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Dehydrocoupling of tris(hydridosilylethyl)boranes with ammonia or amines: a novel route to Si–B–C–N preceramic polymers

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The synthesis of boron-modified polysilazanes of general type $\{B[C_2H_4Si(R)—NR']_3\}_n$ [R = CH_3, $(NR')_{0.5}$; R′ = H, CH_3] by dehydrogenative coupling of tris(hydridosilylethyl)boranes $B[C_2H_4Si(CH_3)_nH_{3-n}]_3$ ($C_2H_4 = CHCH_3$, CH_2CH_2; $n = 0, 1$) and ammonia or methylamine is reported. Detailed characterization of the title compounds was performed using spectroscopic methods such as solid-state NMR spectroscopy, IR spectroscopy, and elemental analysis. Thermolysis produces amorphous Si–B–C–N ceramics with ceramic yields between 25 and 83%, as determined by thermogravimetric analysis (TGA) in argon. High-temperature TGA in an argon atmosphere reveals that a number of the ceramics obtained resist degradation up to ~2000 °C. X-ray diffraction studies of the as-obtained amorphous materials show formation of α-SiC or α-SiC/β-Si_3N_4 crystalline phases between 1600 and 1800 °C, depending on the composition of the materials. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

Precursor thermolysis is a process by which suitable polymers with an inorganic skeleton are converted into a wide variety of amorphous ceramics.[1–5] In particular, silicon-based polymers, such as polysilanes,[6–11] polycarbosilanes,[12–18] polysilazanes,[19–31] and polysiloxanes (for an overview, see Refs 32–35), have proven to be promising precursors for the production of technologically important ceramic components, such as fibers, coatings, infiltrated porous media, or complex-shaped bulk parts.

Recent progress in precursor synthesis has not been focused exclusively on improved selectivity, reduced cost, or production of phase-pure ceramics such as silicon carbide or silicon nitride, but also on the evolution of multinary component ceramics. Within the last decade Si–B–C–N materials, which were obtained from quaternary 'polyborosilazanes', have become of considerable interest owing to their exceptional high temperature and oxidation stability. The structural basis of these compounds is polymeric or cyclic silazanes that are cross-linked via C–B–C bridges[36–43] or N–B–N units.[44–49] Alternatively, borazine-based oligosilazanes[50–58] or boron-modified polysilylcarbodiimides[59–61] served for the synthesis of Si-B-C-N ceramics.

The first cited C–B–C- or N–B–N-bridged polysilazanes were usually obtained by salt elimination reactions, with the inevitable precipitation of solid by-products such as ammonium chloride[36–43] or methylamine hydrochloride.[46–49] The precipitates are separated from the polymer solution by filtration, presuming sufficient solubility of the precursors in the solvent used. This filtration process fails in the case of highly cross-linked

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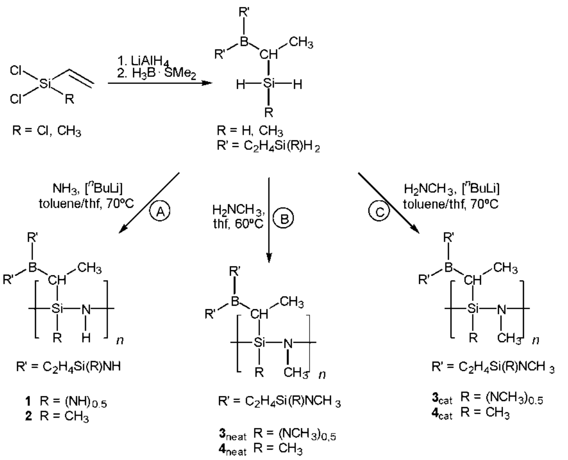


Scheme 1 Synthesis of boron-modified polysilazanes **1–4** by dehydrocoupling of tris(hydridosilylethyl)boranes B[$C_2H_4Si(CH_3)_nH_{3-n}$]$_3$ ($C_2H_4 = CHCH_3$, CH_2CH_2; $n = 0$, 1) and ammonia or methylamine: (A) ammonolysis with catalyst; (B) aminolysis without catalyst; (C) aminolysis with catalyst.

polymers due to their distinct insolubility in common organic solvents.[36–43,46–49] This is a dilemma, since the ceramic yield, which reflects the share of polymer/ceramic residue, depends significantly on the cross-linking of the preceramic polymer. Recently, it was demonstrated that a higher cross-linking efficiently avoids depolymerization of the precursors during thermolysis and consequently inhibits polymer skeleton degradation and volatilization of low-molecular mass species.[39]

The objective of this work is to report a novel approach to highly cross-linked boron-modified polysilazanes of general type $\{B[C_2H_4Si(R)–NR']_3\}_n$ [$R = CH_3$, $(NR')_{0.5}$; $R' = H$, CH_3] as Si–B–C–N ceramic precursors that do not suffer from the above-described drawbacks. This synthetic pathway uses tris(hydridosilylethyl)boranes, $B[C_2H_4Si(CH_3)_nH_{3-n}]_3$ ($n = 0$, 1),[62,63] which were dehydrocoupled with ammonia or methylamine associated with the evolution of molecular hydrogen as the only by-product.

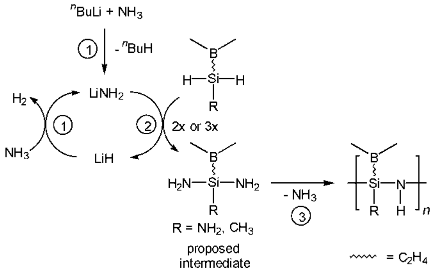
RESULTS AND DISCUSSION

Polymer synthesis and characterization

Boron-modified polysilazanes were synthesized by dehydrocoupling of tris(hydridosilylethyl)boranes and ammonia or methylamine according to Scheme 1. The starting compounds $B[C_2H_4Si(CH_3)_nH_{3-n}]_3$ ($n = 0$, 1) can be obtained by different methods, as described recently.[62,63] We chose synthesis starting from chloro vinylsilanes $(H_2C{=}CH)Si(CH_3)_nCl_{3-n}$ ($n = 0$, 1) that were initially reacted with $LiAlH_4$ in diethyl ether. Since the respective hydrido vinylsilanes $(H_2C{=}CH)Si(CH_3)_nH_{3-n}$ ($n = 0$, 1) are difficult to handle in neat form, they were not isolated but reacted *in situ* by distilling the diethyl ether/hydrido vinylsilane solution into a toluene solution of borane dimethyl sulfide, $BH_3{\cdot}S(CH_3)_2$.

