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Si−B−C−N Ceramic Precursors Derived from Dichlorodivinylsilane and Chlorotrivinylsilane. 1. Precursor Synthesis

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Dichlorodivinylsilane and chlorotrivinylsilane were used as starting materials for the synthesis of Si−B−C−N−H polymers. They were either reacted with ammonia to yield silazanes or with cyanamide to form silylcarbodiimides. The reactions occurred almost quantitatively. Starting from dichlorodivinylsilane, oligomeric or polymeric compounds were obtained, whereas reaction of chlorotrivinylsilane delivered monomers. The products were polymerized into solid Si−B−C−N−H polymers by the addition of borane dimethyl sulfide leading to an almost complete hydroboration of the vinyl groups. The compounds were characterized by chemical analysis and infrared spectroscopy. Boron-free compounds were further analyzed by nuclear magnetic resonance spectroscopy and partly by gas chromatography−mass spectroscopy studies.

1. Introduction

Thermolysis of organometallic polymers containing the elements silicon, nitrogen, carbon, and boron leads to the formation of Si−B−C−N ceramic materials.[1−5] Chemical synthesis gives the possibility to tailor the composition and structure of these molecular precursors which in turn determine the properties of the produced ceramics. In this way, a considerable number of promising materials has been synthesized which are temporarily stable at high temperatures (up to 2000 °C) and resist oxidative attack.[3−10] The reasons for these remarkable properties are not completely understood until now. Boron was shown to be necessary for the development of distinct microstructures.[11−13] By the addition of this element to an Si−C−N precursor, the amorphous state of as-thermolyzed ceramic materials can be stabilized and the decomposition of silicon nitride can be retarded.

The attachment of boron to an Si−C−N precursor can easily be achieved if alkenyl groups are present in the polymer backbone as in oligo(vinylsilazanes) or poly(vinyl)silylcarbodiimides with one vinyl group attached to one silicon atom. Hydroboration of these units with B_2H_6 or H_3B·donor occurs quantitatively and usually yields glasslike polymers[14] with a homogeneous distribution of boron on an atomic scale. The reaction proceeds via the addition of one H−B unit to a vinyl group of the silazane/silylcarbodiimide. Boron containing molecules such as B_2H_6 or H_3B·donor having three H−B bonds per B atom can react with three vinyl groups. Because the number of vinyl groups usually corresponds to the number of silicon atoms in the polymer, these organometallic materials are often characterized by a B/Si atomic ratio of 1:3.

To increase the relative amount of boron in the polymers, substituted boranes “H_2BR” or “HBR_2” (R = organic residue or halogen atom) can be used for the hydroboration of vinyl groups.[15−20] In this way, one

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borane molecule is added to only two or to one vinyl group. The B/Si atomic ratio can thus be increased to 1:2 or even 1:1.

Another possibility to introduce more boron atoms per silicon atom is the use of silazanes or silylcarbodiimides having more than one vinyl group per silicon atom. Starting from divinyl- and trivinylsilazanes or -silylcarbodiimides, Si−B−C−N ceramic precursors are obtained in this study which are characterized by an Si/B atomic ratio of 2:3 or 1:1.

2. Experimental Section

2.1. General Comments. All reactions were carried out in a purified argon atmosphere using standard Schlenk techniques.[21] The chlorovinylsilanes $(H_2C{=}CH)_2SiCl_2$ and $(H_2C{=}CH)_3SiCl$ were obtained from ABCR GmbH & Co. KG, Germany, and freshly distilled before use. ^{n}Butyllithium was purchased as a 2.5 M solution in ^{n}hexane from Merck-Schuchardt, Germany. Borane dimethyl sulfide (2 M solution in toluene) was obtained from Sigma-Aldrich, Germany. Tetrahydrofuran (THF), ^{n}hexane, and toluene were purified by distillation from potassium.

Fourier transform infrared spectra were obtained with a Bruker IFS66 spectrometer as KBr pellets (solids) or as films in NaCl cells (liquids). ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra in solution were recorded on a Bruker Avance 250 spectrometer operating at 250.07, 62.89, and 49.68 MHz, respectively. Chemical shifts are reported in δ relative from tetramethylsilane ($\delta = 0$ ppm) with the solvent as an internal standard.

Mass spectrum-coupled gas chromatography (GC−MS) was performed using a Hewlett-Packard 5890 Series II for GC (column, HP-5 MS 30 m × 0.25 mm; phase thickness, 0.25 μm; carrier gas, helium 0.066 mL/min) and a Finnigan MAT 95 for MS at the Institut für Organische Chemie der Universität Stuttgart. The samples were ionized by electron impact (EI, 70 eV) or by chemical ionization (CI, reactant gas CH_4). Intensity values are reported relative to the base peak.

Chemical analysis was performed using a combination of different analysis equipment (ELEMENTAR Vario EL, ELTRA CS 800 C/S Determinator, LECO TC-436 N/O Determinator) and by atom emission spectrometry (ISA JOBIN YVON JY70 Plus).

