The synthesis, by two different reaction pathways, of boron-modified polysilylcarbodi-imides of general type \{B[C_2H_4Si(R)NCN]_3\}_n (R = singly bonded organic ligand) and the plastic-forming and the thermal behavior of these polymers are described. Compounds \{B[C_2H_4Si(R)NCN]_3\}_n [2a, R = H; 2b, R = CH_3; 2c, R = (NCN)_{0.5}] can be obtained by treatment of the vinyl-substituted polysilylcarbodi-imides [(H_2C=CH)(R)SiN=C=N]_n [1a, R = H; 1b, R = CH_3; 1c, R = (NCN)_{0.5}] with borane dimethylsulfide BH_3. The polysilylcarbodi-imides 1a–1c themselves are accessible via the reaction of vinyl-substituted chlorosilanes (H_2C=CH)(R)SiCl_2 with cyanamide H_2N-C≡N in the presence of pyridine or by a non-oxide sol–gel process of vinylated chlorosilanes and bis(trimethylsilyl)carbodi-imide, (H_3C)₃SiN=C=N-Si(CH_3)_3. In the second method for the synthesis of 2a–2c, hydroboration of vinyl-substituted chlorosilanes (H_2C=CH)(R)SiCl_2 with borane dimethylsulfide, borane trimethylamine or borane triethylamine to yield the tris[(cholorosilyl)ethyl]boranes B[C_2H_4Si(R)Cl_2]_3 (3a, R = H; 3b, R = CH_3; 3c, R = Cl) is followed by treatment of the as-obtained compounds with bis(trimethylsilyl)carbodi-imide, which results in the formation of the hydroborated polysilylcarbodi-imides 2a–2c. The thermogravimetric behavior of the polymers 1a–1c and 2a–2c up to 2300°C is reported. It is shown that boron-modified polysilylcarbodi-imides are suitable precursors for the preparation of dense bulk ceramics. Therefore, the preparation of green bodies of the hydroborated polysilylcarbodi-imides 2a–2c by plastic forming (PF) is described. A series of experiments points to the fact that the microstructure of the as-obtained ceramic monoliths obtained by subsequent thermolysis of the plastic-formed green bodies is strongly influenced by the conditions during plastic forming. © 1998 John Wiley & Sons, Ltd.

Keywords: precursor; ceramic; thermolysis; silicon; carbodi-imide; boron; hydroboration; plastic forming

Received 1 July 1997; accepted 1 August 1997

1 INTRODUCTION

Boron-containing polycarbosilazanes,1–4 carbon-containing polyborosilazanes5,7 and silylated borazine derivatives8–12 have been shown to be excellent precursor molecules to ceramic composite materials in the quaternary system Si–B–C–N. These molecules in general consist of Si–N skeletons, which are more or less crosslinked by B, B–N, B–C or borazine units, carrying different substituents bonded to the silicon centers. The synthesis of the Si–B–C–N precursors is commonly realized either by reaction of chlorosilanes or chloroboranes with amines or ammonia,1–7 or by dehydrogenative coupling reactions of silazanes with derivatives of borane or of borazine.8–12

The polymeric precursors are then transformed
into amorphous Si–B–C–N ceramic materials by subsequent thermolyses (for selected reviews, see Refs 13–16 and literative cited therein). Due to the considerable sensitivity of these compounds towards moisture and oxygen, the ceramization step has to be performed in an inert-gas atmosphere. In some cases, the as-obtained Si–B–C–N ceramic composites exhibit excellent thermochemical properties, which can be attributed to the presence of nanocrystalline SiC and Si₃N₄ surrounded by turbostratic BN(C) segregations. 13,15,17–19 These inhibit the thermodynamically favored decomposition of the Si–B–C–N ceramics kinetically. Therefore, the multicomponent Si–B–C–N ceramics are interesting materials for high-temperature applications in industry.

Moreover, we have shown that solutions of polymers containing the elements silicon, boron, carbon, nitrogen and hydrogen of convenient viscosity are applicable for coatings on non-oxide composite materials in order to protect the substrate efficiently from oxidation and corrosion, especially at very high temperatures. 20–22

In this study, we describe two different syntheses and the plastic-forming and high-temperature behavior of a new class of Si–B–C–N precursors, the boron-modified polysilylcarbodi-imides. In contrast to known Si–B–C–N precursors, these compounds consist of repeating Si-N=C=N units, which are crosslinked by C–B–C bridges. 23,24 Depending on the monomeric starting compounds (H₂C=CH)(R)SiCl₂ (R = H, CH₃, Cl) and the reaction pathway applied, ceramic materials with various compositions, microstructures and thermal behaviors are obtained.