Ammonolysis of $B[C_2H_4Si(CH_3)_nH_{3-n}]_3$ (Scheme 1, route A) does not occur directly and requires catalysts. In earlier publications, Laine, Blum and their coworkers demonstrated that dehydrocoupling of ammonia and alkyl silanes in the presence of transition metal catalysts, such as $Ru_3(CO)_{12}$, occurs under mild conditions, even though the catalyst was used at levels of only 100 to 1000 ppm.[64–67] Alternatively, we used *n*-butyl lithium, similar to a method described by Seyferth and coworkers in which potassium hydride was used for the cross-linking of cyclic silazanes.[68–70] Consequently, 1 mol% of *n*-butyl lithium was added to the toluene/tetrahydrofuran solution of the starting compounds. The reaction mixtures were heated to 70 °C and ammonia was introduced slowly. To avoid the loss of ammonia, the apparatus was equipped with a reflux condenser that was cooled to −78 °C (i-propanol/dry ice). In the case of the synthesis of $\{B[C_2H_4Si(NH)_{1.5}]_3\}_n$ (**1**), strong hydrogen evolution was observed and the precursor precipitated directly from the reaction mixture during the ammonia addition. In contrast, $\{B[C_2H_4Si(CH_3)NH]_3\}_n$ (**2**) remained dissolved. After appropriate work-up, both polymers were obtained as colorless powders in 93% (**1**) or 86% (**2**) yield. They are extremely sensitive to moisture and/or oxygen and insoluble in common organic solvents. **1** does not melt or soften without decomposition (>250 °C), whereas **2** softens at ∼120 °C.

A possible mechanism for the base-catalyzed dehydrocoupling is given in Scheme 2. We suspect that *n*-butyl lithium initially deprotonates ammonia with the formation of lithium amide and evaporation of *n*-butane. The more nucleophilic amide then replaces a silicon-bonded hydride, which subsequently deprotonates ammonia with the evolution of molecular hydrogen. The proposed silyldiamine or -triamine are not stable under the reaction conditions applied and the polymeric precursors form by elimination of ammonia.



Scheme 2 Proposed mechanism for the base-catalyzed dehydrocoupling of ammonia and tris(hydridosilylethyl)boranes. Main steps are (1) deprotonation of ammonia, (2) nucleophilic substitution of a silicon-bonded hydride with an amide, (3) polymerization by ammonia condensation.

The proposed mechanism is supported by the observation that the more highly nucleophilic methylamine and tris(hydridosilylethyl)boranes react without added catalyst (Scheme 1, route B). In contrast to the procedure described above, this reaction was performed in tetrahydrofuran solution at 60 °C. Aminolysis was also performed in the presence of catalytic amounts of *n*-butyl lithium (Scheme 1, route C) according to the procedure applied for the ammonolysis. In both cases, the boron-modified polysilazanes **3** and **4** were obtained in >90% yield. In contrast to polymers **1** and **2**, the *N*-methyl derivatives were obtained as extremely viscous ($\mathbf{3}_{cat}$, 96%; $\mathbf{3}_{neat}$, 100%) or as viscous ($\mathbf{4}_{cat}$, 92%; $\mathbf{4}_{neat}$, 100%) colorless oils that aged rapidly. Even though they are less air-sensitive, they decompose readily when exposed to air.

IR spectroscopy is an ideal tool for monitoring these particular reactions. The decreasing intensity of the Si—H vibration bands, which are present in the starting compounds, directly reflects the progress in the substitution of the silicon-bonded hydride with an amide. As an example, the IR spectra of the starting compound $B[C_2H_4Si(CH_3)H_2]_3$ and the corresponding polymers $\mathbf{4}_{neat}$ and $\mathbf{4}_{cat}$, obtained by the reaction with methylamine, are depicted in Fig. 1.

Whereas the IR spectrum of the monomeric

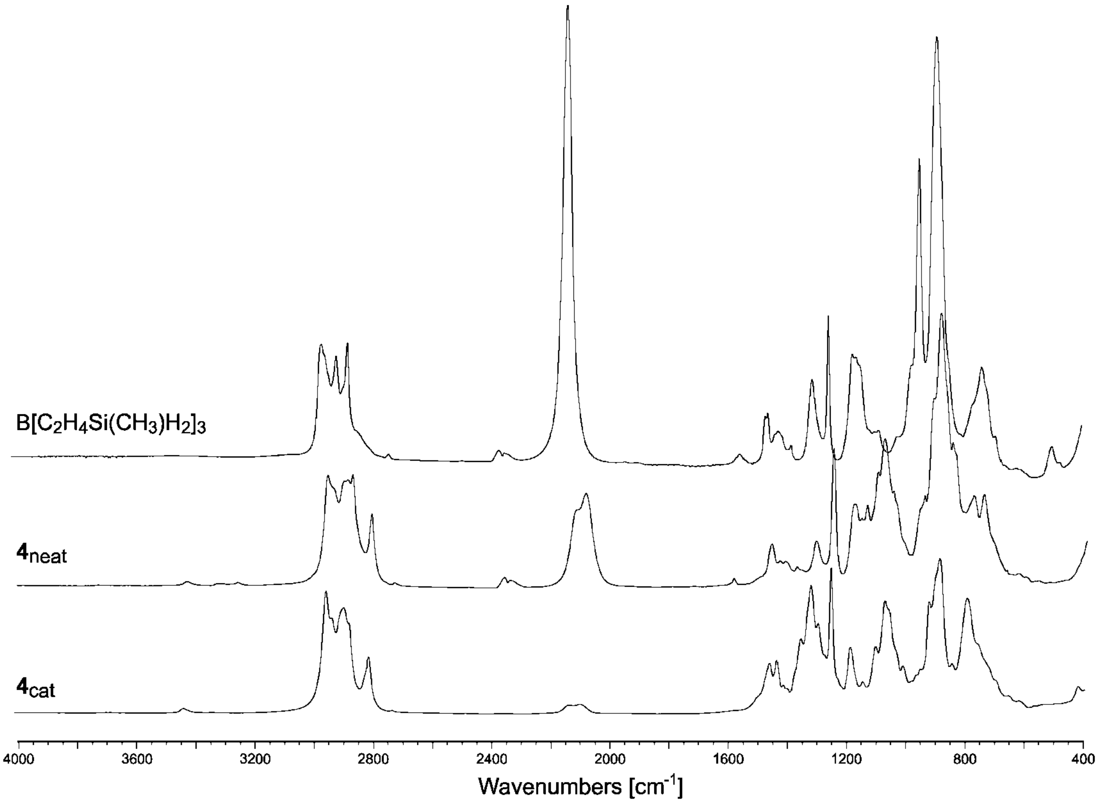


Figure 1 IR spectra (in KBr) of $B[C_2H_4Si(CH_3)H_2]_3$ (top) and the polymers $\mathbf{4}_{neat}$ (mid) and $\mathbf{4}_{cat}$ (bottom).

