

Boron-containing polysilylcarbodi-imides: a new class of molecular precursors for Si-B-C-N ceramics ¹

Markus Weinmann ^a, Rainer Haug ^a, Joachim Bill ^a, Fritz Aldinger ^{a,*}, Jörg Schuhmacher ^b, Klaus Müller ^b

^a Max-Planck-Institut für Metallforschung, Pulvermetallurgisches Laboratorium, and Institut für Nichtmetallische Anorganische Materialien der Universität, Heisenbergstraße 5, D-70569 Stuttgart, Germany

^b Physikalisch-Chemisches Institut der Universität, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

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Abstract

The synthesis of boron-containing polysilylcarbodi-imides of general type $\{B[C_2H_4(R)SiNCN]_3\}_n$ [**6a** R = CH₃, **6b** R = H, **6c** R = (NCN)_{0.5}] by different reactions and their thermal behaviour are discussed. The title compounds **6a-6c** can be obtained by a hydroboration reaction of $BH_3 \cdot S(CH_3)_2$ (**5**) with the vinyl-substituted polysilylcarbodi-imides $[(H_2C=CH)(R)SiNCN]_n$ [**3a** R = CH₃, **3b** R = H, **3c** R = (NCN)_{0.5}], which themselves are accessible from the reaction of the vinyl-substituted chlorosilanes $(H_2C=CH)(R)SiCl_2$ (**1a** R = CH₃, **1b** R = H, **1c** R = Cl) with stoichiometric amounts of $H_2N-C \equiv N$ (**2**). Furthermore, a method for the synthesis of compounds **6a-6c** is given by treatment of compounds **1a-1c** with $(H_3C)_3SiN=C=NSi(CH_3)_3$ (**4**). An alternative reaction sequence, which finally leads to compounds **6a-6c** is the hydroboration of the monomeric vinyl-substituted chlorosilanes **1a-1c** with $BH_3 \cdot S(CH_3)_2$ (**5**) to yield the chlorosilylethylboranes $B[C_2H_4(R)SiCl_2]_3$ (**7a** R = CH₃, **7b** R = H, **7c** R = Cl) at first. Treatment of compounds **7a-7c** with $(H_3C)_3SiN=C=NSi(CH_3)_3$ (**4**), even with or without solvent, stoichiometrically or with excess **4**, produces the hydroborated polysilylcarbodi-imides **6a-6c**. The thermogravimetric behaviour of the polysilylcarbodi-imides **3a-3c** as well as the boron-containing polymers **6a-6c** have been determined by simultaneous TGA (20–1100 °C, argon, heating rate 2 K min⁻¹). The ceramic yields of the polymers are in the range of 53–73%, depending on the structure and the composition of the polymers applied. © 1997 Elsevier Science S.A.

Keywords: Polysilylcarbodi-imides; Thermogravimetric analysis

1. Introduction

The thermolytic conversion of elementorganic or inorganic polymers and oligomers into ceramic materials is a suitable method for the synthesis of inorganic composite materials [1–3]. In particular, the production of binary ceramics such as SiC and Si₃N₄ which can be obtained by thermolysis from polysilanes [4] and polycarbosilanes (SiC) [5] or polysilazanes (Si₃N₄) [6] as well as the ternary Si-C-N ceramics, which are in general synthesised from carbon-containing polysilazanes [7], is well investigated.

Boron-containing polycarbosilazanes are known as precursor molecules for ceramic composite materials in

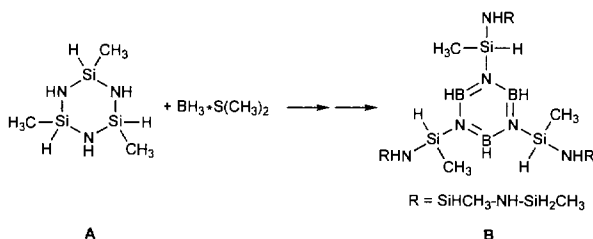
the quaternary system Si-B-C-N [1,8–16,18]. To obtain the ceramic composites, the polymeric precursors are transformed into amorphous ceramic materials by subsequent thermolyses, which are in general performed in an inert gas atmosphere. The as-obtained Si-B-C-N ceramics exhibit excellent thermochemical properties [1,11,13,15] and are therefore interesting materials for high temperature applications in industry. Moreover, solutions of polymers containing silicon, boron, carbon and nitrogen of convenient viscosity are applicable for coatings on non-oxide composite materials e.g. C/C-SiC in order to protect the substrate efficiently from oxidation and corrosion, especially at very high temperatures [1,2,17].

There are several reaction pathways described in the literature, which finally lead to polymers containing silicon, boron, carbon and nitrogen. As some selected examples, the following four routes are described.

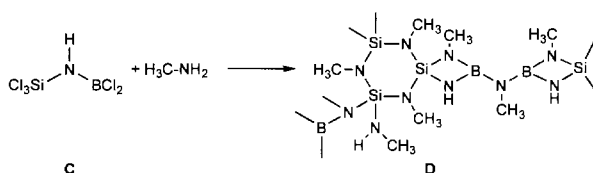
* Corresponding author.

¹ In dedication to Professor Dr. Gottfried Huttner on the occasion of his 60th birthday.

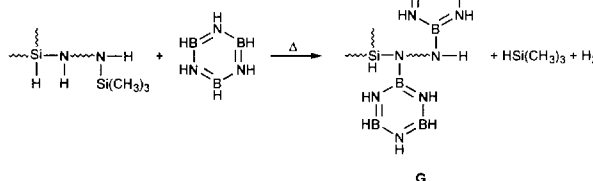
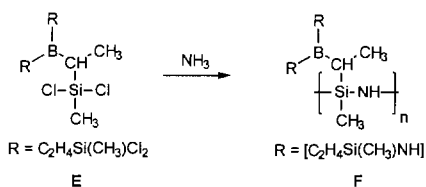
(1) The reaction of cyclic oligomethylsilazanes (**A**) as a Si-C-N source with borane dimethylsulphide leads, under ring opening and elimination of hydrogen, to silylated borazine derivatives of type **B** [9,18]:



(2) [(Trichlorosilyl)amino]dichloroborane (**C**) is a projecting single source precursor for the synthesis of Si-B-N and Si-B-C-N [10,11,13] ceramics. Treatment of this compound with primary and secondary amines (here methylamine) finally leads to a highly cross-linked Si-B-C-N polymer (**D**, idealised structure) [11]:



(3) Treatment of $(\text{H}_2\text{C}=\text{CH})(\text{CH}_3)\text{SiCl}_2$ with borane Lewis base adducts results in the formation of **E**. Amonolysis of this compound leads to the Si-B-C-N polymer **F** in which Si-N chains are linked via C-B-C units [1,14–16]:



(4) Thermal dehydrogenation and dehydrosilylation of hydridosilazanes in the presence of borazines produces polymers of type **G** [12]:

The above-described compounds consist of Si-N skeletons, which are more or less cross-linked via B, B-N, B-C or borazine units and which carry different substituents bonded at the silicon centres. Hence, in this study we mainly focus on the synthesis of a new class of Si-B-C-N ceramic precursors. The syntheses of boron-containing polysilylcarbodi-imides, whose characteristics are repeating Si-N=C=N units, linked via C-B-C bridges, permit an internal comparison to be made of the thermal—and possibly chemical—properties of known Si-B-C-N polymers with this new type of Si-B-C-N pre-ceramic compound.