PRECURSOR SYNTHESIS

Synthesis of vinyl-substituted polysilylcarbodi-imides

We showed previously that boron-modified polysilylcarbodi-imides are accessible by different reaction sequences. 23,24 A possible synthesis of the title compounds \([B(C₃H₆Si(R)NCN)]ₙ\) [2a, R = H; 2b, R = CH₃; 2c, R = (NCN)₀.₅] is given by hydroboration of vinylated polysilylcarbodi-imides of the \([(H₂C=CH)(R)SiNCN]ₙ\) type (R = singly bonded organic ligand) with suitable borane compounds, e.g. borane dimethylsulfide, BH₃*S(CH₃)₂. The syntheses of vinyl-substituted polysilylcarbodi-imides \([(H₂C=CH)(R)SiNCN]ₙ\) [1a, R = H; 1b, R = CH₃; 1c, R = (NCN)₀.₅] themselves, which have been described previously for compound 1b, 25,26,27 can be performed by the reaction of \((H₂C=CH)(R)SiCl₂\) (R = H, CH₃, Cl) with H₂N-C≡N in the presence of pyridine (Py) in tetrahydrofuran (THF) solution, Eqn [1].

\[
\begin{align*}
H₂C=CH₂ & \quad + \quad H₂N-C≡N + \quad Py \quad \rightarrow \quad H₂C=CH₂ \quad - \quad \text{THF, 0°C} \quad - \quad Py·HCl
\end{align*}
\]

\[\text{R = H, CH₃, Cl}\]

\[1a \quad R = H\]

\[1b \quad R = CH₃\]

\[1c \quad R = \text{(NCN)₀.₅}\]

Therefore, the vinylchlorosilanes are dissolved in THF and a pyridine/cyanamide solution is added carefully at 0°C. After appropriate work-up, the polysilylcarbodi-imides 1a–1c are obtained as colorless waxy solids (1a, 1b) and as a colorless powder (1c). Whereas 1a and 1b can be isolated in high yields (1a, 85%; 1b, 78%), the maximum yield for the polysilylcarbodi-imide 1c was 15% via this reaction sequence. This is possibly caused by the higher crosslinkage and therefore the lower solubility of this precursor compared with polymers 1a and 1b. This finally results in a significant product loss during the filtration. Furthermore, compounds 1a–1c are also available by the reaction of bis(trimethylsilyl)carbodi-imide, which itself was synthesized from cyanamide, trimethylchlorosilane and pyridine, with the corresponding vinylchlorosilanes \((H₂C=CH)(R)\text{SiCl₂}\) (Eqn [2]). As-obtained bis(trimethylsilyl) carbodi-imide contains traces of pyridine which catalyze the trans-silylation adequately. In comparison, the use of pure bis(trimethylsilyl)carbodi-imide is less effective for this reaction. Hence, the reaction times increase considerably.

\[
\begin{align*}
H₂C=CH₂ & \quad + \quad (H₂C₂Si₂N=C≡N-Si(CH₃)₂)₂ \quad \rightarrow \quad H₂C=CH₂ \quad - \quad \text{THF, 0°C} \quad - \quad (H₂C₂Si₂N=C≡N-Si(CH₃)₂)₂
\end{align*}
\]

\[\text{Py·HCl} \quad \text{25°C} \quad - \quad (H₂C₂Si₂N=C≡N-Si(CH₃)₂)
\]

\[\text{R = H, CH₃, Cl}\]

\[1a \quad R = H\]

\[1b \quad R = CH₃\]

\[1c \quad R = \text{(NCN)₀.₅}\]

We have shown that this trans-silylation reaction can be carried out under different conditions. Performing the synthesis of compounds 1a–1c in toluene solutions results in the precipitation of the products as colorless powders (1a, 70%; 1b, 58%; 1c, 78%). Therefore, the reaction mixtures have to be refluxed for seven days or longer.