silane possesses a dominant v(Si—H) absorption at 2113 cm^{-1}, there is an Si—H vibration observed at 2086 cm^{-1} in the IR spectrum of $\mathbf{4}_{neat}$ with only medium intensity. This signal additionally has a shoulder at 2108 cm^{-1}. In contrast, very weak Si—H vibrations are observed in the IR spectrum of $\mathbf{4}_{cat}$ at 2098 cm^{-1}. This suggests a quantitative dehydrocoupling of $B[C_2H_4Si(CH_3)H_2]_3$ with methylamine in the presence of catalyst. Similar findings are made in the respective reaction of $B(C_2H_4SiH_3)_3$ with methylamine. Owing to the presence of a strong Si—H vibration at 2138 cm^{-1} in **1**, it can be concluded that ammonolysis of $B(C_2H_4SiH_3)_3$ does not occur quantitatively even in the presence of suitable catalyst. This may be a consequence of the distinct insolubility of this highly cross-linked compound, which precipitates during the reaction, thus causing heterogeneous reaction conditions,[39] as well as by steric effects, as observed in dehydrocoupling reactions of boron-free polysilazanes.[64–67] Accordingly, a strong Si—H vibration is observed in **2** at 2124 cm^{-1} due to the lower reactivity and of the methyl-substituted starting compound $B[C_2H_4Si(CH_3)H_2]_3$ compared with $B(C_2H_4SiH_3)_3$. Full IR spectroscopic details of all compounds are given in Table 3.

The structure of the title compounds was also investigated using solid-state ^{13}C and ^{29}Si cross polarization and magic angle spinning (CP-MAS) NMR (see Table 4). ^{11}B NMR spectra were also recorded, but they are not discussed here since no detailed structural information was obtained due to lack of fine structure in the broad resonance signals.

The most characteristic features recorded in the product spectra are (i) a low-field shift of the ^{29}Si resonance signals compared with the starting compounds, because of the substitution of silicon-bonded hydrogen atoms with amine units and (ii) the appearance of NCH$_3$ resonance signals in the ^{13}C NMR spectra of **3** and **4**. These structural units are not present in tris(hydridosilylethyl)boranes.

Whereas the monomeric silanes exhibit ^{29}Si resonance signals at around −55 ppm ($\sim SiH_3$) and at around −30 ppm ($\sim SiMeH_2$),[63] the corresponding signals of the polymers are observed at −19 ppm (**1**, *Si*N_3C), −6 ppm (**2**, *Si*N_2C_2), −14 ppm (**3**, *Si*N_3C), and at around −0.5–7 ppm (**4**, *Si*N_2C_2). These observations are in good accordance with polymers of comparable composition described in the literature.[36,43] However, as already observed in the IR spectra, resonance signals of very low intensity at unexpected high field point to residual Si—H bonds because of an inadequate Si—N coupling. In particular, the ^{29}Si NMR spectra of **1** and **2** possess weak resonance signals at −44 ppm (**1**, *Si*H_2NC) and −28 ppm (**2**, *Si*H_2C_2, very weak). The absence of high-field shifted resonance signals in silicon NMR spectra of $\mathbf{3}_{cat}$ and $\mathbf{4}_{cat}$ indicates sufficient Si—N coupling, whereas only partial Si—N coupling in the spectra of $\mathbf{3}_{neat}$ and $\mathbf{4}_{neat}$ can be concluded from resonance signals at −28 ppm ($\mathbf{3}_{neat}$, *Si*HN_2C) and at −27.6 ppm ($\mathbf{4}_{neat}$, *Si*H_2C_2).

The ^{13}C NMR spectra of compounds **1–4** appear very similar. The C_2H_4 ($C_2H_4 = CHCH_3$, CH_2CH_2) units that link silicon and boron are already preformed in the starting compounds[62,63] and observed in the 8–25 ppm range. Explicitly, *C*H_3 resonance signals are found at 8–11 ppm, *C*H_2 units show resonance at 13–18 ppm and *C*H carbon atoms appear at around 25 ppm. As expected, Si*C*H_3 resonance signals in **2** and **4** are found around 0 ppm. A less intensive Si*C*H_3 resonance signal at −7.8 ppm in the spectrum of **2** reflects the observation in the ^{29}Si NMR of this compound, pointing to $CSiH_2$*C*H_3 units due to incomplete dehydrocoupling. The N(*C*H_3) units in **3** and **4** are well separated from the *C*H, *C*H_2 and *C*H_3 resonance signals of the C_2H_4 moieties and are observed at around 30 ppm. Full NMR spectroscopic data are given in Table 4.

Elemental analysis (see Table 5) confirms the conclusions obtained from the spectroscopic investigations. As the title compounds are extremely reactive towards moisture and oxygen, the sample preparation was performed within a glove box in an argon environment. For the carbon, hydrogen, nitrogen, and oxygen elemental analysis, only small sample quantities were applied to insure complete decomposition. A homogeneous distribution of the elements under investigation is, therefore, mandatory in order to obtain reliable results. For that reason, solids were carefully ground in an agate mortar and weighed using a precision microbalance with a readability of 10^{-6} g. Under these conditions, a relative standard deviation of the analytical experiments of <1 mass% was achieved.