2.2. Synthesis of Oligo(divinylsilazane), 1a. In a 0.5 L Schlenk flask, equipped with a gas inlet tube, a mechanical stirrer and a dry ice/2-propanol reflux condenser, 21.6 g of $(H_2C{=}CH)_2SiCl_2$ (20 mL, 141 mmol) was dissolved in 250 mL of THF and cooled to 0 °C. A moderate stream of ammonia was introduced under vigorous stirring. Ammonium chloride precipitated immediately. The reaction was complete after 15 min, when liquid ammonia condensed in the reflux condenser. The mixture was allowed to warm to room temperature overnight. After filtration through a pad of Celite, the precipitate was thoroughly washed with THF. The solutions were combined and the solvent was distilled under reduced pressure at 50 °C. The residue was dried at room temperature under reduced pressure (2×10^{-2} mbar). A total of 13.4 g of the title compound was isolated (yield 98%) as a colorless oil. M[C_4H_7NSi] = 97.19 g/mol. Anal. found (calcd) for $C_{4.5}H_{7.2}N_{1.4}Si_1O_{0.1}$ (C_4H_7NSi): C, 49.2 (49.4); H, 6.6 (7.3); N, 17.8 (14.4); Si, 25.4 (28.9); O, 1.0 (0.0) wt %. IR (neat): 3389 m, br (ν N−H), 3049 m (ν_{as} $=CH_2$), 3007 w (ν =C−H), 2966 m (ν C−H), 2943 m (ν_s CH_2), 1592 w (ν C=C), 1403 s (δ_{as} CH_2), 1271 w (δ_s CH_2), 1171 vs, br (δ Si−N−H), 1008 s (δ_{as} CH_2), 957 s (δ_s CH), 924 vs (ν Si−C), 781 m, 720 m (ρ SiCH), 632 m, 547 w cm^{-1}. ^{1}H NMR (C_6D_6, δ): 0.55 (s, br, 1H, NH), 5.88−6.35 (m, 6H, $-CH{=}CH_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, δ): 133.1 ($-CH{=}\mathit{C}H_2$), 139.4 ($-\mathit{C}H{=}CH_2$) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, δ): −25.2, −27.3 ppm. GC−MS (CI), M[SiC_4H_7N], peak 1 (trimer; retention time, 19.7 min; area, 10 383 662) *m/z*: 292 (43%, $(M_3 + H)^+$), 291 (10%, $M_3{}^+$), 265 (23%, $(M_3 + H - Vi)^+$), 264 (100%, $(M_3 - Vi)^+$), 250 (8%, $(M_3 + H - Vi - NH)^+$), 237 (6%, $(M_3 - 2Vi)^+$), 211 (2%, $(M_3 + H - 3Vi)^+$); peak 2 (trimer; retention time, 19.9 min; area, 1 557 714): 294 (57%, $(M_3 + 3)^+$), 267 (24%, $(M_3 + 3 - Vi)^+$), 266 (100%, $(M_3 + 2 - Vi)^+$), 264 (75%, $(M_3 - Vi)^+$), 238 (4%, $(M_3 + H - 2Vi)^+$); peak 3 (tetramer; retention time, 25.3 min; area, 129 927): 391 (1%, $(M_4 + 3)^+$), 390 (5%, $(M_4 + 2)^+$), 389 (18%, $(M_4 + H)^+$), 388 (3%, $M_4{}^+$), 362 (9%, $(M_4 + H - Vi)^+$), 361 (100%, $(M_4 - Vi)^+$), 347 (3%, $(M_4 + H - Vi - NH)^+$), 333 (1%, $(M_4 - H - 2Vi)^+$).

2.3. Synthesis of Poly(borosilazane), 1. To a solution of 7.75 g of oligo(divinylsilazane) **1a** (80 mmol) in 125 mL of toluene, 26.6 mL of a 2 M solution of $H_3B{\cdot}SMe_2$ in toluene (53 mmol) was added at 0 °C under vigorous stirring within 5 min. The solution was allowed to warm to room temperature. Gel formation started after about 1.5 h. After 3 days, the volatile compounds were removed by vacuum distillation at 70 °C. The polymer was dried at 70 °C, 10^{-2} mbar, and isolated as a colorless glasslike material in 99% yield (8.37 g). M[$B_2C_{12}H_{27}N_3Si_3$] = 319.25 g/mol. Anal. found (calcd) for $B_{1.9}C_{11.9}H_{24.5}N_{3.0}Si_3O_{0.2}$ ($B_2C_{12}H_{27}N_3Si_3$): B, 6.4 (6.8); C, 45.0 (45.1); H, 7.8 (8.5); N, 13.2 (13.2); Si, 26.6 (26.4); O, 1.0 (0.0) wt %. IR (KBr): 3410 m, br (ν N−H), 3046 vw (ν =C−H), 2939 s (ν_s C−H), 2908 s (ν_{as} CH_2), 2871 s (ν_s CH_2), 2477 vw, br (ν B−H), 1460 m (ρ CH_2), 1406 m (δ_{as} CH_2), 1379 w, 1309 m, 1158 s, br (δ Si−N−H), 902 s, br (ν Si−C), 789 s cm^{-1}.

2.4. Synthesis of Poly(divinylsilylcarbodiimide), 2a. To a solution of 21.85 g of $(H_2C{=}CH)_2SiCl_2$ (20.2 mL, 143 mmol) in 100 mL of THF, a solution of 6.00 g of H_2NCN (143 mmol), 22.6 g of pyridine (Py) (23.0 mL, 286 mmol), and 25 mL of THF was added dropwise under vigorous stirring at 0 °C. A colorless precipitate formed immediately. After slowly warming to room temperature, the mixture was refluxed for 4 h and subsequently stirred for an additional 3 days at room temperature. The precipitate was filtered of and washed twice with THF. The solutions were combined and all volatile components were removed by distillation under reduced pressure. The remaining suspension which contained the polysilylcarbodiimide and traces of Py·HCl was mixed with 30 mL of ^{n}hexane, stirred for 0.5 h, and filtered. The solution was dried at room temperature, 3×10^{-2} mbar. A total of 16.85 g of highly viscous colorless **2a** was isolated (96%). M[$C_5H_6N_2Si$] = 122.20 g/mol. Anal. found (calcd) for $C_{5.3}H_{5.9}N_{2.2}Si_1O_{0.1}$ ($C_5H_6N_2Si$): C, 49.2 (49.1); H, 4.6 (4.9); N, 23.3 (22.9); Si, 21.6 (23.0); O, 1.6 (0.0) wt %. IR (neat): 3059 m (ν =C−H), 3014 w (ν =C−H), 2978 w (ν_{as} C−H), 2952 m (ν C−H), 2236 vs, br (ν_{as} N=C=N), 2143 vs, br (ν_{as} N=C=N), 1933 w, 1595 s (ν C=C), 1404 s (δ_{as} CH_2), 1269 w (δ_s CH_2), 1002 s (δ_{as} CH_2), 965 s (δ_s CH), 769 s, 746 vs, br (ρ SiCH), 578 s, 545 s cm^{-1}. ^{1}H NMR (C_6D_6, δ): 6.02−6.13 (m, $-CH{=}CH_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, δ): 122.4 (N*C*N), 132.9 ($-CH{=}\mathit{C}H_2$), 136.4 ($-\mathit{C}H{=}CH_2$) ppm.