Much more convenient is the synthesis of compounds 1a–1c without solvent. The educts are carefully mixed at room temperature, even stoichiometrically [1a, 1b, 1 mol bis(trimethylsilyl)-
carbodi-imide per mol \((H_2C=CH)(R)SiCl_2\); 1c, 1.5 mol bis(trimethylylsilyl)carbodi-imide per mol \((H_2C=CH)SiCl_3\) or with a slight excess of bis(trimethylylsilyl)carbodi-imide and stirred for an additional three hours. To quantify the reaction, the material is then slowly heated to 90°C to distill off built-up trimethylchlorosilane. To remove residual \((H_2C)SiCl_3\) and possibly excess bis(trimethylylsilyl)-
carbodi-imide, the as-obtained polymers are finally dried at 70°C in high vacuum. The yields of the products are 80% (1a), 87% (1b) and 85% (1c). These investigations indicate that the syntheses of compounds of the \([H_2C=CH]R)SiNCN\) type [1a, \(R = H\); 1b, \(R = CH_3\); 1c, \(R = (NCN)_{0.5}\)] are best performed by reacting the chlorosilanes \((H_2C=CH)(R)SiCl_3\) and bis(trimethylylsilyl)carbodi-imide without solvent even though the syntheses of 1a–1c by the reaction of cyanamide and the chlorosilanes are somewhat cheaper. The main advantages of the \(trans\)-silylation reactions, compared with the synthesis of the polysilylcarbodi-imides by a salt-elimination process, are the simplified work-up and the possibility of isolating the more highly crosslinked polymer 1c in outstanding yields. This, and especially the possibility of avoiding use of solvent, make these reactions interesting for industrial applications.

**Synthesis of Si–B–C–N precursors from polysilylcarbodi-imides**

The as-obtained polysilylcarbodi-imides carry vinyl units which can easily be hydroborated with suitable borane reagents. It was found that borane dimethylsulfide adds onto the vinyl units fast and selectively; an addition onto the carbodi-imide grouping as described by Kienzle et al., who applied higher temperatures,2,13,14 could not be observed.

Therefore the vinylated polysilylcarbodi-imides were dissolved (1a, 1b) or suspended (1c) in toluene/THF, and a 2 M solution of borane dimethylsulfide was added slowly at 0°C. The reaction mixtures clouded immediately and the products \(\{B[C_2H_4Si(R)NCN]_3\}_{n} 2a, R = H; 2b, R = CH_3; 2c, R = (NCN)_{0.5}\) were directly precipitated from these solutions due to their high degree of crosslinkage (Eqn [3]). After being stirred for an additional 2h at 25°C the solvent and dimethylsulfide could be removed in high vacuum to yield the boron-modified polysilylcarbodi-imides quantitatively as colorless powders. No further work-up was performed.

The less reactive amine trialkylamides of general type \(R_3N*BH_3\) (\(R = H, CH_3, C_2H_5\)) could also be used, but in this case the reaction times increased considerably and for a complete permutation the reaction mixtures had to be refluxed over a period of several days.

The structures of the boron-modified polysilylcarbodi-imides obtained from the vinyl-substituted polymers \([H_2C=CH]R)SiNCN\) [1a, \(R = H\); 1b, \(R = CH_3\); 1c, \(R = (NCN)_{0.5}\)] could be assigned unequivocally by spectroscopic methods. Whereas the C=C stretching vibrations in the FT IR spectra of compounds 1a–1c are observed at approx. 1595 cm\(^{-1}\), these absorption signals are not found in the corresponding product spectra. Moreover, compounds 2a–2c show very strong absorption signals for the asymmetric stretching of the carbodi-imide groupings at 2236 (1a), 2232 (1b) and 2168 cm\(^{-1}\) (1c), respectively. This indicates that the hydroboration takes place exclusively at the vinyl units. Neither addition to the N=C=N grouping nor B–H stretching absorption is observed by this spectroscopic method. Similar observations can be made in the \(^{13}\)C{\(^1\)H} CP-MAS (cross-polarization/magic angle spinning) NMR spectra. While the olefinic carbon atoms of compounds 1a–1c show resonance signals at approx. 130–135 ppm, the signals of the corresponding carbon atoms of the boron-modified products 2a–2c are found at approx. 5.0 (CH\(_3\)), 10.0 (CH\(_2\)) and 25.0 ppm (CH), whereby the boron-bonded carbon atoms are detected with the typical line broadening. Moreover, an addition of the hydroboration reagent boran dimethylsulfide to the carbodi-imide unit, which would directly be reflected in a chemical shift of the carbodi-imide carbons in 1a–1c at approx. 122–125 ppm to higher field, is not observed.