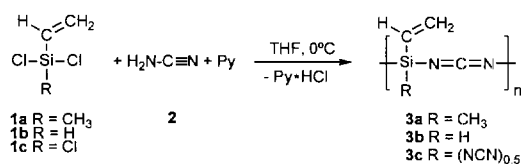
2. Results and discussion

2.1. Synthesis of vinyl-substituted polysilylcarbodi-imides

The synthesis of boron-containing polysilylcarbodi-imides can occur by different reaction sequences. One possible approach is to synthesise polymeric vinyl-substituted polysilylcarbodi-imides which are in a second reaction step hydroborated at the olefinic unit by a suitable boron compound, e.g. borane dimethylsulphide, $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$.

One conceivable exemplary reaction pathway, which finally leads to vinyl-substituted polysilylcarbodi-imides, was described previously for compound $[(\text{H}_2\text{C}=\text{CH})(\text{CH}_3)\text{SiNCN}]_n$ (**3a**) [14,19].

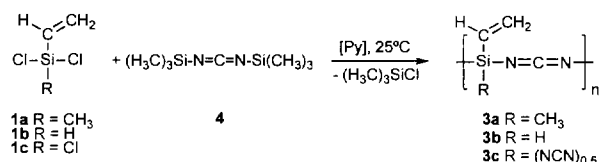
To synthesise the vinyl-substituted polysilylcarbodi-imides, the chlorovinylsilanes $(\text{H}_2\text{C}=\text{CH})(\text{R})\text{SiCl}_2$ (**1a** R = CH_3 , **1b** R = H, **1c** R = Cl) are treated with stoichiometric amounts of cyanamide, $\text{H}_2\text{N-C}\equiv\text{N}$ (**2**) in tetrahydrofuran solutions at 0°C . In the presence of equimolar amounts of pyridine and after appropriate work-up, compounds $[(\text{H}_2\text{C}=\text{CH})(\text{R})\text{SiNCN}]_n$ [**3a** R = CH_3 , **3b** R = H, **3c** R = $(\text{NCN})_{0.5}$] are obtained as colourless waxy solids (**3a**, **3b**) or as a colourless powder (**3c**), which decompose immediately to siloxanes and cyanamide on contact with moisture.



While compounds **3a** and **3b** are obtained in high yields (**3a** 78%, **3b** 85%), the silylcarbodi-imide **3c** is available in maximum 15% yield via this reaction se-

quence. This points to the fact that compound **3c** is probably highly cross-linked, which finally results in a significant product loss during the filtration process due to the low solubility of this polysilylcarbodi-imide.

An alternative reaction sequence for the preparation of compounds **3a–3c** is given by the reaction of compounds **1a** and **1b** in a 1:1 molar ratio with bis(trimethylsilyl)carbodi-imide (**4**) in the presence of catalytic amounts of pyridine [20]. In the case of the synthesis of **3c**, **1c** is reacted with 1.5 parts of **4**.



It turned out that this type of reaction is best performed when the educt bis(trimethylsilyl)carbodi-imide (**4**) is obtained from cyanamide, methyltrichlorosilane and pyridine. As-obtained **4** contains traces of pyridine which catalyse the reaction sufficiently. On the contrary, the addition of pyridine to the reaction mixture of compounds **1a–1c** and highly pure bis(trimethylsilyl)carbodi-imide in order to catalyse the *trans*-silylation reaction is less effective and the reaction times increase considerably.

The yields of the as-obtained polymers **3a** (87%) and **3b** (80%) are comparable with those obtained by the reaction of the vinylchlorosilanes **1a** and **1b** with cyanamide (**2**) and pyridine whereas [(H₂C=CH)Si(NCN)_{1.5}]_n (**3c**) can be isolated in 85% yield on this sequence. The most remarkable advantage of this kind of *trans*-silylation reaction compared to the synthesis of compounds **3a–3c** from the chlorosilanes **1a–1c** and cyanamide (**2**) is the simplified work-up. The by-product chlorotrimethylsilane as well as low-weight oligomeric parts of compounds **3a–3c** can easily be evaporated in high vacuum (10⁻³ mbar) at 70 °C. Solids, which would have to be removed by a filtration step, are not formed. Moreover, these reactions can effectively be performed without solvent, which makes them interesting for industrial applications.

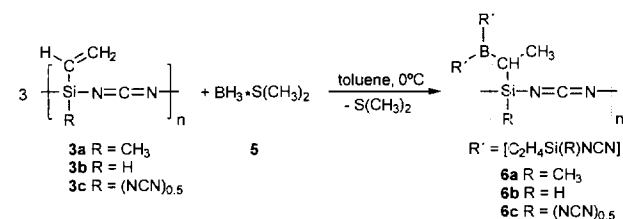
The structures of [(H₂C=CH)(R)SiNCN]_n [**3a** R = CH₃, **3b** R = H, **3c** R = (NCN)_{0.5}] can unequivocally be assigned by IR spectra, which show the expected absorption signals. Typical for this type of compound [20–22] are the very strong and broad asymmetric N=C=N stretching absorptions at 2219 cm⁻¹ (**3a** [14,19]), 2271 cm⁻¹ (**3b**) and 2205 cm⁻¹ (**3c**), the ν_{C=C} absorptions at 1596 cm⁻¹ (**3b**, **3c**) as well as ν_{C-H} in the area of 2950 to 3060 cm⁻¹. In addition, compound **3b** has a very strong absorption band at 2144 cm⁻¹ which

reflects the ν_{Si-H} stretching. The absence of absorption signals in the IR spectra of compounds **3a–3c** in the range of 460–600 cm⁻¹, which would correspond to Si-Cl vibrations (sym. and asym.) indicate that the *trans*-silylation occurred quantitatively.

Moreover, the expected structures of compounds **3a–3c** are confirmed by their NMR spectra. Compared to the resonance signals of the chlorine-containing starting compounds (H₂C=CH(R)SiCl₂ (**1a** R = CH₃, **1b** R = H, **1c** R = Cl), the ²⁹Si{¹H} NMR resonance signals of the vinyl-substituted polysilylcarbodi-imides are significantly shifted to higher field (**3a** -36, -33 ppm [19], **3b** -51, -45 ppm, **3c** -70 ppm) which is due to the substitution of silicon-bonded chlorine atoms towards nitrogen atoms. The ¹³C{¹H} NMR spectra of compounds **3a–3c** show resonance signals for the olefinic carbon atoms in the area of 132–138 ppm, as well as signals of the carbodi-imide carbon atoms that in all cases are observed at 120–122 ppm.

