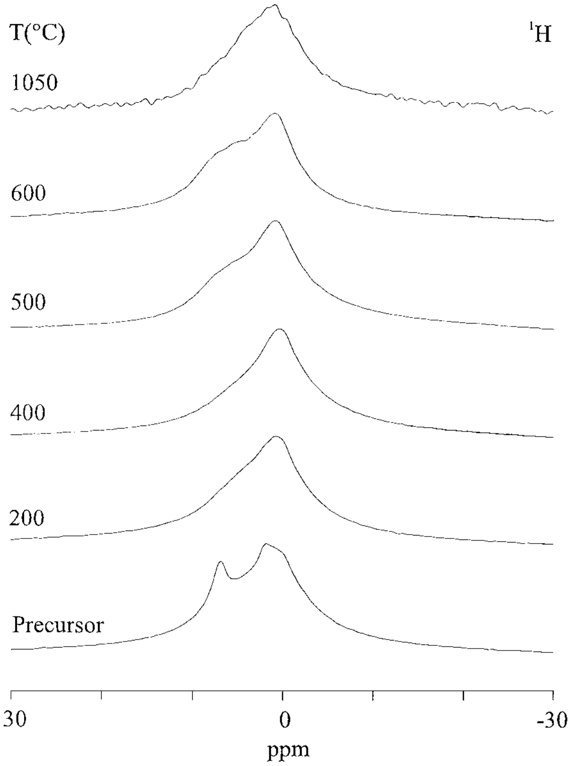


Figure 6 Experimental ^1H NMR spectra of hydroborated polyhydridovinylsilazane at various stages of the thermolysis process. The spectra were obtained under MAS conditions (spinning rate: 12 kHz) and single pulse excitation. Further details are given in the Experimental section.

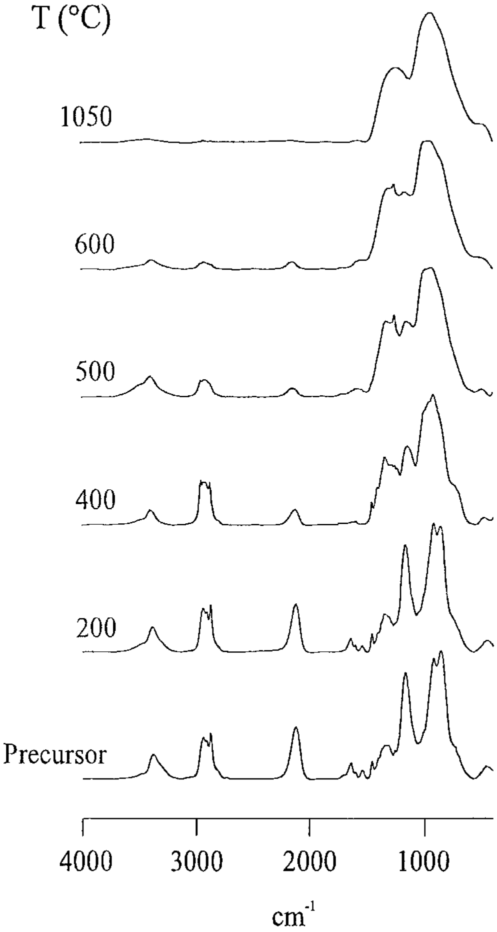


Figure 7 Experimental FT IR spectra of hydroborated polyhydridovinylsilazane at various stages of the thermolysis process. Further details are given in the Experimental section.

In addition, vibration bands of the N—H and Si—H units are observed at 3382 cm^{-1} and 2124 cm^{-1} respectively. For the thermolysis intermediates between 500 and 600 °C it is found that the IR vibration bands of the CH_x ($x = 1, 2, 3$) units have vanished almost completely. These findings again confirm that the transformation of the original polymeric components into the amorphous preceramic network is completed at about 500 °C. In addition, the vibration bands of the N—H and Si—H groups disappear above 600 °C, which is in line with the above-mentioned dehydrocoupling reaction betweeen SiH and NH groups and the formation of Si—N bonds. In the amorphous ceramic at 1050 °C only two broad IR bands are left. They are centered at 1248 cm^{-1} and 941 cm^{-1} and refer to planar BN units — for pure hexagonal boron nitride a vibration band at 1347 cm^{-1} has been reported[49,50] — and a superposition of contributions from $\mathit{Si}C_xN_{4-x}$ ($x = 0, 1, 2$) groups[51,52] respectively.

In the following paragraphs the solid-state NMR data of the transformation to the thermodynamically stable crystalline ceramic are discussed briefly. Figure 8 gives representative ^{29}Si and ^{11}B NMR spectra covering the temperature range between 1050 and 2000 °C. At $T \geq 1600$ °C a narrowing of the broad ^{29}Si NMR line, due to the $SiC_x(sp^3)N_{4-x}$ units, occurs along with a splitting into two resonances at −19 and −49 ppm. These signals can be attributed to the formation of crystalline $\mathit{Si}C_4$ (β-SiC: −20 ppm[53]) and $\mathit{Si}N_4$ units (Si_3N_4: −48 ppm[41]), resulting from a demixing of the $SiC_x(sp^3)N_{4-x}$ ($x = 1, 2$) units into silicon carbide and silicon nitride. In the crystalline ceramic at 1800 °C, therefore, only two, well separated signals remain. At the same time, the experimental ^{29}Si NMR spectrum exhibits considerable smaller linewidths, which also can be traced back to the presence of SiC and Si_3N_4 crystallites. Obviously, all structural components with silicon in mixed coordination, such as $SiC_x(sp^3)N_{4-x}$ ($x = 1, 2, 3$), are disintegrated at this temperature, as also found by recent X-ray studies on the same samples.[10]