**Synthesis of Si–B–C–N precursors from tris[(chlorosilyl)ethyl]boranes**

An alternative process which finally results in the formation of boron-modified polysilylcarbodi-imides involves reaction of tris[(chlorosilyl)ethyl]boranes\(^{28}\) of the general type \(B[C_2H_4Si(R)Cl]_3\) (3) with bis(trimethylylsilyl)carbodi-imide.\(^{23,24}\) The pro-

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products \(3\) are available on adding a toluene solution of borane dimethylsulfide, borane trimethylamide or borane triethylamine to the corresponding vinylated chlorosilanes \((H_2C=CH(R)SiCl_2; R = H, CH_3, Cl)\) in a 1:3 molar ratio (Eqn [4]). After distillation in vacuum \((10^{-2}\ \text{mbar}; \ 3a, \ 102^\circ\text{C}; \ 3b, \ 105^\circ\text{C}; \ 3c, \ 115^\circ\text{C})\), compounds \(B(C_2H_4Si(R)Cl_2)_3\) \((3a, R = H; \ 3b, R = CH_3; \ 3c, R = Cl)\) are obtained as colorless, highly air-sensitive oils in 95% yield.

\[
\begin{align*}
3 & \text{Cl-Si-Cl + BH_2} + \text{Do} \rightarrow \text{H}_2C=CH\text{Si-Do-Cl} \\
\text{Do} & = \text{SiMe}_2, \text{NMe}_3, \text{NIT}_3,
\end{align*}
\]

![Reaction Scheme](image)

In contrast to the well-known hydroboration of olefinic hydrocarbons, the addition of \(B-H\) to a silylated olefin is not regioselective. Depending on the silicon-bonded substituent \(R\), \(\alpha\) and \(\beta\)-hydroboration both take place to various extents, directly reflected in the multiplet character of the \(C_2H_2\) and \(CH_3\) resonance signals in the \(^1\text{H}\) NMR and \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra in which the boron-bonded carbon atoms once more show the typical line broadening as mentioned above. The lower regioselectivity of the hydroboration of vinyl-substituted silanes compared with terminal olefinic hydrocarbons, which can result in the formation of \(\alpha\alpha\alpha\), \(\alpha\alpha\beta\), \(\alpha\beta\beta\) and \(\beta\beta\beta\)-hydroboration products, can also be observed in the \(^{29}\text{Si}\{^1\text{H}\}\) NMR spectra. Moreover, the \(\alpha\alpha\alpha\) and \(\alpha\beta\beta\) products exist as diastereotopic isomers which can also be distinguished in the NMR spectra. As an example, \(B(C_2H_4SiHCl_2)\) \((3a)\) obtained from \((H_2C=CH)SiHCl_2\) shows resonance signals at \(-6.5\) to \(-7.9\ \text{ppm} (\text{Si-CH}_3; \ \beta\)-hydroboration) and at approx. \(10.3\) to \(11.6\) and \(15.0\) to \(16.1\ \text{ppm} (\text{CH}_3); \ \alpha\)-hydroboration).\(^{23}\)

The pyridine-catalyzed synthesis of the boron-modified compounds \(\{B[C_2H_4Si(R)NCN]_3\}_n\) \((2a, R = H; \ 2b, R = CH_3; \ 2c, R = (NCN)_{0.5}\) from the reaction of the tris[(chlorosilyl)ethyl]boranes \(3a-3c\) and a slight excess of bis(trimethylsilyl)carbodi-imide (Eqn [5]) can be performed under various conditions. Whereas their reaction in boiling toluene solution leads to the precipitation of the precursors as colorless powders, the reaction without solvent results in the formation of compounds \(3a-3c\) as hard, glass-like materials. The greatest disadvantage of the former process is the slow reaction rate. Against this, the reaction of the educts without solvent occurs immediately and has finished in special cases within a few minutes. In a series of experiments it was found that the reaction time depends on the one hand on the tris[(chlorosilyl)ethyl]borane used: the reactivity of the starting compounds \(B[C_2H_4Si(R)Cl_2]_3\) towards bis(trimethylsilyl)carbodi-imide increases with respect to the substituent \(R\) in the order \(CH_3 < H < Cl\). Additionally, the reaction time is strongly influenced by the temperature applied and the size of the batch, so the latter has a direct effect upon the former: with increasing batch size, effective cooling of the viscous reaction mixture becomes more difficult. This finally results in a higher reaction temperature, which is directly reflected in an increased reaction rate.