2.2. Synthesis of boron-containing polysilylcarbodi-imides from **3a–3c**

To transform compounds [(H₂C=CH)(R)SiNCN]_n [**3a** R = CH₃, **3b** R = H, **3c** R = (NCN)_{0.5}] into boron-containing polymers, the as-obtained polysilylcarbodi-imides can be hydroborated at the vinyl unit by the reaction with a suitable hydroboration reagent, e.g. borane-dimethylsulphide (**5**) in toluene solutions. Therefore the polymer is suspended in toluene and the borane-dimethylsulphide is dropwise added at 0 °C. After stirring for an additional 2 h, the solvent and dimethylsulphide are removed in vacuum at 50 °C. Any further work-up for the purification of the isolated boron-containing polysilylcarbodi-imides {B[C₂H₄(R)SiNCN]₃]_n [**6a** R = CH₃, **6b** R = H, **6c** R = (NCN)_{0.5}], which are obtained as colourless powders in 100% yield, is not necessary and was not performed. The high degree of cross-linkage of the Si-B-C-N polymers, which is caused by the hydroboration of the vinyl units, is directly reflected in the very low solubility of compounds **6a–6c** in most common polar as well as non-polar organic solvents.



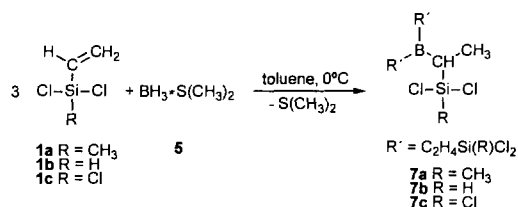
From the IR spectra of compounds **6a–6c**, one can conclude that BH₃·S(CH₃)₂ reacted selectively with

the vinyl group in a quantitative manner. No $\nu_{C=C}$ absorptions found for **3a-3c** nor B-H stretching absorptions can be detected in the IR spectra of compounds **6a-6c**. Moreover, B-N absorptions, which should have been obtained in the case of a hydroboration of the carbodi-imide units, as was reported by Kienzle and coworkers [14,22], are not observed.

Identical findings are made in the $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR spectra of compounds **6a-6c**. Resonance signals, which may arise from olefinic carbon atoms, are not found, whereas the carbodi-imide carbon atoms are observed as broad resonance signals. For a detailed discussion of the spectroscopic data of **6a-6c** see Section 2.3.

2.3. Synthesis of boron-containing polysilylcarbodi-imides from tris[(chlorosilyl)ethyl]boranes

A further possibility for the synthesis of boron-containing polysilylcarbodi-imides is given by the reaction of bis(trimethylsilyl)carbodi-imide with boron-substituted chlorosilanes of type $\text{B}[\text{C}_2\text{H}_4(\text{R})\text{SiCl}_2]_3$ (**7a** $\text{R} = \text{CH}_3$, **7b** $\text{R} = \text{H}$, **7c** $\text{R} = \text{Cl}$). These molecules are accessible by the reaction of the according chlorosilanes **1a-1c** with borane-dimethylsulphide in a 3:1 molar ratio. Therefore, at 0°C a solution of **5** in toluene is slowly added to the chlorovinylsilane dissolved in toluene. After purification by distillation in vacuum (10^{-2} mbar; **7a** 105°C , **7b** 102°C , **7c** 115°C), compounds **7a-7c** are obtained as colourless oils which are very sensitive to oxygen and moisture.



Compounds **7a** and **7c** were first described by Jones and Myers in 1972 [23] and are therefore not discussed here in detail. It is remarkable that in contrast to the hydroboration of alkenes, which are in general borated in the terminal position, the hydroboration of vinylsilanes is not regioselective [23]. In the case of the hydroboration of vinylsilanes, there is, depending on the nature of the silicon-bonded substituents, a mixture of α - and β -hydroboration products observed. This is reflected in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound **7b**, where resonance signals at 15.0–16.1 (SiCH), 10.3–11.6 (SiCH) and -6.5 – -7.9 ppm (SiCH₂) are observed. This is possibly due to the formation of $\alpha\alpha\alpha$ -, $\alpha\alpha\beta$ -, $\alpha\beta\beta$ - and $\beta\beta\beta$ -hydroboration products. Moreover, the

$\alpha\alpha\alpha$ - and $\alpha\alpha\beta$ -products exist in diastereotopic isomers which can be distinguished in the NMR spectra.

Because of the different isomers, the ^1H NMR spectrum of compound **7b** only shows proton resonance signals with multiplet character. While the protons of the C_2H_4 unit are observed in the region of 0.78–1.86 ppm, the silicon-bonded hydrogen atoms show resonance signals at 5.22–5.38 ppm. Both the multiplets of the carbon-bonded protons as well as the silicon-bonded proton are obtained in the expected 4:1 ratio. Moreover, CH, CH₂ and CH₃ are observed in a 1:1:3 ratio. This indicates that α -hydroboration occurs in 2/3, while β -hydroboration is only observed in 1/3. Resonance signals according to olefinic protons are not found.

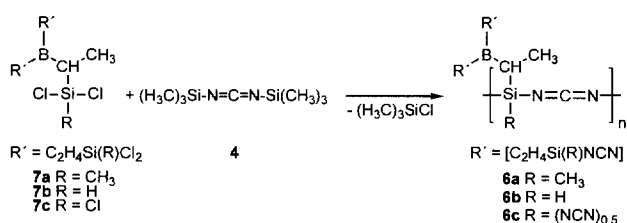
Similar observations are made in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **7b**. The absence of olefinic resonance signals indicates that the hydroboration occurred quantitatively. The carbon resonance signals of the C_2H_4 unit are found in the area of 27.9–31.3 (CH), 15.8–21.5 (BCH₂), 12.7–14.7 (SiCH₂) and 9.0–9.3 ppm (CH₃) whereby the boron-bonded carbon atoms show the typical line broadening.

The observed ^{11}B chemical shift at 85.8 ppm rel. $\text{B}(\text{OH})_3$ is typical for these types of compound and is similar to that for $\text{B}[\text{C}_2\text{H}_4(\text{CH}_3)\text{SiCl}_2]_3$ [14,15].

The molecule ion of compound **7b** $\text{B}[\text{C}_2\text{H}_4(\text{H})\text{SiCl}_2]_3^+$ is observed in the EI-MS spectrum with 10% rel. intensity. The most intensive fragment ions are $\text{M}^+ - \text{Cl}$ 359 (100% rel. Intens.), $\text{M}^+ - \text{C}_2\text{H}_5\text{SiCl}_2$ 267 (33% rel. Intens.), $\text{C}_2\text{H}_5\text{SiCl}_2^+$ 127 (18% rel. Intens.), HSiCl_2^+ 99 (31% rel. Intens.) and HSiCl^+ 63 (35% rel. Intens.).