It is found that the Si:B ratio at 3:1 in the starting compounds is sustained in all the polymers. There is, in contrast, a deviation of the determined and calculated nitrogen and carbon values. The nitrogen contents of the polymers **1** and **2**, obtained by ammonolysis, and those of $\mathbf{3}_{neat}$ and $\mathbf{4}_{neat}$, synthesized by aminolysis without catalyst, are too low, whereas the respective values in $\mathbf{3}_{cat}$ and $\mathbf{4}_{cat}$ are too high. In the first case it has to be presumed that only partial Si—N coupling is responsible, whereas $NHCH_3$ end groups in $\mathbf{3}_{cat}$ and $\mathbf{4}_{cat}$ are most likely the reason for excessive nitrogen contents. The latter argument is very pronounced for both $\mathbf{3}_{\text{cat}}$ and $\mathbf{4}_{\text{cat}}$. The ideal formula of $\mathbf{3}_{\text{cat}}$ is $Si_3BC_{10.5}N_{4.5}H_{25.5}$, whereas the measured formula is $Si_3BC_{12.5}N_{5.7}H_{32.2}$. This is very close to $Si_3BC_{12}N_6H_{33}$, derived from $\{B[C_2H_4Si(NHCH_3)NCH_3]_3\}_n$. The latter structure can be deduced from the ideal structure $\{B[C_2H_4Si(NCH_3)_{1.5}]_3\}_n$ by assuming that the *trans*-amination of initially formed $B[C_2H_4Si(NHCH_3)_{1.5}]_3$ (see Scheme 2, step 3) did not proceed quantitatively, possibly due to steric reasons or the decreasing solubility of the polymer with increasing cross-linking. This conclusion is also valid for $\mathbf{4}_{\text{cat}}$. The measured composition of $Si_3B_{1.2}C_{14.7}N_{4.7}H_{37}$ is very close to $Si_3BC_{13.5}N_{4.5}H_{37.5}$, which can be attributed to $\{B[C_2H_4Si(CH_3)(NHCH_3)(NCH_3)_{0.5}]_3\}_n$, which itself can be traced back to incomplete *trans*-amination of $B[C_2H_4Si(CH_3)(NHCH_3)_2]_3$.

Ceramic materials

Ceramic materials of **1–4** were obtained by thermolysis of the polymeric precursors in an argon atmosphere. The precursors were heated in alumina Schlenk tubes to 1400 °C with a heating rate of 1 °C min^{-1} and held at the final temperature for an additional 3 h to ensure complete ceramization. A critical point with respect to obtaining ceramic parts by this process is an accompanying mass loss of the materials during thermolysis due to the formation of gaseous by-products. Evaporation of the gases during the heat treatment of the materials frequently results in the formation of unfavorable cracks and pores. To determine the amount of gaseous by-products that form, thermolysis was monitored using thermogravimetric analysis (TGA), as shown in Fig. 2.

A number of factors, such as polymer structure, molecular weight (which could only be determined by cryoscopic methods in benzene for $\mathbf{4}_{\text{neat}}$), the degree of cross-linking, *i.e.* the structure of the polymer backbone and the nature of the functional groups that are attached to silicon and/or nitrogen strongly influence the ceramic yields.[39] An additional important issue in this regard is the decomposition chemistry of the precursors, including the ability to cross-link further during the heat treatment. The evaluation of structural intermediates that arise during the various stages of thermolysis was performed by using multinuclear solid-state NMR and FT-IR spectroscopy and will be published soon.[71]

In general, it is observed that increased cross-linking of the precursors avoids depolymerization during thermolysis and low weight substituents that split off as gaseous by-products cause a lower weight loss than bulk groups. Compounds **1** and **3**, which were obtained from $B(C_2H_4SiH_3)_3$, are more highly cross-linked than the precursors **2** and **4**, which were obtained from $B[C_2H_4Si(CH_3)H_2]_3$; consequently, it is presumed that the ceramic yields of **1** and **3** are higher than those of **2** and **4**. On the other hand, the silicon-bonded methyl groups in **2** and **4**, as well as the nitrogen-bonded methyl groups in **3** and **4**, can easily split off during thermolysis and evaporate as methane. Considering the findings in the TGA shown in Fig. 2, the ceramic yields increase in the expected sequence **4** (25%) $<\mathbf{3}_{\text{neat}}$ (73%) $\sim$**2** (73%) $<$**1** (83%). $\mathbf{3}_{\text{cat}}$ does not fit in this sequence. This is most probably a consequence of incomplete *trans*-amination, as discussed above, and thus insufficient cross-linking, which is responsible for volatilization of low molecular species. In contrast to its isostructural polymer $\mathbf{3}_{\text{neat}}$, the ceramic yield is only 58%.

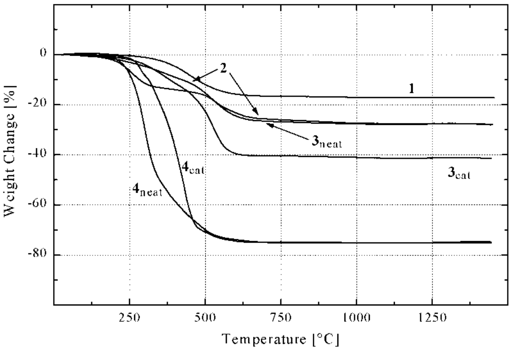


Figure 2 TGA of $\{B[C_2H_4Si(R)NR']_3\}_n$ [R = CH_3, $(NR')_{0.5}$; R′ = H, CH_3], heating rate: 5 °C min^{-1}; atmosphere: flowing argon.

As-obtained ceramics are black amorphous materials with a metallic gloss. Chemical compositions are given in Table 1. Calculated phase fractions [moles of atom%] were determined using the Calphad (*cal*culation of *pha*se *d*iagrams[72–74]) approach and are given in Table 2. The high-temperature mass stability was investigated by high-temperature TGA (HT-TGA, Fig. 3) over the temperature range 25–2150 °C in an argon atmosphere. The thermally induced formation of crystalline phases, such as silicon carbide or silicon carbide/silicon nitride, was monitored using X-ray diffraction (XRD, Fig. 4).

A comparison of the elemental composition of

Table 1 Chemical analysis and empirical formula of the ceramic materials obtained from compounds **1–4**

Ceramic	Analysis found[a]	Empirical formula[b,c]
1	C: 22.9; N: 26.1; B: 6.3; Si: 44.7 mass% C: 32.1; N: 31.4; B: 9.8; Si: 26.7 at. %	$Si_3B_{1.1}C_{3.5}N_{3.6}$ $(Si_3BC_{7.3}N_{3.1})$
2	C: 35.9; N: 16.1; B: 6.0; Si: 42.0 mass% C: 48.2; N: 18.6; B: 9.0; Si: 24.2 at. %	$Si_3B_{1.1}C_6N_{2.3}$ $(Si_3BC_{9.7}N_{2.1})$
$\mathbf{3}_{neat}$	C: 36.7; N: 20.2; B: 5.0; Si: 38.1 mass% C: 48.4; N: 22.8; B: 7.3; Si: 21.5 at. %	$Si_3BC_{6.7}N_{3.2}$ $(Si_3BC_{9.5}N_{3.0})$
$\mathbf{3}_{cat}$	C: 24.5; N: 33.0; B: 5.0; Si: 37.5 mass% C: 32.9; N: 38.0; B: 7.5; Si: 21.6 at. %	$Si_3BC_{4.6}N_{5.3}$ $(Si_3BC_{12.5}N_{5.7})$
$\mathbf{4}_{neat}$	C: 40.4; N: 15.7; B: 5.2; Si: 38.7 mass% C: 53.0; N: 17.7; B: 7.6; Si: 21.7 at. %	$Si_3BC_{7.3}N_{2.4}$ $(Si_3BC_{11.3}N_{2.6})$
$\mathbf{4}_{cat}$	C: 32.3; N: 24.6; B: 6.1; Si: 37.0 mass% C: 42.5; N: 27.8; B: 8.9; Si: 20.8 at. %	$Si_3B_{1.2}C_{6.0}N_{4.0}$ $(Si_3B_{1.2}C_{14.7}N_{4.7})$

[a] Referenced to 100%; oxygen values were determined to be <2 at. %, hydrogen <0.1 at. %; both values are neglected.