2.5. Synthesis of Poly(borosilylcarbodiimide), 2. To a solution of 11.46 g of poly(divinylsilylcarbodiimide) **2a** (94 mmol) in 100 mL of toluene, 31 mL of a 2 M solution of $H_3B{\cdot}SMe_2$ in toluene (62 mmol) was added dropwise at 0 °C under vigorous stirring. Spontaneous gelation occurred instantly. After warming to room temperature, the mixture was stirred for 3 days. During this time, a suspension of a fine-grained colorless precipitate was produced. The volatile compounds were removed by vacuum distillation at 50 °C. After drying the residue at 100 °C and 3×10^{-2} mbar, 11.88 g of **2** was isolated as a very fine-grained powder (96%). M[$B_2C_{15}H_{24}N_6Si_3$] = 394.28 g/mol. Anal. found (calcd) for $B_{2.0}C_{14.4}H_{24.3}N_{5.8}Si_3O_{0.2}$ ($B_2C_{15}H_{24}N_6Si_3$): B, 5.5 (5.5); C, 44.5 (45.7); H, 6.3 (6.1); N, 20.8 (21.3); Si, 21.7 (21.4); O, 0.7 (0.0) wt %. IR (KBr): 2957 m (ν_s C−H), 2919 m (ν_{as} CH_2), 2878 m (ν_s CH_2), 2218 vs (ν_{as} N=C=N), 2125 sh (ν_{as} N=C=N), 1459 w (ρ CH_2), 1406 w (δ_{as} CH_2), 1263 m (δ_s CH_2), 1299 w, 1167 m (ν C−C), 1102 m (δ_{as} CH_2), 759 s, 585 m cm^{-1}.

2.6. Synthesis of Trivinylsilylamine, 3a. In a 1 L Schlenk flask equipped with a gas inlet tube, a mechanical stirrer, and a dry ice/2-propanol reflux condenser, 50.0 g of $(H_2C{=}CH)_3$-

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[20] Matsumoto, R. L.; Schwark, J. M. U.S. Patent 5,386,006, 1995.

[21] All apparatus are equipped with sidearms for pumping out the air and moisture and introducing inert gas. See also: Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

SiCl (53.5 mL, 346 mmol) was dissolved in 0.5 L of THF and cooled to 0 °C. A moderate stream of ammonia was introduced under vigorous stirring. Ammonium chloride precipitated immediately. The reaction was complete after 0.5 h, when liquid ammonia condensed in the reflux condenser. The mixture was allowed to warm to room temperature within 2 h, then it was filtered through a pad of Celite. The precipitate was washed 3 times with THF, and the combined liquid phases fractionated with a Vigreux column. The distillation delivered THF, and at 127 °C 33.8 g (270 mmol) of **3a** (78%) as a colorless liquid which contained traces of ammonium chloride. This impurity precipitates in the main after addition of some milliliters of ^{n}hexane or upon storage for several days and can easily be filtered of. M[$C_6H_{11}NSi$] = 125.25 g/mol. Anal. found (calcd) for $C_{6.0}H_{9.8}N_{1.0}Si_1O_{0.1}$ ($C_6H_{11}NSi$): C, 57.7 (57.5); H, 7.9 (8.9); N, 11.0 (11.2); Si, 22.5 (22.4); O, 1.1 (0.0) wt %. IR (neat): 3472 m (ν_{as} NH_2), 3397 m (ν_s NH_2), 3050 s (ν_{as} $=CH_2$), 3008 m (ν $=C-H$), 2968 s (ν C−H), 2944 s (ν C−H), 1917 w, 1592 m (ν C=C), 1551 m (δ NH_2), 1402 s (δ_{as} CH_2), 1271 w (δ_s CH_2), 1178 w, 1067 s, 1009 s (δ_{as} CH_2), 958 s (δ_s CH), 846 s (ν Si−N), 768 m, 716 s (ρ SiCH), 609 m (ν_s SiC_3), 551 m cm^{-1}. ^{1}H NMR (C_6D_6, δ): 0.40 (t, br, 2H, $^1J_{N-H}$ = 49 Hz, NH_2), 5.89−6.50 (m, 9H, $-CH=CH_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 134.4 ($-CH=CH_2$), 137.1 ($-CH=CH_2$) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, δ): −24.3 ppm. GC−MS (CI), M[$SiC_6H_{11}N$], peak 1 (retention time, 5.3 min; area, 28 479 138) *m/z*: 126 (16%, $(M + H)^+$), 125 (1%, M^+), 109 (27%, $(M - NH_2)^+$), 108 (41%, $(M - H - NH_2)^+$), 98 (100%, $(M - Vi)^+$), 97 (40%, $(M - H - Vi)^+$), 72 (20%, $(M + H - 2Vi)^+$), 71 (9%, $(M - 2Vi)^+$); peak 2 (retention time, 5.6 min; area, 624 141); peak 3 (retention time, 6.1 min; area, 4 682 059).

2.7. Synthesis of Poly(borosilylamine), 3. To a solution of 15.03 g of trivinylsilylamine **3a** (120 mmol) in 120 mL of toluene, 60 mL of a 2 M solution of $H_3B{\cdot}SMe_2$ in toluene (120 mmol) was added under vigorous stirring at 0 °C within 10 min. After warming to room temperature, gel formation started within 4 h. After 16 h, the volatile compounds were distilled in a vacuum at 50 °C and the residue dried at 90 °C (3×10^{-2} mbar). A total of 15.88 g of the glasslike colorless polymer was isolated (95%). M[$BC_6H_{14}NSi$] = 139.08 g/mol. Anal. found (calcd) for $BC_{6.1}H_{13.0}N_{1.0}Si_{0.8}O_{0.2}$ ($BC_6H_{14}NSi$): B, 7.7 (7.8); C, 52.6 (51.8); H, 9.3 (10.1); N, 9.7 (10.1); Si, 15.9 (20.2); O, 2.8 (0.0) wt %. IR (KBr): 3423 m, br (ν_{as} NH_2), 3047 m (ν $=C-H$), 3008 w (ν $=C-H$), 2905 s (ν C−H), 2866 s (ν C−H), 2478 w, br (ν B−H), 1605 m (ν C=C), 1460 m (ρ CH_2), 1401 vs (δ_{as} CH_2), 1271 w (δ_s CH_2), 1156 s (δ Si−N−H, ν C−C), 1095 s, 1009 s (δ_{as} CH_2), 954 s (δ_s CH), 924 s (ν Si−C), 727 s (ρ SiCH) cm^{-1}.