The conversion of compounds **7a-7c** into boron-containing polysilylcarbodi-imides is best performed by their reaction with bis(trimethylsilyl)carbodi-imide (**4**) even with or without solvent, stoichiometrically or with excess **4**. The reactions in toluene solutions have to be achieved in the boiling solvent from which the products separate as colourless powders. The most remarkable disadvantage of this reaction compared to the solvent-free reactions is the long time the experiment takes (7 days). On the other hand, the stoichiometric solvent-free reaction of **7a-7c** and **4** in the presence of catalytic amounts of pyridine produces compounds **7a-7c** as hard glass-like materials. This reaction is cheap and is finished in a few hours. If the chlorosilylboranes **7a-7c** are reacted with a ten-fold excess of bis(trimethylsilyl)carbodi-imide (**4**), compounds **6a-6c** are obtained first as rubber-like products. We suspect that in this state the products are oligomeric and not very highly cross-linked. Heating these compounds to 70°C in high vacuum produces compounds **6a-6c** in quantitative yields under elimination of **4**. With regard to industrial applications of these compounds, it is remarkable that eliminated chlorotrimethylsilane and bis(trimethylsilyl)carbodi-imide can efficiently be recycled.

In addition, a reaction as described for the synthesis of compounds $[(H_2C=CH)(R)SiNCN]_n$ [**3a** R = CH₃, **3b** R = H, **3c** R = (NCN)_{0.5}] which makes use of the cheaper cyanamide is inapplicable for the synthesis of compounds **6a–6c** from **7a–7c**, because the obtained products have very low solubility in common organic solvents and therefore are difficult to separate from the by-product pyridine hydrochloride.



The spectra of compounds $\{B[C_2H_4(R)SiNCN]_3\}_n$ [**6a** R = CH₃, **6b** R = H, **6c** R = (NCN)_{0.5}] which were obtained by the reaction of the boranes **7a–7c** with bis(trimethylsilyl)carbodi-imide are similar to those obtained by the reaction of compounds **3a–3c** with $BH_3 \cdot S(CH_3)_2$.

The IR spectra clearly show vibrations of the different groupings: $\nu(C-H)$ for compounds **6a–6c** are observed at approx. 2960 and 2880 cm⁻¹ as medium or weak absorption peaks, whereas the asymmetric N=C=N vibrations are reflected in very strong and broad absorption signals at 2232 cm⁻¹ (**6a**), 2236 cm⁻¹ (**6b**) and 2168 cm⁻¹ (**6c**, very broad). Other characteristic group frequencies of compounds **6a–6c** are $\delta(CH_3)$ at approx. 1450 cm⁻¹ and $\nu(Si-C)$ at 1260 cm⁻¹. In addition, the IR spectrum of compound $\{B[C_2H_4(H)SiNCN]_3\}_n$ (**6b**), shows a very strong absorption band at 2171 cm⁻¹, which is due to the Si-H stretching vibration. Si-Cl, C=C, B-H or B-N vibrations are not observed.

Moreover, the molecular structure of compounds **6a–6c** can be assigned by their ¹³C{¹H} CP-MAS NMR spectra where the resonance signals of the methyl, methylene and methine carbon atoms are obtained in predicted values. The chemical shifts of the carbodi-imide carbon atoms at 123.0 ppm (**6a**) 123.5 ppm (**6b**) and 125.0 ppm (**6c**) are nearly identical to those of the polymeric silylcarbodi-imides **3a–3c** (see Section 2.1). This indicates that the hydroboration reactions of the olefinic groupings do not seriously influence the magnetic environment of these atoms in the polymeric state. Likewise, the different silicon-bonded substituents R do not significantly influence the ¹¹B{¹H} CP-MAS NMR chemical shift of compounds **6a–6c** at about 0 ppm rel. Et₂O * BF₃. Against this, the ²⁹Si{¹H} CP-MAS NMR resonance signals of the silicon atom of compounds **6a**

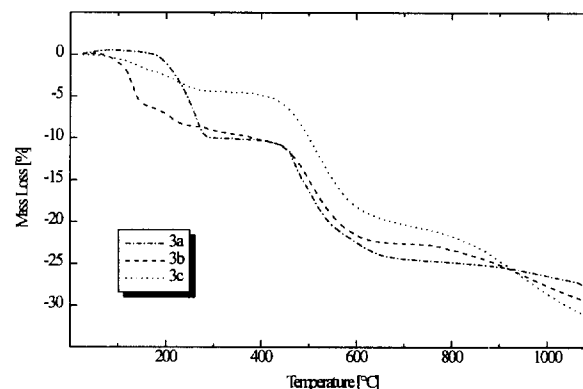


Fig. 1. TGA of $[(H_2C=CH)(R)SiNCN]_n$ [**3a** R = CH₃, **3b** R = H, **3c** R = (NCN)_{0.5}]; heating rate 2°C min⁻¹, argon.

with an SiN₂C₂ environment and **6b** with an SiN₂HC environment are observed at -23.0 and -36.2 ppm whereas the silicon resonance of compound **6c** with an SiN₃C environment is observed at $\delta = -55.4$.

2.4. Thermogravimetric analysis (TGA) investigations

The general applicability of an organoelement polymer as a pre-ceramic material can be proved by several analytical and mechanical methods.

First, the thermal conversion of the precursor molecules into the ceramic material can be monitored by simultaneous TGA. In this paper TGA was performed in a purified argon atmosphere in a temperature range of 25–1100°C (heating rate: 2°C min⁻¹) for compounds $[(H_2C=CH)(R)SiNCN]_n$ [**3a** R = CH₃, **3b** R = H, **3c** R = (NCN)_{0.5}; Fig. 1] obtained from the reaction of $(H_2C=CH)(R)SiCl_2$ (**1a** R = CH₃, **1b** R = H, **1c** R = Cl) and $(H_3C)_3SiN=C=NSi(CH_3)_3$ (**4**) as well as for compounds $\{B[C_2H_4(R)SiNCN]_3\}_n$ [**6a** R = CH₃, **6b** R = H, **6c** R = (NCN)_{0.5}; Fig. 2] synthesised from $B[C_2H_4(R)SiCl_2]_3$ (**7a** R = CH₃, **7b** R = H, **7c** R = Cl) and $(H_3C)_3SiN=C=NSi(CH_3)_3$ (**4**).

The thermolysis of **3a–3c** (Fig. 1) results in a two

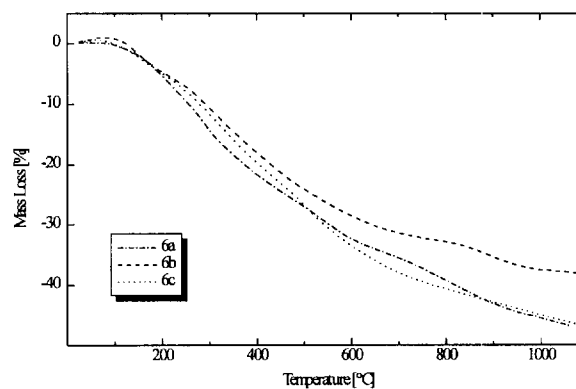


Fig. 2. TGA of $\{B[C_2H_4(R)SiNCN]_3\}_n$ [**6a** R = CH₃, **6b** R = H, **6c** R = (NCN)_{0.5}]; heating rate 2°C min⁻¹, argon.

step decomposition of these compounds. The ceramic yields are **3a** 73%, **3b** 71% and **3c** 69%. TG-MS studies indicate that in the temperature range of 150–250 °C, mass losses of 5% (**3c**) and 10% (**3a**, **3b**) are observed which are caused by the elimination of hydrogen and hydrocarbons. The elimination of nitrogen and dicyan takes place at temperatures around 450–650 °C. Even though the composition of the pre-ceramic polymers is different, the mass losses of compounds **3a–3c** in this temperature range are comparable (**3a** 15%, **3b** 13%, **3c** 16%). At temperatures above 900 °C, again the elimination of nitrogen as well as of dicyan is observed.