[b] Referenced to Si_3.

[c] Polymer composition in parentheses, hydrogen values are neglected.

the polymers and the respective polymer-derived materials (Table 1) shows that the Si:B ratio ∼3:1 in the starting polymers is retained in the ceramics. The different nitrogen contents in the polymers are reflected in corresponding nitrogen values in the ceramic materials, since the Si:N ratio likewise remains almost unchanged. A slight deviation from this series is only observed for materials derived from the nitrogen-rich polymers $\mathbf{3}_{cat}$ and $\mathbf{4}_{cat}$, most likely due to thermally induced *trans*-amination reactions that occurred during thermolysis. The lower nitrogen contents in $\mathbf{3}_{neat}$ and $\mathbf{4}_{neat}$ polymers, compared with the $\mathbf{3}_{cat}$ and $\mathbf{4}_{cat}$ polymers (compare Tables 1 and 5), result in lower nitrogen contents of the corresponding ceramics: 22.8 at. % ($\mathbf{3}_{neat}$) versus 38.0 at. % ($\mathbf{3}_{cat}$) and 17.7 at. % ($\mathbf{4}_{neat}$) versus 27.8 at. % ($\mathbf{4}_{cat}$). In contrast, there is no clear trend observed for the carbon contents in the polymers and the polymer-derived materials. This is a consequence of the evaporation of gaseous species during thermolysis, which are primarily composed of carbon and hydrogen, as was determined by TGA coupled with mass spectrometry for structurally comparable precursors.[37–39] However, even though fragment ions with $m/z > 58$ were not observed, it cannot be excluded that heavy monomers or oligomers are also volatilized but not detected due to their condensation in colder parts of the apparatus.

The results of the HT-TGA are presented in Fig. 3. They reveal a significant difference in the high-temperature mass stability of the materials. Ceramics derived from **1**, $\mathbf{3}_{cat}$ and $\mathbf{4}_{cat}$ decompose around 1450–1550 °C, which is the typical temperature range where ternary SiCN materials decompose.[75–77] Materials obtained from **2**, $\mathbf{3}_{neat}$ and $\mathbf{4}_{neat}$, in contrast, start to decompose above 1900 °C.

The first steps in the decomposition of **1** (20 mass%) and $\mathbf{3}_{cat}$ (30 mass%) are caused by the

Table 2 Calculated phase fractions (moles of atom%)[72–74] of ceramic materials obtained from polymers **1–4**, presuming complete crystallization into thermodynamically stable phases

	1	**2**	$\mathbf{3}_{neat}$	$\mathbf{3}_{cat}$	$\mathbf{4}_{neat}$	$\mathbf{4}_{cat}$
BN	19.6	18.0	14.6	15.0	15.2	17.8
Si_3N_4	37.8	16.8	27.1	50.4	17.7	33.1
SiC	21.0	34.0	19.8	0	28.3	13.2
C	21.6	31.2	39.5	32.9	38.8	35.9
(N_2)				(1.7)		

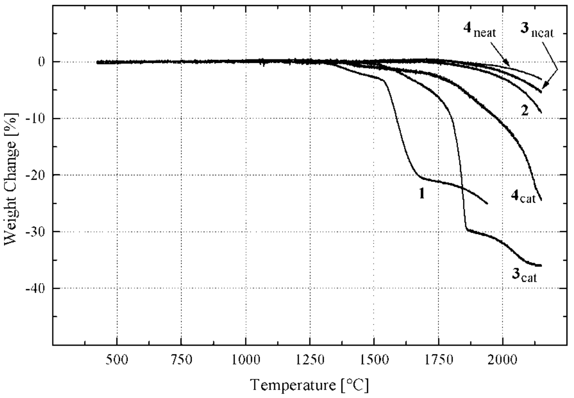


Figure 3 HT-TGA of the ceramic materials obtained from **1**–**4**. Heating rate $T < 1400$ °C: 5 °C min^{-1}, $T > 1400$ °C: 2 °C min^{-1}; argon atmosphere.

reaction of silicon-bonded nitrogen with carbon. By presuming de-mixing of the amorphous materials into thermodynamically stable phases, these reactions proceed according to $Si_3N_4 + 3C \rightarrow 3SiC + 2N_2$. The calculated phase fractions of the materials obtained from **1–4** are given in Table 2. From these data it can be concluded that silicon nitride decomposition in **1** causes the loss of 21.6 at. % (18 mass%) of nitrogen, whereas the loss of 30.5 at. % (27 mass%) of nitrogen is expected for $\mathbf{3}_{cat}$ ceramic. Both values are roughly observed in the HT-TGA depicted in Fig. 3. The second step in the decomposition of the materials is not understood in detail, but is most likely due to the reaction of carbon and boron nitride with the formation of boron carbide and nitrogen. An unusual finding in the calculated phase composition of $\mathbf{3}_{cat}$ ceramic is the presence of 1.7 mol at. % of nitrogen (see Table 2, value in parentheses) and the lack of a silicon carbide phase. However, this finding may be due to the 1.0 mass% relative error in the measurements of the elemental analysis and must thus be discussed carefully.

It was published recently that the extraordinary high-temperature stability in Si–B–C–N ceramics can be explained by the presence of a turbostratic non-stoichiometric B–C–N phase that inhibits diffusion processes and decreases the activity of free carbon,[78,79] which is present in all known Si–B–C–N ceramics of that general type.[36–43,59–61] A further important prerequisite for obtaining high-temperature stable materials is that the amount of silicon nitride does not exceed a certain value.[39] This is also valid for the materials described here. Whereas the least stable ceramics derived from **1** and $\mathbf{3}_{cat}$ contain silicon nitride phase fractions of 37.8 mol at. % and 50.4 mol of at. % respectively, this value is 33 mol at. % for the $\mathbf{4}_{cat}$ material. Its decomposition also starts at 1550 °C, but in comparison with **1** and $\mathbf{3}_{cat}$ ceramics the process is retarded. In contrast, the amount of silicon nitride in materials **2**, $\mathbf{3}_{neat}$ and $\mathbf{4}_{neat}$, which decompose between 1900 and 2000 °C, is below 30 mol at. % (see Table 2).