\[
\begin{align*}
R' &= B(C_2H_4Si(R)Cl_2) \\
R' &= (CH_2)\cdot R \\
R' &= (NCN)_{0.5}
\end{align*}
\]

Riedel and co-workers investigated in detail the reaction coordinates of this kind of non-oxide sol–gel process for the synthesis of \(Si-C-N\) ceramic precursors from chlorosilanes and bis(trimethylsilyl)carbodi-imide.\(^{29-32}\) However, in this study the concentration of pyridine was identical in all experiments (bis[trimethylsilyl]carbodi-imide is obtained by the reaction of chlorotrimethylsilane, cyanamide and pyridine and therefore contains 0.5–1 mol% of the catalyst).

With respect to possible industrial applications of the boron-modified precursors, it should be mentioned that in addition to the very short reaction times observed for the synthesis of the polymers \(\{B[C_2H_4Si(R)NCN]_3\}_n\) from \(2a-2c\) and the elimination of the need for solvents, an attractive property of the whole process is that it works without waste: the chlorotrimethylsilane eliminated and the excess bis(trimethylsilyl)carbodi-imide can be recycled efficiently by distillation after the reactions have finished.

Compounds \(\{B[C_2H_4Si(R)NCN]_3\}_n\) \((2a, R = H; \ 2b, R = CH_3; \ 2c, R = (NCN)_{0.5})\) were identified by various spectroscopic methods and elemental analysis. First, solid-state \(^{13}\text{C}\{^1\text{H}\}\) CP-MAS NMR spectra of compounds \(2a-2c\) each depicted the resonance signal of the carbodi-imide carbon atoms at approx. 125 ppm (Table 1). This is very close to the resonances obtained for the boron-free...
vinyl-substituted polysilylcarbodi-imides of the \([\text{H}_2\text{C}=	ext{CH})(\text{R})\text{SiNCN}]_n\) type as well as those of the \(\text{CH}_3, \text{CH}_2\) and \(\text{CH}\) carbonatoms of the borated \(\text{C}_2\text{H}_4\) unit at 0–5, 10–12 and 24–27 ppm (Table 1). Terminal NCN-Si(\(\text{CH}_3\))\(3\) in compounds \(2a–2c\) as well as Si\(\text{CH}_3\) in compound \(2b\) overlap with \(\text{CH}_3\) from the \(\text{C}_2\text{H}_4\) units and cannot be separated.

Second, the \(^{29}\text{Si}\{^1\text{H}\} \text{CP-MAS NMR}\) spectra of the title compounds also showed the expected signals at 1–3 ppm for terminal NCN-Si(\(\text{CH}_3\))\(3\) groups and the silicon atoms bound in the polymer framework in the expected area (Table 1). Surprisingly, for compound \(2c\) a resonance signal was found at \(-36.2\) ppm which may correspond to a silicon with an \(\text{HCN}_2\) environment. The identity of this moiety is not clarified yet.

Finally, the \(^{11}\text{B}\{^1\text{H}\} \text{CP-MAS NMR}\) spectra of the boron-modified compounds \(2a–2c\) show resonances at approx. \(-12\) to \(+8\) ppm.

Moreover, FT IR spectroscopy identified the different functional groups in compounds \(2a–2c\), confirming the proposed structures of the isolated boron-modified polysilylcarbodi-imides. The most remarkable absorption signals detected are \(v(\text{C-H})\), \(v_{\text{as}}(\text{N}=\text{C}=\text{N})\), \(v(\text{Si-H})\) \((2a)\), \(\delta(\text{CH}_3)\), \(v(\text{Si-C})\) and \(v(\text{B-C})\) (Table 2). Signals for \(\text{Si-Cl}, \text{C}=\text{C}, \text{B-H}\) or \(\text{B-N}\) vibrations, which would indicate unintended side-reactions or non-quantitative educt-to-polymer conversions, were not observed.