While the thermolyses of compounds **3a–3c** occur in two steps, the thermal behaviour of compounds **6a–6c** is characterised by a continuous mass loss over the full temperature range from 25–1100 °C. The ceramic yields of these polymers are lower (**6a** 53%, **6b** 63%, **6c** 53%) than those of the polysilylcarbodi-imides **3a–3c** even though compounds **6a–6c** are more highly cross-linked.

Due to the absence of reflections in the XRD patterns of the ceramic materials obtained from the thermolysis of compounds **3a–3c** and **6a–6c** one can suggest that these ceramics are amorphous up to 1100 °C in an argon atmosphere. Several publications have shown that the amorphous state is an essential prerequisite to obtaining ceramic materials that are stable at high temperatures [1,2,13,16]. The thermal behaviour (crystallisation, decomposition) at temperatures up to 2300 °C of the amorphous ceramics obtained from the thermolysis of **3a–3c** and **6a–6c** will be published soon [24].

3. Experimental part

3.1. General comments

All reactions were carried out in a purified argon atmosphere using standard Schlenk techniques. Tetrahydrofuran was purified by distillation from sodium/benzo-phenone ketyl; toluene was purified by distillation from potassium; pyridine (stored over KOH) was refluxed with 1 wt.% of NaNH₂ for 1 week and then distilled. Fourier-infrared spectra were obtained with a Perkin-Elmer IFS66 spectrometer as KBr pellets (solids) or as film in NaCl cells (liquids). NMR spectra were recorded on a Bruker AC250 spectrometer operating at 250.133 MHz (¹H NMR) in the Fourier transform mode, 62.896 MHz (¹³C{¹H} NMR), 49.694 MHz (²⁹Si{¹H} NMR) or 80.253 MHz (¹¹B{¹H} NMR). Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane (δ = 0) with the solvent as the reference signal): ¹H NMR, C₆D₆ δ = 7.17; ¹³C NMR, C₆D₆ δ = 127.0; ²⁹Si NMR: standard external rel. tetramethylsilane (δ = 0), ¹¹B NMR: standard rel. B(OH)₃. Solid state NMR spectra were obtained on a Bruker CXP 300 spectrometer at a static

magnetic field strength of 7.05 T using a 4 mm magic angle spinning probe head. ²⁹Si and ¹³C data were performed at 59.60 MHz and 75.47 MHz respectively, using the cross-polarization technique with a ¹H 90° pulse length of 4.5 μs, a spin locking field of 55.5 kHz and a contact time of 3 ms. Typical recycle delays were 8 s. The sample spinning rates were 6 kHz. ²⁹Si and ¹³C chemical shifts were determined relative to the external standards Q₈M₈ the trimethylsilyl ester of octameric silicate, and adamantane. ²⁹Si and ¹³C chemical shift values were then expressed relative to the reference compound trimethylsilane TMS (0 ppm). The ¹¹B MAS NMR spectroscopy was carried out at 96.29 MHz. The samples were spun at speeds of 10 to 12 kHz. Single pulse excitation using a 45° (1.75 μs) pulse and a recycle delay of 3 s was employed. All chemical shifts were determined relative to an aqueous solution of boric acid, which has a chemical shift of 19.60 ppm relative to the ¹¹B reference compound BF₃·OEt₂ (0 ppm). EI mass spectra (70 eV) were recorded on a MAT 8230 (Finnigan) mass spectrometer at the Anorganisch-Chemisches Institut der Universität Heidelberg operating in the positive ion mode. TGA was carried out on a Netzsch STA 409 or STA 410 with coupled MS Balzer QMG 520 in an argon atmosphere (temperature range 25–1100 °C, heating rate 2 °C min⁻¹). Microanalyses were performed by the microanalytical department of the Max-Planck-Institut für Metallforschung in Stuttgart. The molecular weights \bar{M} of soluble compounds were determined by cryoscopic methods in benzene as solvent [25].

3.2. Synthesis of [(H₂C=CH)(R)SiNCN]_n [**3a** R = CH₃, **3b** R = H, **3c** R = (NCN)_{0.5}] from (H₂C=CH)(R)SiCl₂ (**1a** R = CH₃, **1b** R = H, **1c** R = Cl) and H₂N-C≡N (**2**)

At 0 °C a solution of 200 mmol (8.4 g) H₂N-C≡N (**2**) and 400 mmol (31.6 g) pyridine in 300 ml of tetrahydrofuran is dropwise added to (H₂C=CH)(R)SiCl₂ (**1a** 200 mmol, 28.2 g; **1b** [26] 200 mmol, 25.4 g; **1c** 133 mmol, 21.6 g) dissolved in 500 ml of tetrahydrofuran. The reaction takes place by the precipitation of pyridine hydrochloride which clouds the reaction mixture immediately. After the addition of **2** is finished, the reaction mixture is allowed slowly to warm up to 25 °C. To complete the procedure, the reaction mixture is stirred for an additional 3 h. The polymer solution is separated from the precipitate by filtration through 5 cm of Celite. Finally, all volatile components of the filtrate are removed in vacuum at 70 °C. Compounds [(H₂C=CH)(R)SiNCN]_n are obtained as colourless waxy solids (**3a** R = CH₃, 78%; **3b** R = H, 85%) or as a colourless powder [**3c** R = (NCN)_{0.5}; max. 15%]. The analytical and spectroscopic data of compound [(H₂C=CH)(CH₃)SiNCN]_n (**3a**) are described elsewhere [14,15].

3.2.1. $[(H_2C=CH)(H)SiNCN]_n$ (**3b**)

Anal. Found: C, 39.4; H, 4.7; N, 27.8. $[C_3H_4N_2Si]_n$ ([96.12]_n) calc.: C, 37.48; H, 4.18; N, 29.13. IR (KBr): $\nu(C-H) = 3060$ m, 3116 w; 2956 s; $\nu_{as}(N=C=N)$, $\nu(Si-H) = 2190$ vs, vbr; $\nu(C=C) = 1596$ s; $\nu(C-H, \text{in plane}) = 1404$ s; $\nu(Si-C) = 1254$ s; $\nu(C-H, \text{trans wagging}) = 1006$, $\delta(Si-H) = 878$ s cm^{-1} . 1H NMR (C_6D_6): $\delta = 4.6\text{--}5.1$ (m, 1H, SiH), 5.5–6.1 (m, 3H, C_2H_3). $^{29}Si\{^1H\}$ NMR (THF– D_2O): $\delta = -51.0, -49.2, -45.3$. $\bar{M} = 780$ g mol^{-1} ; $\bar{n} = 8.1$. TGA (1100 °C, 71% ceramic yield): 25–300 °C, -10%; 300–700 °C, -13%; 700–1100 °C, -6%.