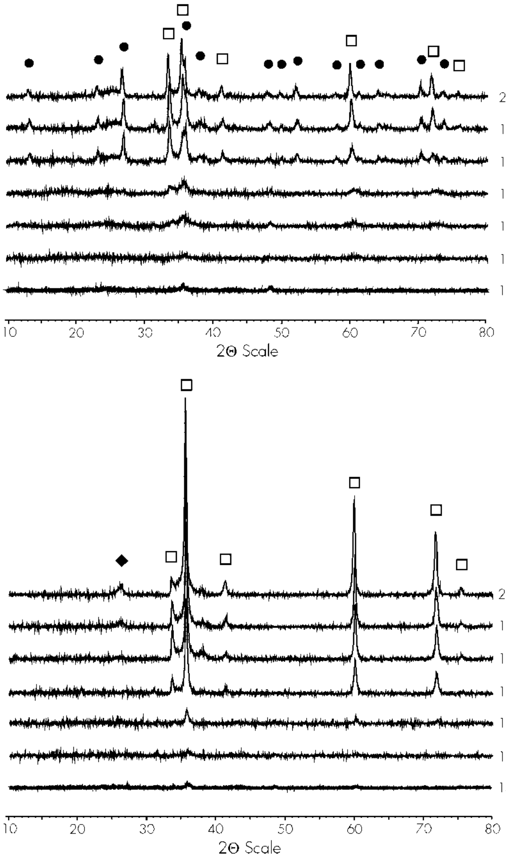


Figure 4 XRD patterns of annealed ceramics obtained from $\mathbf{3}_{neat}$ (top) and $\mathbf{3}_{cat}$ (bottom) at 1400–2000 °C (100 °C steps, 1 bar nitrogen) each for 3 h. In the case of the $\mathbf{3}_{neat}$ material α/β-SiC (□) and β-Si_3N_4 (●) reflections are observed, whereas in the case of the $\mathbf{3}_{cat}$ ceramic α/β-SiC (□) reflections are found. A reflection at $2\Theta = 26.3$ ° in the latter materials arising at 1900 and 2000 °C points to the crystallization of graphite (◆).

The different thermal stabilities of the ceramics observed by HT-TGA are nicely reflected in their crystallization behavior. For this, ceramics were annealed for 3 h in carbon crucibles in a purified nitrogen atmosphere (1 bar) at various temperatures in the range 1400–2000 °C.

The above-mentioned trend, i.e. the dependence of the high-temperature stability on the silicon nitride content, is supported by comparing the phase evolution of annealed silicon-nitride-'poor' $\mathbf{3}_{neat}$ and silicon-nitride-'rich' $\mathbf{3}_{cat}$ material using XRD. As-obtained $\mathbf{3}_{neat}$ ceramic is fully amorphous. Very broad reflections arising at 1600 °C at $2\Theta = 36°$ and $60.5°$ point to the formation of nanocrystalline silicon carbide (□). At 1800 °C these reflections sharpen remarkably and confirm the proposed silicon carbide crystallization. Moreover, β-silicon nitride reflections (●) appear at this temperature and remarkably do not decrease in intensity, even at 2000 °C. This observation is very unusual, since under the conditions applied it is expected that silicon nitride decomposes into the elements according to $Si_3N_4 \rightarrow 3Si + 2N_2$. In contrast to $\mathbf{3}_{neat}$ ceramic, $\mathbf{3}_{cat}$ material starts to crystallize at lower temperature. There are sharp silicon carbide reflections (□) observed already at 1600 °C. These increase substantially in intensity at 1700 °C. Considering the results of the elemental analysis and the thermodynamic calculations given in Table 2, the appearance of silicon carbide reflections can be traced to silicon nitride decomposition in the presence of free carbon, as mentioned above. As a consequence, the most distinctive difference in the X-ray patterns of annealed $\mathbf{3}_{neat}$ and $\mathbf{3}_{cat}$ ceramic is the absence of silicon nitride reflections in the latter material. In addition, the remarkably lower signal-to-noise ratio in $\mathbf{3}_{neat}$ ceramic indicates a lower crystallinity, *i.e.* smaller crystallite sizes in this material. A surprising finding in the XRD patterns of the $\mathbf{3}_{cat}$ material is the appearance of a broad reflection at $2\Theta = 26.3°$ (◆) evolving at 1900 °C and further sharpening at 2000 °C. This reflection can unequivocally be assigned to crystalline graphite. It is, to our knowledge, the first time that crystalline carbon has been observed in Si–B–C–N ceramics. In contrast, the presence of crystalline boron-containing phases can be excluded in all materials.

Summarizing the findings of the HT-TGA and the X-ray investigations, it can be assumed that a rearrangement of the amorphous materials with formation of crystalline phases is not necessarily accompanied by the degradation of the ceramic composites, *i.e.* the loss of nitrogen due to silicon nitride decomposition. However, it is an important detail that materials that have a retarded mass loss up to or exceeding 1900 °C crystallize around 1800 °C, forming both silicon nitride and silicon carbide crystalline phases, whereas the less thermally stable Si–B–C–N ceramics that lose nitrogen crystallize around 1600 °C.

Conclusions

Dehydrocoupling of tris(hydridosilylethyl)boranes and ammonia or amines is a suitable method for synthesizing highly cross-linked boron-modified polysilazanes. Depending on the nucleophilic strength of the amine used, this reaction has to be performed either with or without catalyst. Suitable catalysts are strong bases, such as *n*-butyl lithium, which initially deprotonate ammonia, or amines to originate more highly nucleophilic amides. These replace silicon-bonded hydrides and form the polymer skeleton. The ceramic yield after the polymer-to-ceramic conversion depends strongly on the molecular structure of the polymers. Increased cross-linking of the polymeric framework and low molecular silicon- or nitrogen-bonded substituents cause high ceramic yields. In contrast, insufficient cross-linking and bulky groups, such as methyl, that are attached to the polymer skeleton cause a significant mass loss during thermolysis, and thus low ceramic yields. The chemical composition of the ceramics is affected strongly by the molecular structure and the composition of the preceramics. Whereas the Si:B ratio in all precursors is at ~3:1, carbon and nitrogen contents vary over a wide range. The high-temperature stability of the as-obtained materials essentially depends on their nitrogen content, *i.e.* the amount of silicon nitride that can be calculated thermodynamically. Excessive silicon nitride causes degradation of the ceramics by either decomposition into the elements or, more likely, reaction with free carbon with the formation of silicon carbide and molecular nitrogen.