2.8. Synthesis of Bis(trivinylsilyl)amine, 4a. (a) The residue obtained after distillation of **3a** was distilled under reduced pressure (3×10^{-2} mbar) at about 50 °C to yield 2.70 g of colorless liquid **4a** (12 mmol, 17%). (b) To a solution of 11.27 g of trivinylsilylamine **3a** (90 mmol) in 50 mL of ^{n}hexane, 36.0 mL of a 2.5 M solution of ^{n}BuLi in ^{n}hexane was slowly added within 1 h at room temperature, whereby a colorless precipitate formed. After additional stirring for 2 h, 11.9 g of chlorotrivinylsilane (12.7 mL, 95 mmol) was added dropwise at room temperature. The mixture was stirred overnight and subsequently heated to reflux for 5 h. After filtration, the solvent was removed by distillation under reduced pressure at room temperature. The residue was fractioned at about 50 °C (2×10^{-2} mbar) to yield 17.00 g of colorless liquid **4a** (73 mmol, 81%). M[$C_{12}H_{19}NSi_2$] = 233.46 g/mol. Anal. found (calcd) for $C_{11.6}H_{17.8}N_{1.1}Si_2O_{0.2}$ ($C_{12}H_{19}NSi_2$): C, 59.0 (61.7); H, 7.6 (8.2); N, 6.8 (6.0); Si, 23.8 (24.1); O, 1.5 (0.0) wt %. IR (KBr): 3367 w, br (ν N−H), 3051 m (ν $=C-H$), 3008 w (ν $=C-H$), 2969 w (ν C−H), 2945 m (ν C−H), 1916 w, 1592 m (ν C=C), 1402 s (δ_{as} CH_2), 1271 w (δ_s CH_2), 1177 s, br (δ Si−N−H), 1008 s (δ_{as} CH_2), 957 vs (δ_s CH), 935 s (ν Si−C), 767 s, 727 s (ρ SiCH), 615 w (ν_s SiC_3), 553 m cm^{-1}. ^{1}H NMR (C_6D_6, δ): 0.61 (s, br, 1H, NH), 5.9−6.7 (m, 18H, $-CH=CH_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 134.4 ($-CH=CH_2$), 137.2 ($-CH=CH_2$) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, δ): −24.6 ppm. MS (EI), M[$Si_2C_{12}H_{19}N$], *m/z*: 233 (2%, M^+), 206 (25%, $(M - Vi)^+$), 179 (100%, $(M - 2Vi)^+$), 152 (30%, $(M - 3Vi)^+$), 151 (48%, $(M - 3Vi - H)^+$), 125 (21%, $(M - 4Vi)^+$), 109 (32%, $(SiVi_3)^+$), 98 (23%, $(M - 5Vi)^+$), 83 (30%, $(HSiVi_2)^+$), 72 (15%, $(M - 6Vi)^+$).

2.9. Synthesis of Poly(borodisilylamine), 4. To a solution of 10.74 g of bis(trivinylsilyl)amine **4a** (46 mmol) in 270 mL of toluene, 46 mL of a 2 M solution of $H_3B{\cdot}SMe_2$ in toluene (92 mmol) was added dropwise at 0 °C within 10 min. The mixture was allowed to warm to room temperature. Beginning gelation was observed within 1 h. After 3 days, volatile compounds were removed by distillation under reduced pressure at 50 °C. The residue was dried at 100 °C, 10^{-2} mbar. The title compound was isolated as a colorless glasslike material in 100% yield (11.97 g). M[$B_2C_{12}H_{25}NSi_2$] = 261.13 g/mol. Anal. found (calcd) for $B_2C_{12.3}H_{24.4}N_{1.0}Si_{2.0}O_{0.2}$ ($B_2C_{12}H_{25}NSi_2$): B, 8.1 (8.3); C, 55.2 (55.2); H, 9.2 (9.6); N, 5.5 (5.4); Si, 21.3 (21.5); O, 0.9 (0.0) wt %. IR (KBr): 3401 w, br (ν N−H), 3046 vw (ν $=C-H$), 2939 s (ν C−H), 2908 s (ν C−H), 2871 s (ν C−H), 2477 vw, br (ν B−H), 1461 m (ρ CH_2), 1408 m (δ_{as} CH_2), 1379 w, 1306 m, 1162 s, br (δ Si−N−H), 916 s, br (ν Si−C), 770 s (ρ SiCH) cm^{-1}.

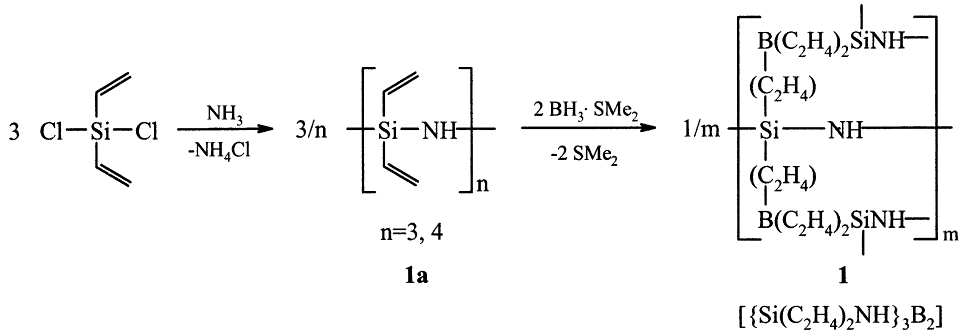
2.10. Synthesis of Bis(trivinylsilyl)carbodiimide, 5a. To a solution of 15.11 g of $(H_2C=CH)_3SiCl$ (16.2 mL, 104 mmol) in 100 mL of THF, a solution of 2.19 g of H_2NCN (52 mmol) and 8.26 g of pyridine (8.4 mL, 104 mmol) in 20 mL of THF was added dropwise under vigorous stirring at 15 °C during 20 min. A colorless precipitate formed immediately. After complete addition, the reaction mixture was heated to reflux for 3 h and allowed to cool to room temperature overnight. After removal of solid products by filtration through a pad of Celite, THF was removed by distillation at 70 °C. The residue was distilled at 100 °C under reduced pressure (5×10^{-2} mbar). The raw product was mixed with 10 mL of ^{n}hexane, and the mixture was stirred for 12 h and subsequently filtered. The solvent was removed by distillation under reduced pressure to yield 12.03 g of colorless air- and moisture-sensitive oily **5a** (49 mmol, 95%). M[$C_{13}H_{18}N_2Si_2$] = 258.47 g/mol. Anal. found (calcd) for $C_{13.3}H_{18.0}N_{2.0}Si_2O_{0.2}$ ($C_{13}H_{18}N_2Si_2$): C, 59.9 (60.4); H, 6.8 (7.0); N, 10.4 (10.8); Si, 21.1 (21.7); O, 1.2 (0.0) wt %. IR (KBr): 3676 m, br, 3179 w, 3055 s (ν $=C-H$), 3010 s (ν $=C-H$), 2974 s (ν_{as} C−H), 2949 s (ν C−H), 2206 vs, br (ν_{as} N=C=N), 1924 m, 1593 s (ν C=C), 1403 s (δ_{as} CH_2), 1269 m (δ_s CH_2), 1005 s (δ_{as} CH_2), 959 s (δ_s CH), 737 s (ρ SiCH), 647 s (ν_s SiC_3), 534 s cm^{-1}. ^{1}H NMR (C_7D_8, δ): 5.85−6.18 (m, $-CH=CH_2$) ppm. $^{13}C\{^1H\}$ NMR (C_7D_8, δ): 124.3 (N=C=N), 133.9 ($-CH=CH_2$), 135.5 ($-CH=CH_2$ ppm). $^{29}Si\{^1H\}$ NMR (C_7D_8, δ): −31.1 ppm.