3.2.2. $[(H_2C=CH)Si(NCN)_{1.5}]_n$ (**3c**)

Anal. Found: C, 35.7; H, 3.6; N, 32.1. $[C_{3.5}H_3N_3Si]_n$ ([115.15]_n) calc.: C, 36.5; H, 2.62; N, 36.47. IR (KBr): $\nu_{as}(N=C=N) = 2205$ vs. $^{13}C\{^1H\}$ CP-MAS NMR: $\delta = 2.0$ ($SiCH_3$), 121.5 ($N=C=N$), 131.8 ($C=C$), 138.4 ($C=C$). $^{29}Si\{^1H\}$ CP-MAS NMR: $\delta = -69.8$. TGA (1100 °C, 69% ceramic yield): 25–300 °C, -5%; 300–680 °C, -15%; 700–1100 °C, -11%.

3.3. Synthesis of $[(H_2C=CH)(R)SiNCN]_n$ [**3a** $R = CH_3$, **3b** $R = H$, **3c** $R = (NCN)_{0.5}$] from $(H_2C=CH)(R)SiCl_2$ (**1a** $R = CH_3$, **1b** $R = H$, **1c** $R = Cl$) and $(H_3C)_3SiN=C=NSi(CH_3)_3$ (**4**)

At 25 °C 100 mmol (18.6 g) of $(H_3C)_3SiN=C=NSi(CH_3)_3$ (**4**) [14] are added in one portion to the chlorovinylsilane $(H_2C=CH)(R)SiCl_2$ (**1a** 100 mmol, 14.1 g; **1b** 100 mmol, 12.7 g; **1c** 67 mmol, 10.8 g) under vigorous stirring. After approx. 3–5 h an exothermic reaction starts and the viscosity of the liquid mixture increases significantly under elimination of chlorotrimethylsilane, which can readily be monitored by ^{29}Si NMR. Two days later, the reaction mixtures of the polymers are slowly heated up to 70 °C to remove all volatile components (residual chlorotrimethylsilane and oligomers) in vacuum (10^{-3} mbar). The as-obtained polysilylcarbodi-imides $[(H_2C=CH)(R)SiNCN]_n$ are colourless waxy solids (**3a** $R = CH_3$, 87%; **3b** $R = H$, 80%) or a colourless powder [**3c** $R = (NCN)_{0.5}$, 85%]. The analytical and spectroscopic data of compounds $[(H_2C=CH)(R)SiNCN]_n$ are identical with those described in Section 3.2.

3.4. Synthesis of $[B(C_2H_4(R)SiNCN)_3]_n$ [**6a** $R = CH_3$, **6b** $R = H$, **6c** $R = (NCN)_{0.5}$] from $[(H_2C=CH)(R)SiNCN]_n$ [**3a** $R = CH_3$, **3b** $R = H$, **3c** $R = (NCN)_{0.5}$] and $BH_3 \cdot S(CH_3)_2$ (**5**)

At 0 °C, a solution of 50 mmol of borane dimethylsulphide (**5**) in 100 ml toluene is added dropwise to the appropriate vinyl-substituted polysilylcarbodi-imide $[(H_2C=CH)(R)SiNCN]_n$ (**3a** 16.5 g, **3b** 14.4 g, **3c** 17.3 g) in 200 ml of toluene. The reaction mixture, from which

the product precipitates spontaneously, is then allowed slowly to warm up to 25 °C. After stirring for an additional 2 h at room temperature the solvent as well as dimethylsulphide are removed in vacuum (10^{-2} mbar). The residual is dried for 24 h at 70 °C/ 10^{-3} mbar. Compounds **6a–6c** are obtained in quantitative yields as colourless powders, which are extremely sensitive to moisture and oxygen.

3.4.1. $[B(C_2H_4(CH_3)SiNCN)_3]_n$ (**6a**)

Anal. Found: C, 39.8; H, 6.5. $[C_{12}H_{21}BN_6Si_3]_n$ ([344.37]_n) calc.: C, 41.85; H, 6.15. IR (KBr): $\nu(C-H) = 2963$ m, 2880 w; $\nu_{as}(N=C=N) = 2232$ vs; 1636 vs; $\nu_s(N=C=N) = 1560$ m; $\delta(CH_3) = 1457$ m; $\nu(Si-C) = 1260$ m; $\nu(B-C) = 1051$ m; $\nu(Si-C) = 788$ s cm^{-1} . $^{13}C\{^1H\}$ CP-MAS NMR: $\delta = 5.0$ (CH_3), 10.6 (CH_2), 26.6 (CH), 123.0 ($N=C=N$). $^{11}B\{^1H\}$ CP-MAS NMR: $\delta = -0.1, 8.1$. $^{29}Si\{^1H\}$ CP-MAS NMR: $\delta = -23.0$ (C_2SiN_2), 2.0 (C_3SiN). TGA (1100 °C, 53% ceramic yield): 25–1100 °C, -47%.

3.4.2. $[B(C_2H_4(H)SiNCN)_3]_n$ (**6b**)

Anal. Found: C, 37.0; H, 4.8; N, 27.9. $[C_9H_{15}BN_6Si_3]_n$ ([302.29]_n) calc.: C, 35.76; H, 5.00; N, 27.79. IR (KBr): $\nu(C-H) = 2961$ m, 2873 w; $\nu_{as}(N=C=N) = 2236$ vs, br; $\nu(Si-H) = 2171$ vs, br; $\nu_s(N=C=N) = 1578$ m; $\delta(CH_3) = 1457$ m; $\nu(Si-C) = 1260$ m; $\nu(B-C) = 1090$ br; $\delta(Si-H) = 845$ s; $\nu(Si-C) = 756$ cm^{-1} . $^{13}C\{^1H\}$ CP-MAS NMR: $\delta = 3.0$ (CH_3), 11.2 (CH_2), 24.1 (CH), 123.5 ($N=C=N$). $^{11}B\{^1H\}$ CP-MAS NMR: $\delta = -6.5$. $^{29}Si\{^1H\}$ CP-MAS NMR: $\delta = -36.2$ ($HCSiN_2$). TGA (1100 °C, 63% ceramic yield): 25–1100 °C, -37%.