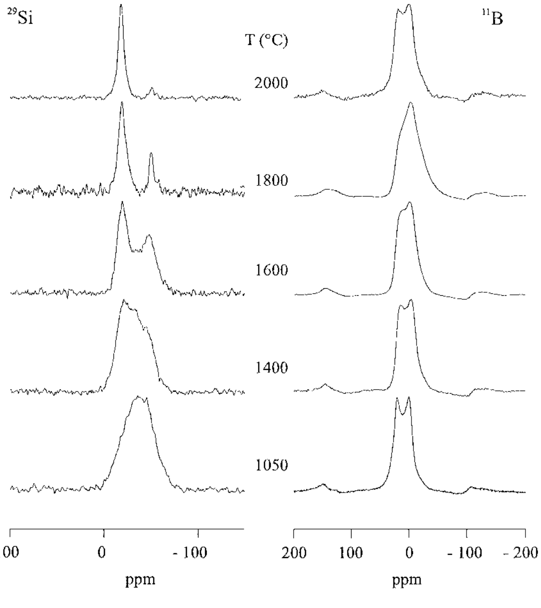


Figure 8 Experimental ^{29}Si (left) and ^{11}B NMR spectra (right) of hydroborated polyhydridovinylsilazane between 1050 and 2000 °C. The spectra were obtained under MAS conditions and single pulse excitation. Further details are given in the Experimental section.

At 2000 °C the decomposition of the crystalline ceramic sets in, as reflected by the intensity decay of the ^{29}Si NMR signal due to Si_3N_4 at −49 ppm. Silicon nitride thus either reacts with carbon to give silicon carbide and nitrogen or decomposes into its elements. It is interesting to note that, unlike the situation in Si–C–N systems,[7,54] in the present Si–B–C–N ceramics the decomposition occurs at much higher temperatures (about 200 °C) than crystallization.[10] Whether this observation is related to the high-temperature stability of such systems is the subject of further investigations.

The ^{11}B NMR spectra, given in the right column in Fig. 8, exhibit line broadening effects between 1400 and 1800 °C, at which crystallization occurs. Eventually, at 2000 °C the typical ^{11}B NMR spectrum of trigonal-coordinated boron reappears. This latter observation is surprising, since, according to X-ray studies,[10] (crystalline) hexagonal boron nitride is absent at such high temperatures. However, turbostratic BN(C) interface layers exist under such conditions, as shown recently by high-resolution transmission electron microscopy.[44] At present, it is still open as to whether such structural changes from the planar BN domains to the turbostratic BN(C) phase are responsible for the observed ^{11}B NMR spectral effects. Here again, ^{15}N NMR would be of considerable help, and these measurements are scheduled for the near future. Finally, it should be noted that we were unable to record ^{13}C NMR spectra beyond 1050 °C due to the extremely long ^{13}C spin-lattice relaxation times (>60 min). Likewise, the information content of the FT IR spectra was very limited, since only very broad and overlapping IR bands were detectable.

CONCLUSIONS

Multinuclear solid-state NMR and FT IR experiments have been performed to follow the thermolysis of boron-modified polyhydridovinylsilazane between room temperature and 2000 °C. It has been found that the disintegration of the original precursor polymer is completed at about 500 °C, at which an amorphous pre-ceramic network is formed. Likewise, boron is found to exhibit a strong affinity to nitrogen, which results in a reduction of nitrogen in the vicinity of silicon atoms below 500 °C. The amorphous ceramic at 1050 °C is characterized by the presence of an Si–C–N matrix (i.e. SiC_xN_{4-x} with $x = 0$, 1, 2), amorphous (graphite-like) carbon and planar BN domains, as clearly shown by the NMR and IR data. It is argued that the formation of carbon-enriched Si–C–N domains, with a homogeneous element distribution, is a major reason for the observed high-temperature stability of Si–B–C–N ceramics. The same is true for the BN domains, which are considered as diffusion barriers at higher temperatures, thus inhibiting decomposition reactions. However, so far, it is not known whether separate amorphous carbon and BN domains exist or whether a homogeneous B–C–N phase is built up by interdigitated carbon and BN layers.

The study has been further extended to the temperature range between 1050 and 2000 °C, where a crystallization of the amorphous ceramic sets in. The ^{29}Si NMR studies could prove that the crystallization is accompanied by a demixing of the SiC_xN_{4-x} domains and formation of silicon carbide and silicon nitride. The ceramic decomposition at 2000 °C is characterized by the reaction of the latter component to give silicon carbide or its disintegration to yield elemental silicon.

In summary, the present study has demonstrated that the combination of multinuclear solid-state NMR and FT IR techniques is a powerful method for the study of ceramization processes. From this, a detailed picture about the structural changes that occur during the precursor thermolysis up to the crystalline ceramic is available. It should be emphasized that such methods are of particular help for the characterization of the amorphous intermediates, for which most other experimental techniques fail.

Acknowledgements Financial support for this project by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. The authors are also grateful to Professor M. Kaupp (Universität Würzburg) for the support during the quantum chemical calculations.

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