EXPERIMENTAL SECTION

General comments

All reactions were carried out in a purified argon atmosphere using standard Schlenk techniques. This preparative method is based on experiments developed by the German chemist Wilhelm Schlenk. All apparatus is equipped with sidearms for pumping out the air and moisture and introducing inert gas. See also: Ref 80. Tris(hydridosilylethyl)boranes, $B[C_2H_4Si(CH_3)_nH_{3-n}]_3$ ($n = 0,\ 1$) were obtained according to Ref 63. Ammonia and methylamine were dried with KOH prior to their use. Tetrahydrofuran and toluene were purified by distillation from potassium; hexane was distilled

Table 3 IR spectroscopic data of compounds **1–4**

	1	**2**	$\mathbf{3}_{\mathrm{neat}}$	$\mathbf{3}_{\mathrm{cat}}$	$\mathbf{4}_{\mathrm{neat}}$	$\mathbf{4}_{\mathrm{cat}}$
ν(N—H)	3384 br	3380 br	3422 vw	3402 vw	3406 vw	3410 vw
ν(C—H)	2949 s, 2906 m, 2869 m	2954 m, 2905 m, 2868 m	2928 m, 2882 s, br	2949 sh, 2929 s, 2882 s	2954 m, 2893 m, 2870 m	2952 s, 2940 sh, 2893 s
ν(NC—H)			2804 m	2807 m	2807 m	2810 m
νSi—H	2138 s	2124 s	2091 s	2085 w	2108 sh, 2086 m	2120 sh, 2098 vw
δ_a(C—) CH_3	1462 m	1459 m	1461 w	1460 w	1460 w	1460 m
δ_s(C—) CH_3	1378 m	1409 s	1374 w	1363 m	n.o.	1396 s
δ_s(Si—) CH_3	–	1252 s	–	–	1252 s	1252 s
$\delta SiCH_2C$		1167 s	1181 w	1192 m	1181 m	1189 m
νC—B—C	1081 w	1180 s	1083 s	1069 s	1080 s	1093 m
δN—H	1164 vs, br	n.o.	n.o.	n.o.	n.o.	n.o.
νN—Si—N		893 vs	884 vs, 844 vs	942 s, 897 vs	923 sh, 890 vs	923 sh, 887 vs

n.o. not observed.

from calcium hydride. *n*-Butyl lithium from Sigma Aldrich GmbH was used as a 2 M solution in *n*-hexane.

Fourier-transformed IR spectra were obtained with a Bruker IFS66 spectrometer using a KBr matrix. Solid-state NMR experiments were performed with a Bruker CXP 300 or a Bruker MSL 300 spectrometer operating at a static magnetic field of 7.05 T (nominal ^1H frequency: 300.13 MHz) using a 4 mm MAS probe. ^{29}Si and ^{13}C NMR spectra were recorded at 59.60 and 75.47 MHz using the CP technique, in which a spin lock field of 62.5 kHz and a contact time of 3 ms were applied. Typical recycle delays were 6 to 8 s. All spectra were acquired using the MAS technique with a sample rotation frequency of 5 kHz. ^{29}Si and ^{13}C chemical shifts were determined relative to external standard Q_8M_8, the trimethylsilylester of octameric silicate, and adamantane. These values were then expressed relative to the reference compound tetramethylsilane (0 ppm).

Elemental analysis was performed using various apparatus (ELEMENTAR, Vario EL CHN-Determinator; ELTRA, CS 800, C/S Determinator; LECO, TC-436, N/O Determinator) and by atom emission spectrometry (ISA JOBIN YVON JY70 Plus). TGA of the polymer-to-ceramic conversion was carried out in flowing argon atmosphere (50 cm^3 min^{-1}) in alumina crucibles with Netzsch STA 409 (25–1450 °C; heating rate 2 °C min^{-1}) equipment. Bulk ceramization of preceramic material was performed in alumina Schlenk tubes in flowing argon at 25–1400 °C, heating rate 1 °C min^{-1} and a dwell time of 3 h. HT-TGA of the as-obtained ceramic samples was performed using carbon crucibles in an argon atmosphere (25–2150 °C; heating rate $T < 1400$ °C: 5 °C min^{-1}; $T > 1400$ °C: 2 °C min^{-1}) using a Netzsch STA 501 equipment. The crystallization of as-obtained amorphous ceramics was investigated in graphite furnaces using graphite crucibles at 1400 °C and 1500–2000 °C (100 °C steps; heating rate $T < 1400$ °C: 10 °C min^{-1}; $T > 1400$ °C: 2 °C min^{-1}). The XRD was performed using a Siemens D5000/Kristalloflex diffractometer (Cu Kα_1 radiation), equipped with an OED and a quartz primary monochromator.

Synthesis of $\{B[C_2H_4Si(R)NH]_3\}_n$ [1, R = $(NH)_{0.5}$; 2, R = CH_3]

In a 1000 ml Schlenk flask equipped with a CO_2/i-PrOH reflux condenser and a gas inlet tube, 20 g of $B(C_2H_4SiH_3)_3$ (106.4 mmol) or 15.8 g $B[C_2H_4Si(CH_3)H_2]_3$ (68.6 mmol) were dissolved in a mixture 400 ml of toluene and 100 ml of tetrahydrofuran. After adding 2 M *n*-BuLi in *n*-hexane (1 mol% relative to the starting compounds), the colorless solutions were heated to 70 °C and excess ammonia was slowly introduced. During the synthesis of $\{B[C_2H_4Si(NH)_{1.5}]_3\}_n$ (**1**) strong hydrogen evolution was observed, whereas only moderate hydrogen evolution was observed during the synthesis of $\{B[C_2H_4Si(CH_3)NH]_3\}_n$ (**2**). In both reactions, precipitation of a white solid was observed After approximately 6 h all volatile components were removed in vacuum (50 °C/ 10^{-2} mbar) and the colorless residues were ex-