3.4.3. $[B(C_2H_4Si(NCN)_{1.5})_3]_n$ (**6c**)

Anal. Found: C, 35.3; H, 5.7. $[C_{10.5}H_{12}BN_9Si_3]_n$ ([359.27]_n) calc.: C, 35.10; H, 3.37. IR (KBr): $\nu(C-H) = 2962$ m, 2877 w; $\nu_{as}(N=C=N) = 2168$ vs, vbr; $\delta(CH_3) = 1488$ m; $\nu(Si-C) = 1255$ m; $\nu(B-C) = 1164$ m; $\nu(Si-C) = 770$ vs cm^{-1} . $^{13}C\{^1H\}$ CP-MAS NMR: $\delta = 1.7$ (CH_3), 10.7 (CH_2), 125.8 ($N=C=N$). $^{11}B\{^1H\}$ CP-MAS NMR: $\delta = -12.1$. $^{29}Si\{^1H\}$ CP-MAS NMR: $\delta = -55.4$ ($CSiN_3$), -36.2 (SiN_2), 2.7 (C_3SiN). TGA (1100 °C, 53% ceramic yield): 25–1100 °C, -47%.

3.5. Synthesis of $[B(C_2H_4(H)SiCl_2)_3]_n$ (**7b**)

At 0 °C 137 ml (274 mmol) of a 2 M $BH_3 \cdot S(CH_3)_2$ (**5**) solution in toluene are added dropwise to 104 g (820 mmol) $(H_2C=CH)(H)SiCl_2$ dissolved in 300 ml of toluene. After the addition of the borane solution has finished, the reaction mixture is carefully warmed up to 25 °C and stirred for an additional 2 h. The solvent as well as dimethylsulphide are evaporated in vacuum (10^{-2} mbar) at room temperature and the residual cloudy oil is purified by vacuum distillation

(102 °C/10⁻² mbar). B[C₂H₄(H)SiCl₂]₃ (**7b**) is obtained in 96% yield as a colourless oil, which is very sensitive to moisture. Compounds B[C₂H₄(CH₃)SiCl₂]₃ (**7a**) and B(C₂H₄SiCl₃)₃ (**7c**) are synthesised in a similar manner. Their spectroscopic data are described in the literature [14,23].

Anal. Found: C, 17.3; H, 3.9; N, 1.0. C₆H₁₅BCl₆Si₃ (394.96) calc.: C, 18.25; H, 3.83; N, 0.0. IR (NaCl): ν (C-H) = 2965 m, 2939 m, 2911 w; 2877 m; ν (Si-H) = 2207 vs; δ (CH₃) = 1456 m; ν (Si-C) = 1285 s; ν_{as} (C-B-C) 1167 vs; δ (Si-H) = 800 vs; ν (Si-Cl) 557 vs cm⁻¹. ¹H NMR (C₆D₆): δ = 0.78–1.10 (m, 7.2 H, CH₃), 1.14–1.39 (m, 2.4 H, CH₂), 1.57–1.86 (m, 2.4 H, CH), 5.22–5.38 (m, 3 H, SiH). ¹³C{¹H} NMR (C₆D₆): δ = 8.8 (CH₃), 9.0 (CH₃), 9.1 (CH₃), 9.3 (CH₃), 12.7 (SiCH₂), 13.7 (SiCH₂), 14.5 (SiCH₂), 14.7 (SiCH₂), 15.8 (br, BCH₂), 18.3 (br, BCH₂), 21.5 (br, BCH₂), 27.9 (br, CH), 28.5 (br, CH), 29.0 (br, CH), 31.3 (br, CH). ¹¹B{¹H} NMR (THF/D₂O): δ = 85.5 (br). ²⁹Si{¹H} NMR (THF/D₂O): δ = -6.5–-7.9 (SiCH₂), 10.3–11.6 (SiCH), 15.0–16.1 (SiCH). \bar{M} = 400 g mol⁻¹. EI-MS [*m/e* (rel. Int.)]: M⁺ 394 (10), M⁺-Cl 359 (100), M⁺-2Cl 325 (11), M⁺-C₂H₅SiCl₂ 267 (33), C₂H₅SiCl₂⁺ 127 (18), HSiCl₂⁺ 99 (31), C₂H₅SiCl⁺ 92 (14), HSiCl⁺ 63 (35).

3.6. Synthesis of {B[C₂H₄(R)SiNCN]₃]_n [**6a** R = CH₃, **6b** R = H, **6c** R = (NCN)_{0.5}] from B[C₂H₄(R)SiCl₂]₃ (**7a** R = CH₃, **7b** R = H, **7c** R = Cl) and (H₃C)₃SiN=C=NSi(CH₃)₃ (**4**) [14]

Under vigorous stirring 100 mmol (18.6 g) of (H₃C)₃SiN=C=NSi(CH₃)₃ (**4**) [14] are added in one portion to compounds **7a–7c** (**7a** 33 mmol, 14.4 g; **1b** 33 mmol, 13.0 g; **1c** 22 mmol, 11.0 g) at 25 °C. 30–60 min later, the reaction mixtures significantly begin to increase their viscosity under elimination of chlorotrimethylsilane and finally result in hard glass-like product mixtures. Compounds **6a–6c** are purified by heating to 70 °C/10⁻³ mbar and then by freeze drying at -178 °C. After repeating this procedure three times **6a–6c** are obtained as colourless powders in quantitative yields. The analytical and spectroscopic data of the as-obtained polymers are identical with those described in Section 3.4.