2.11. Synthesis of Polyboro(disilylcarbodiimide), 5. To a solution of 8.98 g of bis(trivinylsilyl)carbodiimide **5a** (35 mmol) in 130 mL of toluene, 35 mL of a 2 M solution of $H_3B{\cdot}SMe_2$ (70 mmol) in toluene was added dropwise under vigorous stirring at 0 °C. The mixture was allowed to warm to room temperature. Within 15 min, the viscosity increased and a gel was formed. After 3 days, the volatile components were removed under reduced pressure. The residue was dried in a vacuum (2×10^{-2} mbar) at 70 °C to yield 9.65 g of pale yellow glassy grains and colorless powder (96%). M[$B_2C_{13}H_{24}N_2Si_2$] = 286.14 g/mol. Anal. found (calcd) for $B_2C_{13.3}H_{24.1}N_{2.0}Si_{2.0}O_{0.2}$ ($B_2C_{13}H_{24}N_2Si_2$): B, 7.4 (7.6); C, 54.6 (54.6); H, 8.3 (8.5); N, 9.6 (9.8); Si, 19.2 (19.6); O, 1.3 (0.0) wt %. IR (KBr): 2948 m (ν C−H), 2905 m (ν C−H), 2872 m (ν C−H), 2189 vs, br (ν_{as} N=C=N), 1459 w (ρ CH_2), 1406 m (δ_{as} CH_2), 1294 m, 1269 m (δ_s CH_2), 1163 m (ν C−C), 1005 s (δ_{as} CH_2), 958 m (δ_s CH), 743 s (ρ SiCH), 578 m cm^{-1}.

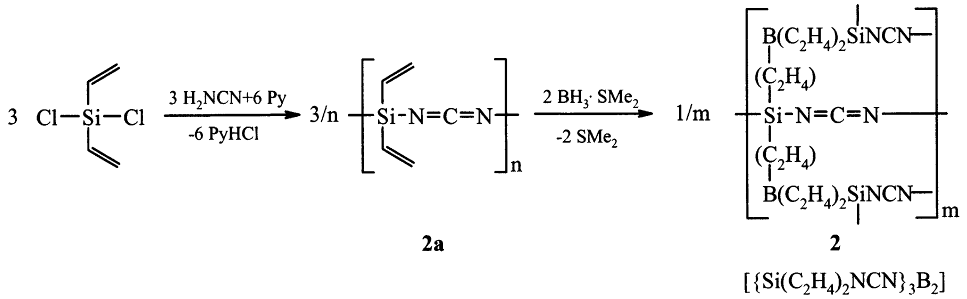
3. Results and Discussion

Polymers Derived from Dichlorodivinylsilane. The reaction of dichlorodivinylsilane with ammonia was performed in THF at 0 °C. A solution of liquid oligodivinylsilazanes **1a** was produced (see reaction Scheme 1[22]), which could easily be separated from ammonium chloride by filtration. The dried colorless oil was isolated in 98% yield and characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy as well

Scheme 1



Scheme 2



as by mass spectrometry. The IR spectrum of **1a** shows a broad absorption at 3389 cm^{-1} characteristic for the N−H stretching vibration in oligosilazanes. Besides, sharp bands with low intensity at 3049, 3007 (ν =C−H), and 1592 cm^{-1} (ν C=C) indicate the presence of vinyl groups. The Si−N−H deformation vibration causes a very intensive broad band at 1171 cm^{-1}. In the ^{1}H NMR spectrum of **1a**, the nitrogen bonded protons show a broad resonance without fine structure centered at 0.55 ppm. The signal of the vinyl group H atoms occurs as a multiplet between 5.88 and 6.35 ppm. The ^{13}C{^{1}H} NMR spectrum as expected exhibits two resonances for the vinyl group C atoms at 133.1 and 139.4 ppm. In the ^{19}Si{^{1}H} NMR spectrum of **1a**, two signals at −25.2 and −27.3 ppm were observed, the latter in much lower intensity. They can be assigned to silicon atoms in six- and eight-membered silazanerings, respectively. To further characterize the molecular structure of the silazane mixture, GC−MS experiments were performed. Two compounds separated by gas chromatography have very similar retention times and were identified by CI−MS as trimer ring molecules [SiVi$_2$NH]$_3$. A third compound with a significantly longer retention time occurred in a small amount and could be identified as the tetramer [SiVi$_2$NH]$_4$. The intensity ratio of the GC peaks shows that, during ammonolysis, the formation of six-membered [SiVi$_2$NH]$_3$ rings is clearly preferred over formation of eight-membered rings; the molecular trimer/tetramer ratio is 92:1. The MS pattern of all three components is characterized by (protonated) molecular ion peaks at 292 and 291 u (M$_3^+$) for the first trimer compound, at 294 u for the second trimer and at 391, 390, 389, and 388 u (M$_4^+$) for the tetramer. The respective base peaks at 264/266 (trimers) and 361 u (tetramer) can be assigned to (protonated) molecule ions minus one vinyl group. The fragmentation pattern corresponds to subsequent elimination of vinyl groups.