### THERMOGRAVIMETRIC INVESTIGATIONS

The thermal conversion of elementorganic polymers into ceramics usually results in amorphous materials (see, for example, Refs 13–16 and 33–38). During this process, the oligomeric or polymeric precursors decompose with elimination of gaseous species. For the production of dense precursor-derived bulk ceramics, it is of interest to design the preceramics so that the mass loss during thermolysis is low, in order to inhibit the appearance of cracks and to minimize open porosity.

The polymer-to-ceramic conversion was monitored using thermogravimetric analysis (TGA), which was performed in a purified argon atmosphere in the temperature range 25–1100°C (heating rate 2°C min\(^{-1}\), Figs 1 and 2) for compounds \([\text{H}_2\text{C}=	ext{CH})(\text{R})\text{SiNCN}]_n\) \([1a, \text{R} = \text{H}; 1b, \text{R} = \text{CH}_3; 1c, \text{R} = (\text{NCN})_{0.5}]\ obtained from (\(\text{H}_2\text{C}=	ext{CH})(\text{R})\text{SiCl}_2\) and (\(\text{H}_3\text{C}\))\(3\)\(\text{SiN}=\text{C}=\text{NSi}(\text{CH}_3)\)\(3\).

### Table 1

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<th>(2a)</th>
<th>(2b)</th>
<th>(2c)</th>
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<td>26.6</td>
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</table>

### Table 2

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<th>(^{11}\text{B}{^1\text{H}} \text{NMR})</th>
<th>(2a)</th>
<th>(2b)</th>
<th>(2c)</th>
</tr>
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<tbody>
<tr>
<td>(\text{BC}_3)</td>
<td>(-6.5)</td>
<td>(-0.1, 8.1)</td>
<td>(-12.1)</td>
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</tbody>
</table>

\(a\) Intensity in parentheses.

as well as for compounds {B[C₂H₄Si(R)NCN]₃}ₙ [2a, R = H; 2b, R = CH₃; 2c, R = (NCN)₀.₅] synthesized by the reaction of B[C₂H₄Si(R)Cl₂]₃ (3a, R = H; 3b, R = CH₃; 3c, R = Cl) and (H₃C)₃SiN=C=NSi(CH₃)₃.

The thermal behavior of compounds 1a–1c (Fig. 1) is very similar and results in two-step decompositions of these compounds. The ceramic yields are (1a) 71%, (1b) 73% and (1c) 69%. In the temperature range 150–250°C, mass losses of 5% (1c) and 10% (1a, 1b) are observed which are mainly caused by the elimination of hydrogen and hydrocarbons as identified by TG–MS studies. At temperatures around 450–650°C, elimination of nitrogen and cyanogen (C₂N₂) takes place.

Even though the compositions of the preceramic polymers are different, the mass losses of compounds 1a–1c in this temperature range are comparable (1a, 13%; 1b, 15%; 1c, 16%). It is remarkable that at temperatures above 900°C the elimination of nitrogen as well as of cyanogen is again observed.

In contrast to compounds 1a–1c, for which the thermolyses take place in two steps, the thermal behavior of compounds 2a–2c is characterized by a continuous mass loss over the full temperature range from 25 to 1100°C. The ceramic yields of these polymers are lower (2a, 63%; 2b, 53%; 2c, 53%) than those of the polysilylcarbodi-imides 1a–1c, even though compounds 2a–2c are more highly crosslinked.

To investigate the high-temperature stability of the ceramic monoliths (monoliths were obtained by plastic forming of the preceramic polymer powders and then subsequently heated to 1400°C; heating rate 1°C min⁻¹) obtained from compounds 1a–1c and 2a–2c, thermogravimetric analysis was carried out for these materials in the temperature range 25–2200°C (argon; heating rate at 25–1200°C, 20°C min⁻¹, and at 1200–2100°C, 2°C min⁻¹). The results of these investigations for the materials obtained from the boron-free polysilylcarbodi-imides 1a–1c are shown in Fig. 3. Surprisingly, the molecular structure of the precursor has only a negligible influence on the thermal stability of the as-synthesized ceramic powders. (In contrast to compounds 2a–2c, intact green bodies from the boron-free polysilylcarbodi-imides 1a–1c have not yet been obtainable. The ceramic materials decompose at approx. 1540°C (1a, 1c) and 1570°C (1b). This is possibly due to the decomposition of Si₃N₄ in the presence of free carbon according to Eqn [6].)¹³ Weight losses during the thermal analyses were 25% (1a), 28% (1c) and 35% (1b) respectively.