Table 4 NMR spectroscopic data (ppm) of compounds **1–4**

	1	**2**	$\mathbf{3}_{\mathrm{neat}}$	$\mathbf{3}_{\mathrm{cat}}$	$\mathbf{4}_{\mathrm{neat}}$	$\mathbf{4}_{\mathrm{cat}}$
^{13}CNMR						
$\mathrm{Si}\mathit{C}\mathrm{H}_3$	–	−7.8, 2.2	–	–	−2.7	−3.3
$\mathrm{CH}\mathit{C}\mathrm{H}_3$	11.1	10.7	11.9^{a}	8.8	10.9	7.8
$\mathrm{N}\mathit{C}\mathrm{H}_3$	–	–	28–33^{a}	28.9	31.1	29.3
$\mathit{C}\mathrm{HCH}_3$	25.1	^{b}	25.5^{a}		24.7 sh	25.5 sh
$\mathit{C}\mathrm{H}_2{}^{b}$	16.7 sh	15.6 sh	15.5^{a}	13.3	17.8	15.3 sh
^{29}SiNMR						
	−44.0 sh	−28.4	−14.0 vbr	−14.4	−0.5–7.0	0–2.5
	$\mathit{Si}\mathrm{HN}_2\mathrm{C}$	$\mathit{Si}\mathrm{H}_2\mathrm{C}_2$	$\mathit{Si}\mathrm{N}_3\mathrm{C}$	$\mathit{Si}\mathrm{N}_3\mathrm{C}^{c}$	$\mathit{Si}\mathrm{N}_2\mathrm{C}_2{}^{c}$	$\mathit{Si}\mathrm{N}_2\mathrm{C}_2$
	−19.5 vbr	−6.8 to −4.3	−28.4		−27.6	
	$\mathit{Si}\mathrm{N}_3\mathrm{C}$	$\mathit{Si}\mathrm{N}_2\mathrm{C}_2$	$\mathit{Si}\mathrm{HN}_2\mathrm{C}$		$\mathit{Si}\mathrm{H}_2\mathrm{C}_2$	

[a] Spectrum recorded in C_6D_6 solution.
[b] These signals overlap with $CHCH_3$.
[c] Spectrum recorded in tetrahydrofuran solution.

tracted three times each with 50 ml of *n*-hexane to deliver 24.2 g of compound **1** (98.1 mmol, 93%) and 15.8 g of compound **2** (58.8 mmol, 86%), each as a colorless solid. Both polymers are extremely sensitive to moisture and/or oxygen and insoluble in common organic solvents. Whereas **1** does not melt or soften without decomposition (>250 °C), **2** softens at ~120 °C. For spectroscopic details see Tables 3 and 4; for elemental analysis see Table 5.

Synthesis of $\{B[C_2H_4Si(R)NCH_3]_3\}_n$ [3, $R = (NCH_3)_{0.5}$; 4, $R = CH_3$]

The synthesis of **3** and **4** was performed under differing conditions. First, according to the procedure described for the synthesis of **1** and **2**, and second because of the more highly nucleophilic character of methylamine compared with ammonia, it was carried out in tetrahydrofuran solution without catalyst. To differentiate between the formally equal polymers the subscripts 'cat' (synthesis in the presence of catalyst, *e.g.* $\mathbf{3}_{\mathrm{cat}}$) and 'neat' (synthesis without catalyst, *e.g.* $\mathbf{3}_{\mathrm{neat}}$) are used. For the reaction without catalyst, $B(C_2H_4SiH_3)_3$ or $B[C_2H_4Si(CH_3)H_2]_3$ were dissolved in tetrahydrofuran and a twofold excess of methylamine was introduced at 0 °C. The reaction mixtures were then heated to 60 °C for 6 h.

Table 5 Calculated and analyzed elemental composition and formulas of polymers **1–4**

Polymer	*Calculated* (Found)^{a} (mass%)	*Ideal formula*^{b} (Found)
1	H: 6.74; C: 29.20; N: 25.53; B: 4.38; Si: 34.15 (H: 7.7; C: 29.7; N: 19.5; B: 4.7; Si: 38.4)	$Si_3BC_6N_{4.5}H_{16.5}$ $(Si_3BC_{7.3}N_{3.1}H_{16.8})$
2	H: 8.98; C: 40.13; N: 15.60; B: 4.01; Si: 31.28 (H: 9.35; C: 43.75; N: 11.0; B: 4.30; Si: 31.60)	$Si_3BC_9N_3H_{24}$ $(Si_3BC_{9.7}N_{2.1}H_{25})$
$\mathbf{3}_{\mathrm{neat}}$	H: 8.29; C: 40.70; N: 20.33; B: 3.49; Si: 27.19 (H: 9.66; C: 41.00; N: 15.14; B: 4.03; Si: 30.17)	$Si_3BC_{10.5}N_{4.5}H_{25.5}$ $(Si_3BC_{9.5}N_{3.0}H_{26.8})$
$\mathbf{3}_{\mathrm{cat}}$	H: 8.29; C: 40.70; N: 20.33; B: 3.49; Si: 27.19 (H: 9.05; C: 42.0; N: 22.42; B: 3.05; Si: 23.40)	$Si_3BC_{10.5}N_{4.5}H_{25.5}$ $(Si_3BC_{12.5}N_{5.7}H_{32.2})$
$\mathbf{4}_{\mathrm{neat}}$	H: 9.71; C: 46.28; N: 13.49; B: 3.47; Si: 27.05 (H: 10.17; C: 45.5; N: 12.3; B: 3.72; Si: 28.33)	$Si_3BC_{12}N_3H_{30}$ $(Si_3BC_{11.3}N_{2.6}H_{30})$
$\mathbf{4}_{\mathrm{cat}}$	H: 9.71; C: 46.28; N: 13.49; B: 3.47; Si: 27.05 (H: 10.12; C: 46.63; N: 17.48; B: 3.48; Si: 22.30)	$Si_3BC_{12}N_3H_{30}$ $(Si_3B_{1.2}C_{14.7}N_{4.7}H_{37})$

[a] Referenced to 100%; oxygen values are <2 mass% and neglected.
[b] Chemical formula per monomer unit.

Subsequently, all the volatile components were removed in high vacuum (80 °C/10^{-2} mbar). The precursors were obtained as extremely viscous ($\mathbf{3}_{\mathrm{cat}}$, 96%; $\mathbf{3}_{\mathrm{neat}}$, 100%) or as viscous ($\mathbf{4}_{\mathrm{cat}}$, 92%; $\mathbf{4}_{\mathrm{neat}}$, 100%) colorless and air-sensitive oils, which aged rapidly. For spectroscopic details see Tables 3 and 4; for elemental analysis see Table 5.

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