The reaction of **1a** with borane dimethyl sulfide was carried out in toluene at 0 °C in a Si(silazane)/B(H$_3$B·SMe$_2$) = 3:2 stoichiometric ratio to achieve complete hydroboration of all vinyl groups (reaction Scheme 1). The viscosity of the mixture slowly increased after complete addition of the borane. The produced gel was dried to yield poly(borosilazane) **1** in 99% yield as a colorless glasslike material. The IR spectrum of **1** shows a plain band at 1460 cm^{-1}, which is characteristic for the CH$_x$ rocking vibration in aliphatic hydrocarbon chains. Besides, very weak absorption bands at 3046 (ν =C−H) and 2477 cm^{-1} (ν B−H) indicate, that a small amount of vinyl and H−B groups remained unreacted, even after a period of 3 days. This may be a consequence of the steric hindrance in the forming highly cross-linked polymer and the increasing viscosity of the solution during gelation. Furthermore, the IR spectrum of **1** shows a broad absorption at 3410 cm^{-1} assigned to N−H stretching vibrations which is slightly shifted to higher wavenumbers compared to **1a**. In contrast, the Si−N−H deformation vibration in **1** exhibits a bathochromic shift to 1157 cm^{-1} in comparison with **1a** (1171 cm^{-1}).

In the second scheme (Scheme 2) the reaction of equimolar amounts of dichlorodivinylsilane with cyanamide is shown. In analogy to the synthesis of recently described poly(silylcarbodiimides),[23−28] pyridine (Py)

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(22) Please note: All chemical formulas and reaction schemes for the synthesis of the chemical substances are schematic representations and may include simplifications. No evidence was obtained if hydroboration occurs regioselectively. Furthermore, it is not clear if further reactions of H$_2$B(C$_2$H$_4$)SiViR$_2$ with vinyl groups are inter- or intramolecular.

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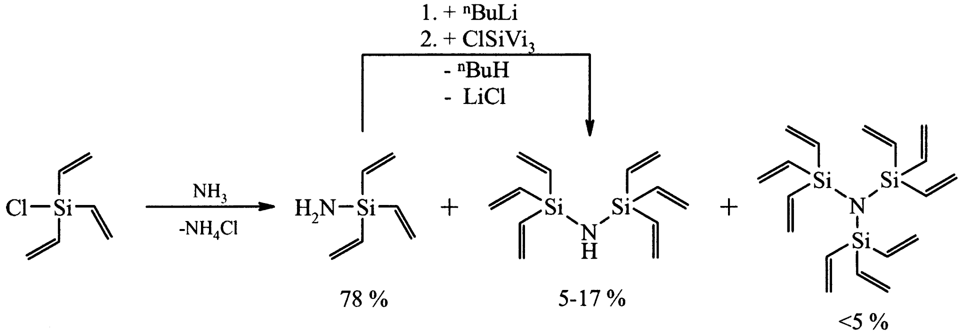
Scheme 3



3a **4a**

was used in stoichiometric amount as auxiliary base to bind hydrogen chloride that is formed during the polymerization. After filtration of precipitated pyridinium hydrochloride and evaporation of the solvent THF, the raw product was isolated. To remove dissolved Py·HCl which partly precipitates after some days, ^{n}hexane was added and the mixture was filtrated again. After appropriate workup, poly(divinylsilylcarbodiimide) **2a** could be isolated in 96% yield as a colorless highly viscous oil. In the IR spectrum, two very intensive absorptions appear at 2236 and 2143 cm^{-1} which can be attributed to asymmetric carbodiimide stretching vibrations. The presence of two of these bands was already observed in the spectra of similar polysilylcarbodiimides and is explained by coupling phenomena between neighboring N=C=N units.[29] C−H stretching vibration bands of the vinyl groups in **2a** were detected at 3059, 3014, 2978, and 2952 cm^{-1}, whereas the C=C vibration causes a band at 1595 cm^{-1}. In the ^{1}H NMR spectrum of **2a**, resonances of the vinyl protons were observed as a multiplet between 6.02 and 6.13 ppm. Compared to the vinyl group proton resonances of the silazanes **1a**, **3a**, and **4a** which stretch over at least 0.5 ppm, the proton signals in the spectra of silylcarbodiimides appear in a more restrained chemical shift range of 0.1 to 0.3 ppm. ^{13}C{^{1}H} NMR spectroscopy revealed the presence of the carbodiimide group by a weak absorption at 122 ppm. Besides, two intensive resonances were detected at 132.9 and 136.4 ppm that are attributed to the vinyl C atoms.

The hydroboration of **2a** was carried out by addition of borane dimethyl sulfide in a Si/B = 3:2 ratio in toluene solution (Scheme 2). During the reaction, waxy grains formed that aged and precipitated within 1 day as a colorless powder. After 3 days, the material was dried in a vacuum to deliver **2** in 96% yield. Emphasis has to be placed on the fact that **2** is the only polymer described in this study which forms a very fine-grained solid in contrast to the other boron-containing polymers obtained as glassy millimeter-sized particles. About 25 wt % of material **2** formed grains in the 0.1−0.5 mm range. A second sieving fraction of 15 wt % was obtained between 80 and 32 μm. The grain size of 60 wt % of **2** was determined to be below 32 μm.

The absence of both ν(=C−H) and ν(B−H) absorption bands in the IR spectrum indicates that the reaction occurred quantitatively and selectively. This finding suggests that the steric hindrance in **2** which increases with ongoing hydroboration seems to be less pronounced than in the polymer **1**. This phenomenon is probably due to the linear carbodiimide unit acting efficiently as a spacer group between reaction centers. The IR spectrum of **2** shows a very intensive absorption band at 2218 cm^{-1} with a shoulder at about 2125 cm^{-1}. These carbodiimide vibration bands exhibit a slight bathochromic shift of about 20 cm^{-1} compared to the absorption bands of the starting compound **2a**.