![Figure 1](image1.jpg)

**Figure 1** Thermogravimetric analysis of [(H₂C=CH)(R)-SiNCN]ₙ [1a, R = H; 1b, R = CH₃; 1c, R = (NCN)₀.₅]; heating rate 2°C min⁻¹, argon.

![Figure 2](image2.jpg)

**Figure 2** Thermogravimetric analysis of {B[C₂H₄Si(R)-NCN]₃}ₙ [2a, R = H; 2b, R = CH₃; 2c, R = (NCN)₀.₅]; heating rate, 2°C min⁻¹, argon.

From a few examples it is known that Si–C–N ceramics can be stabilized thermally by adding the element boron.¹–⁷ These composites, in general obtained from the thermolysis of boron-containing polysilazanes,²–⁶ silylated borazine derivatives⁸–¹² or highly crosslinked polysilazanes/borazines,⁵–⁷ are composed of Si₃N₄, SiC, BN and free carbon. The as-obtained materials sometimes show excellent thermal stability up to 2000°C⁴,⁷ which thermodynamically cannot be sufficiently explained. It is supposed that the incorporation of boron leads to a stabilization of the amorphous state...
and shifts the temperature of the crystallization of the thermodynamically stable phases to higher values. High-resolution transmission electron microscopy (HRTEM) investigations carried out with a precursor-derived ceramic material obtained from the ammonolysis of B[Si(CH 3 )Cl 2 ] 3 point to the fact that (turbostratic) BN(C) segregations, which surround nanosized crystalline areas of SiC and Si 3 N 4 , inhibit diffusion processes efficiently. 17,18,19 These processes, however, would finally lead to the thermal decomposition of Si 3 N 4. 

Figure 4 depicts the results of the high-temperature thermogravimetric investigations of the ceramics obtained from the boron-modified polysilylcarbodi-imides 2a–2c. It is observed that the decomposition of these materials begins around 1500°C (2b, 2c) whereas the ceramic obtained from the hydrogen-substituted precursor 2a starts to decompose at approx. 1600°C. These results are comparable with those found for the boron-free materials. In conclusion, a significant increase in the thermal stability due to the modification of compounds 1a–1c with boron could not be detected. Likewise, the thermogravimetric yields, at approx. 70% (2000°C), are comparable with those of the ceramics obtained from compounds 1a–1c.

As mentioned above, one can presume that the decomposition of the ceramics, whether obtained from the boron-free or from the boron-modified polysilycarbodi-imides, is caused by the elimination of nitrogen. In Fig. 4 it is shown that, in a first decomposition step, mass losses of approx. 25% (2a, 2c) and 28% (2b) are detected. These findings are in a good accord with the results of the elemental analysis performed for the ceramics obtained from 2a (found: 23.5 wt% N), 2b (found: 25 wt% N) and 2c (found: 23.4 wt% N).

Remarkably, monoliths obtained from the title compounds did not tend to crack at temperatures up to 2300°C in an argon atmosphere, although the shrinkage was roughly proportional to the mass loss during thermolysis. The crystallization of these materials, investigated by X-ray diffraction (XRD), began at approx. 1650–1700°C and finally resulted in the formation of SiC. Crystalline phases containing boron were not observed, possibly because of the low boron contents (5–6 wt%) of the materials.
With respect to the above-mentioned decomposition of Si₃N₄ in the presence of free carbon, it is of general interest to investigate the influence of the atmosphere on the thermal behavior of the ceramic materials obtained. For example, a comparison was made for the ceramic obtained from the boron-modified precursor {B[C₂H₄Si(H)NCN]}ₙ (2a) which is shown in Fig. 5. It is observed that in contrast to the thermal decomposition of this material which occurred in an argon atmosphere at approx. 1600°C, thermal decomposition in nitrogen began at 1700°C.

PLASTIC FORMING OF BORON-MODIFIED POLYSILYCARBODI-IMIDES

To obtain precursor-derived bulk ceramic materials, preceramics are in general shaped by cold isostatic pressing (CIP). The as-obtained green bodies are then transformed into amorphous ceramic monoliths by subsequent thermolysis. However, a remarkable disadvantage of this method is that it is less applicable for the densification of highly crosslinked polymer powders such as the title compounds 2a–2c because of their inelastic nature. Yet a high degree of crosslinkage in the polymeric state is needed to avoid softening of the green parts during thermolysis. Therefore, plastic forming (PF), has been applied for the shaping of green bodies from boron-modified polysilylcarbodi-imide powders.