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References

- [1] J. Bill, F. Aldinger, *Adv. Mater.* 7 (1995) 775.
- [2] J. Bill, F. Aldinger, *Z. Metallk.* 87 (1996) 827.
- [3] (a) D. Segal, *Chemical Synthesis of Advanced Ceramic Materials*, Cambridge University Press, 1987. (b) M. Birot, J.-P. Pillot, J. Dunoguès, *Chem. Rev.* 95 (1995) 1443. (c) P. Wisian-Neilson, H.R. Allcock, K.J. Wynne (Eds.), *Inorganic and Organometallic Polymers II, Advanced Materials and Intermediates*, ACS Symposium Series 572, American Chemical Society, Washington, DC, 1994. (d) M. Zeldin, K.J. Wynne, H.R. Allcock (Eds.), *Inorganic and Organometallic Polymers, Advanced Materials and Intermediates*, ACS Symposium Series 360, American Chemical Society, Washington, DC, 1988. (e) R.M. Laine, *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*, Proc. NATO Advanced Research Workshop, Cap d'Agde, France, 1986. (f) W. Toreki, *Poly. News* 16 (1991) 6. (g) M. Peuckert, T. Vaahs, M. Brück, *Adv. Mater.* 2 (1990) 398. (h) S. Yajima, *Am. Ceram. Soc. Bull.* 62 (1983) 893. (i) R.R. Wills, R.A. Markle, S.P. Mukherjee, *Am. Ceram. Soc. Bull.* 62 (1983) 905. (j) B.E. Walker Jr., R.W. Rice, P.F. Becher, B.A. Bender, W.S. Coblenz, *Am. Ceram. Soc. Bull.* 62 (1983) 916.
- [4] (a) S. Yajima, J. Hayashi, M. Omori, *Chem. Lett.* (1975) 93. (b) S. Yajima, J. Hayashi, M. Omori, German Patent 2618150, 1976. (c) S. Yajima, J. Hayashi, M. Omori, German Patent 2618246, 1976. (d) R.D. Miller, J. Michl, *Chem. Rev.* 89 (1989) 1359. (e) R.D. Miller, *Angew. Chem. Adv. Mater.* 101 (1989) 1773. (f) R. West, *J. Organomet. Chem.* 300 (1986) 327.
- [5] (a) C.L. Shilling Jr., J.P. Wesson, T.C. Williams, *Am. Ceram. Soc. Bull.* 62 (1983) 912. (b) B. Boury, L. Carpenter, R.J.P. Corriu, *Angew. Chem.* 102 (1990) 818. (c) C.K. Whitmarsh, L.V. Interrante, *Organometallics* 10 (1991) 1336. (d) B. Boury, R.J.P. Corriu, W.E. Douglas, *Chem. Mater.* 3 (1991) 487. (e) E. Boullion, R. Pailler, R. Naslain, E. Bacqué, J.-P. Pillot, M. Birot, J. Dunoguès, P.V. Huong, *Chem. Mater.* 3 (1991) 356. (f) D. Seyferth, H. Lang, *Organometallics* 10 (1991) 551. (g) D. Seyferth, M. Tasi, H.-G. Woo, *Chem. Mater.* 7 (1995) 236.
- [6] (a) D. Seyferth, G.H. Wiseman, C. Prud'homme, *J. Am. Ceram. Soc.* 66 (1983) C-13. (b) D. Seyferth, G.H. Wiseman, C. Prud'homme, *Mater. Sci. Res.* 17 (1984) 263. (c) D. Seyferth, G.H. Wiseman, *Am. Chem. Soc. Polym. Div. Polym. Prepr.* 25 (1984) 10. (d) R.M. Laine, Y.D. Blum, A. Chow, R. Hamlin, K.B. Schwartz, D.J. Rowcliffe, *Am. Chem. Soc. Polym. Div. Polym. Prepr.* 28 (1987) 393. (e) Y.D. Blum, K.B. Schwartz, R.M. Laine, *J. Mater. Sci.* 24 (1989) 1707. (f) E. Werner, U. Klingebiel, F. Pauer, D. Stalke, R. Riedel, S. Schaible, *Z. Anorg. Allg. Chem.* 596 (1991) 35.
- [7] (a) B.G. Penn, F.E. Ledbetter III, J.M. Clemons, J.G. Daniels, *J. Appl. Polym. Sci.* 27 (1982) 3751. (b) D. Seyferth, G.H. Wiseman, *J. Am. Ceram. Soc.* 67 (1984) C-132. (c) A. Lavedrine, D. Bahloul, P. Goursat, N.S. Choong Kwet Yive, R.J.P. Corriu, D. Leclerq, P.H. Mutin, A. Vioux, *J. Eur. Ceram. Soc.* 8 (1991) 221. (d) N.S. Choong Kwet Yive, R.J.P. Corriu, D. Leclerq, P.H. Mutin, A. Vioux, *New J. Chem.* 15 (1991) 85. (e) T. Vaahs, M. Brück, W.D.G. Böcker, *Adv. Mater.* 4 (1992) 224. (f) N.S. Choong Kwet Yive, R.J.P. Corriu, D. Leclerq, P.H. Mutin, A. Vioux, *Chem. Mater.* 4 (1992) 141. (g) D. Bahloul, M. Pereira, P. Goursat, N.S. Choong Kwet Yive, R.J.P.

- Corriu, J. Am. Ceram. Soc. 76 (1993) 1156. (h) D. Bahloul, M. Pereira, P. Goursat, J. Am. Ceram. Soc. 76 (1993) 1163. (i) D. Mocaer, R. Pailler, R. Naslain, C. Richard, J.-P. Pillot, J. Dunoguès, C. Gerardin, F. Taulelle, J. Mater. Sci. 28 (1993) 2615.
- [8] (a) M. Takamizawa, T. Kobayashi, A. Hayashida, Y. Takeda, US Patent 4604367, 1986. (b) T. Wideman, K. Su, E.E. Remsen, G.A. Zank, L.G. Sneddon, Chem. Mater. 7 (1995) 2203.
- [9] D. Seyferth, H. Plenio, W.S. Rees Jr., K. Büchner, Silicon ceramics with a dash of boron, in: *Frontiers of Organosilicon Chemistry*, The Royal Society of Chemistry, Cambridge, 1991.
- [10] M. Jansen, H.-P. Baldus, German Patent DE 4 107 108 A1, 1992.
- [11] H.-P. Baldus, O. Wagner, M. Jansen, Mater. Res. Soc. Symp. Proc. 271 (1992) 821.
- [12] K. Su, E.E. Remsen, G.A. Zank, L.G. Sneddon, Chem. Mater. 5 (1993) 547.
- [13] H.-P. Baldus, M. Jansen, O. Wagner, Key Eng. Mater. 89-91 (1994) 75.
- [14] A. Kienzle, Thesis, Universität Stuttgart, 1994.
- [15] R. Riedel, A. Kienzle, W. Dressler, L. Ruwisch, J. Bill, F. Aldinger, Nature 382 (1996) 796.
- [16] R. Riedel, J. Bill, A. Kienzle, Appl. Organomet. Chem. 10 (1996) 241.
- [17] (a) D. Heimann, J. Bill, F. Aldinger, Fortschrittsberichte der Deutschen Keramischen Gesellschaft, Werkstoffe-Verfahren-Anwendungen, Bd. 10, Keramische Schichten, 1995. (b) D. Heimann, Thesis, Universität Stuttgart, 1996.
- [18] D. Seyferth, H. Plenio, J. Am. Ceram. Soc. 73 (1990) 2131.
- [19] A. Kienzle, A. Obermeyer, R. Riedel, F. Aldinger, A. Simon, Chem. Ber. 126 (1993) 2569.
- [20] A. Obermeyer, A. Kienzle, J. Weidlein, R. Riedel, A. Simon, Z. Anorg. Allg. Chem. 620 (1994) 1357.
- [21] (a) A. Kienzle, J. Bill, F. Aldinger, R. Riedel, Nanostructured Mater. 6 (1995) 349. (b) R. Riedel, A. Greiner, G. Miede, W. Dreßler, H. Fueß, J. Bill, F. Aldinger, Angew. Chem. in press.
- [22] A. Kienzle, K. Wurm, J. Bill, F. Aldinger, R. Riedel, From molecules to materials, in: N. Auner, J. Weis (Eds.) *Organosilicon Chemistry II*, Verlag Chemie, Weinheim, 1996, p. 725.
- [23] P.R. Jones, J.K. Myers, J. Organomet. Chem. 34 (1972) C9.
- [24] M. Weinmann, R. Haug, J. Bill, F. Aldinger, Appl. Organomet. Chem. in press.
- [25] G.M. Barrow, Physikalische Chemie, Bohmann Verlag, Wien, 1983.
- [26] H. Berger, US Patent 3465019, 1969.