Polymers Derived from Chlorotrivinylsilane. The ammonolysis reaction of chlorotrialkyl- or arylsilanes $ClSiR_3$ ($R \neq CH_3$) generally produces primary silylamines as main products.[30,31] In the case of chlorotrivinylsilane, ammonolysis in THF yielded 5−17% of the disubstitution product bis(trivinylsilyl)amine **4a** and a small amount of tris(trivinylsilyl)amine (identified by NMR) besides the main product trivinylsilylamine **3a** (reaction Scheme 3) which was obtained in 78% yield. Compounds **3a** and **4a** were separated by fractionated distillation and identified by chemical analysis, IR, and NMR spectroscopy.

In the IR spectrum of trivinylsilylamine **3a**, two $-NH_2$ stretching vibrations at 3472 and 3397 cm^{-1} were detected characteristic for primary amines. The ^{1}H NMR spectra of **3a** in benzene or toluene (not shown here) show a broad structured triplet absorption for the NH_2 group at 0.40 ppm with a coupling constant J = 49 Hz. With increasing temperature, the half-width of this 1:1:1 triplet decreases. The multiplicity of the signal is due to direct ^{1}J coupling between the amine protons and the ^{14}N atom (I = 1).

GC−MS of **3a** revealed that three different compounds formed which could be characterized by EI as well as CI−MS. They have monomeric structures Vi_3SiNH_2 with very similar fragmentation patterns. In all spectra, the molecular ion peak at m/z = 125 was detected in about 1% relative intensity. The signal of the protonated molecule ion $(M + H)^+$ occurring in CI−MS spectra was observed in about 15% intensity. Decomposition is characterized by the subsequent loss of either NH_2 or vinyl groups.

The IR spectrum of bis(trivinylsilyl)amine **4a** as expected shows one broad ν (N−H) vibration band at 3367 cm^{-1} and a broad δ (Si−N−H) band at 1177 cm^{-1}.

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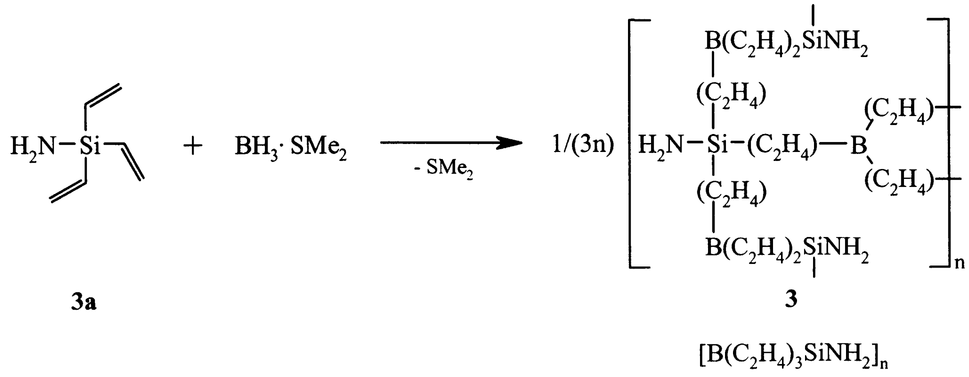
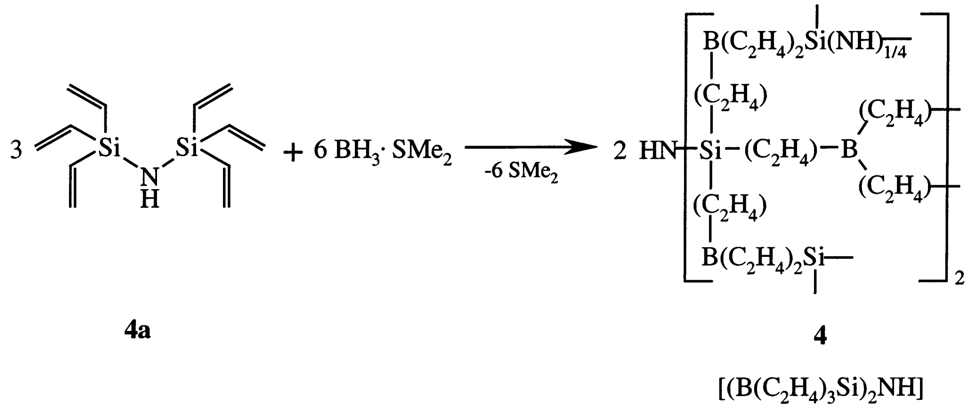
Scheme 4



$[B(C_2H_4)_3SiNH_2]_n$

Scheme 5



$[(B(C_2H_4)_3Si)_2NH]$

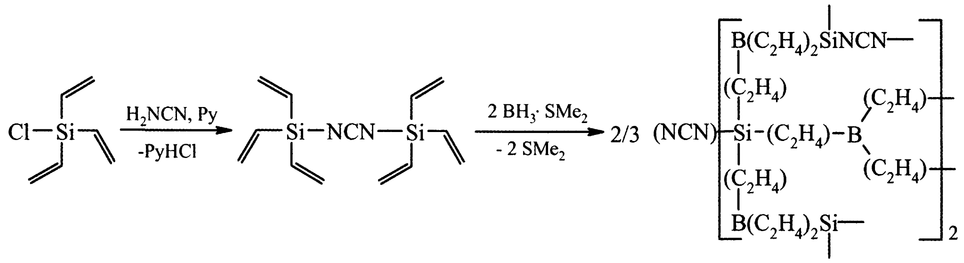
C−H stretching vibrations of the vinyl groups were detected at 3051, 3008, 2969, and 2945 cm^{-1}. In the ^{1}H NMR spectrum, one broad absorption was observed for the nitrogen-bonded H atom at 0.61 ppm. The multiplet signal of the vinyl protons was observed between 5.9 and 6.7 ppm. ^{13}C{^{1}H} resonances for the vinyl C atoms appeared at 134.4 and 137.2 ppm. The ^{29}Si{^{1}H} spectrum of **4a** shows a signal at −24.6 ppm. In the EI mass spectrum, the molecule ion peak at 233 u in 2% intensity was identified by the isotope distribution pattern. Fragmentation proceeds via elimination of vinyl groups (m = 27 u), leading to the formation of signals at 206 u (**4a** − Vi)$^+$ in 25% intensity, 179 u (**4a** − 2 Vi)$^+$ as base peak, 152 u (**4a** − 3 Vi)$^+$ in 30% intensity, 125 (21%) and 98 u (23%).