For the determination of optimized conditions for this process, TMA investigations of the green bodies obtained by CIP were performed. These studies indicate that the title compounds soften in the range 100–180°C, but melting is not observed. At temperatures above 180°C the decomposition of the precursors begins (Fig. 2). Hence, the densification of the polymer powders, which were first milled using a ball mill and then sieved (mesh size 0.16 mm) in order to obtain a homogeneous grain size distribution, was achieved at temperatures around 100–150°C at various pressures. Accordingly the as-obtained fine-grained powders were compacted by uniaxial pressing in graphite dies and then pyrolyzed at 1400°C (25–1400°C, heating rate 1°C min⁻¹) in an argon atmosphere. Due to the significant sensitivity of the boron-modified polymers towards oxygen and moisture, the complete process was carried out in an inert-gas atmosphere or in vacuum.

To investigate the microstructure of the as-synthesized monoliths, scanning electron microscopy (SEM) and mercury pressure porosimetry were carried out for the ceramics obtained from compound {B[C₂H₄Si(H)NCN]}ₙ (2a; Table 3, Fig. 6). The results of the mercury pressure porosimetry show that the microstructure of the precursor-derived monolith is strongly influenced by the pressing temperatures applied. Increasing the pressing temperature results in a lower specific

<table>
<thead>
<tr>
<th>Pressing temp. (°C)</th>
<th>100</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td>31.0</td>
<td>38.7</td>
</tr>
<tr>
<td>Spec. surface area (m² g⁻¹)</td>
<td>17.64</td>
<td>7.67</td>
</tr>
<tr>
<td>Average pore radius (µm)</td>
<td>0.028</td>
<td>0.033</td>
</tr>
<tr>
<td>Bulk density (g cm⁻³)</td>
<td>1.43</td>
<td>1.72</td>
</tr>
<tr>
<td>Corr. bulk density (g cm⁻³)</td>
<td>1.77</td>
<td>1.995</td>
</tr>
<tr>
<td>Total sample porosity (%)</td>
<td>19.26</td>
<td>13.79</td>
</tr>
</tbody>
</table>

Figure 6 Correlation of pressure applied for PF and total sample porosity of ceramic monoliths obtained from {B[C₂H₄Si(H)NCN]}ₙ (2a).
surface area as well as in a decrease of the average pore size, which is correspondingly directly reflected in an increased bulk density of the monoliths. Furthermore, the total sample porosity also decreases with increasing pressure, as expected. As depicted in Fig. 6 there is a linear correlation of the pressure applied for PF and the total sample porosity after thermolysis.

From Fig. 6 one should conclude that additionally increasing the pressing temperature and the pressure applied results in samples with further increased density and decreased porosity. With respect to the preparation of dense and crack-free ceramic monoliths it soon became clear that there is a limit to densifying the green bodies. Our investigations reveal that open porosity is needed to allow the release of gaseous decomposition products during thermolysis and therefore to prevent bloating of the monoliths (Fig. 7).

SEM investigations show that ceramic monoliths obtained from boron-modified polysilylcarbodiimides possess a very homogeneous microstructure (Figs 8 and 9). Figure 8 shows a cross-section through a complete specimen which emphasizes the homogeneity of the whole bulk material. No cracks nor bubbles are observed. The impurities (white layer) at the surfaces of the material are residual boron nitride with traces of graphite. These are caused by the use of boron nitride-treated graphite dies for powder densification.

Figure 9 shows the monolith cross-section of Fig. 8 at higher magnification. The homogeneous microstructure suggests that ceramics obtained from boron-modified polysilylcarbodi-imides are suitable for the preparation of dense bulk materials.

Acknowledgments We thank the Deutsche Forschungsgemeinschaft (DFG) and the Japan Science and Technology Corporation (JST) for financial support. For many discussions we are grateful to Professor Dr Gerd Becker. Furthermore, the authors thank Sabine Katz warmly for supporting us in preparative chemistry and for carrying out the mercury pressure porosimetry. Horst Kummer is acknowledged for performing the high-temperature thermogravimetric analysis. The authors also thank Martina Thomas for performing the XRD studies and Alf Breitschwerdt for performing the FT IR analysis.

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