An improved procedure which delivers **4a** in almost quantitative yield was realized by a two-step reaction starting from **3a** (see Scheme 3); trivinylsilylamine **3a** was first deprotonated with 1 equiv of ^{n}butyllithium to produce the corresponding lithiumamide which was subsequently mixed in a one-pot reaction with a small excess of chlorotrivinylsilane. After appropriate workup, **4a** was isolated in 81% yield as a colorless viscous oil.

The monomeric compounds **3a** and **4a** were reacted with $H_3B \cdot SMe_2$ in toluene solution (see Schemes 4 and 5) in a stoichiometric ratio Si/B of 1:1. To prevent immediate gelation during addition of borane dimethyl sulfide, the reactions were performed in diluted solution. The hydroboration reaction of **3a** was stopped after 16 h by removing the solvent, whereas the mixture containing **4a** was allowed to react for 3 days. As evidenced from IR spectroscopy, both reactions did not occur quantitatively under the reaction conditions applied. The spectra of both precursors show vibration bands at around 3050, 2500, and 1600 cm^{-1} due to =C−H, B−H, and C=C stretching vibrations, indicating the presence of residual B−H and vinyl groups (see Experimental Section). The amount of these unreacted groups was very small in the case of polymer **4** but considerable in the case of **3**. This difference may be due to the inadequate reaction time chosen for the synthesis of **3**. The presence of vinyl groups and B−H units was observed in all boron-modified silazanes investigated in this study, whereas the vinyl groups of the silylcarbodiimides **2a** and **5a** (see the following discussion) reacted completely with the borane. Progressing hydroboration leads to an increase of the viscosity of both polymer and reaction mixture, thus retarding further reactions of the functional groups. Although the second hydroboration step is possibly facilitated if a $H_2C=CH-$ unit is located in the vicinity of the H_2BR center, the bulky substituents of the boron and the silicon atoms will sterically hinder further reactions. This steric hindrance is possibly more pronounced during the reaction of **3a** → **3** than that of **4a** → **4**, thus explaining the reduced reactivity of partially hydroborated **3a** compared to partially reacted **4a** toward further hydroboration. The increase of viscosity or sterical hindrance is obviously less pronounced in boron-modified polysilylcarbodiimides than in silazanes because of the larger N=C=N unit which separates the reaction centers.

Beside =C−H, B−H, and C=C vibration bands, the IR spectrum of **3** shows an absorption at 1460 cm^{-1} indicating the presence of saturated CH_x units which result of B−H addition to vinyl groups. Furthermore, a

Scheme 6



5a

5

$[\{B(C_2H_4)_3Si\}_2NCN]$

broad structured band centered at 3443 cm^{-1} can be assigned to different N−H stretching vibrations.

Characteristic features in the IR spectrum of **4** are two broad absorption bands at 3423 and 1162 cm^{-1} which trace back to SiNH units (N−H stretching and Si−N−H deformation vibration, respectively). The frequencies of these absorptions are almost the same in all of the boron-modified polysilazanes investigated here (3410 and 1158 cm^{-1} in **1**, 3423 and 1156 cm^{-1} in **3**), which indicates that these vibrations are widely independent from those of the rest of the molecules. The deformation vibration absorption band of the aliphatic CH_x units in **4** at 1460 cm^{-1} is present in the spectra of all of the boron-containing polymers in this study.

Chlorotrivinylsilane was also reacted with an equimolar amount of cyanamide. Pyridine was used in stoichiometric amount as auxiliary base (see reaction Scheme 6). The synthesis was performed following a route described in the literature for the preparation of bis(trimethylsilyl)carbodiimide.[23,27,32] The main product bis(trivinylsilyl)carbodiimide **5a** was purified by distillation and isolated in 95% yield as a colorless liquid. The IR and NMR spectroscopic data of **5a** are very similar to those observed for **2a** and for other polymeric silylcarbodiimides described in the literature.[28] However, the IR spectrum of **5a** shows only one strong broad carbodiimide stretching vibration band at 2206 cm^{-1}. This is in accordance with the theory mentioned previously which explains the band splitting of the asymmetric N═C═N stretching band in **2a** by vibrational coupling of vicinal N═C═N units. This coupling being obviously not possible in a monomeric disilylcarbodiimide, only one band appears at average wavenumbers.

C−H stretching bands of the vinyl groups appear at 3055, 3010, 2974, 2949, and 2877 cm^{-1} and the C═C double bond stretching causes absorption at 1593 cm^{-1}. These values are comparable to those of the starting compound Vi_3SiCl. The ^1H NMR spectrum of **5a**, as expected, shows a multiplet signal at 5.85−6.18 ppm for the vinyl group protons. The presence of the carbodiimide group was evidenced in the $^{13}C\{^1H\}$ NMR spectrum by a resonance signal at 124 ppm, whereas signals of the vinyl group carbon atoms were found at 131.9 and 135.5 ppm. The $^{29}Si\{^1H\}$ NMR spectrum of **5a** exhibits a resonance signal at −31.1 ppm.

The hydroboration of **5a** with 2 equiv of $H_3B{\cdot}SMe_2$ (Scheme 6) was performed in toluene solution at 0 °C. After addition of the borane, gel formation started within 15 min at room temperature. After 3 days the reaction was stopped by removing all volatile components. The poly(borosilylcarbodiimide) was isolated in nearly quantitative yield as a colorless glasslike material **5**.

As in the case of boron-modified polysilylcarbodiimide **2**, the IR spectrum of **5** reveals the absence of unreacted functional groups; absorption bands of residual B−H or vinyl units were not detected, indicating complete hydroboration of all vinyl groups. Furthermore, the positions of observed absorption bands in the spectra of **2** and **5** are very similar in the 4000−1100 cm^{-1} range. However, again, only one N═C═N vibration band at 2189 cm^{-1} was detected in the spectrum of **5**, whereas two overlapping bands at about 2218 and 2125 cm^{-1} appeared in the spectrum of **2**.

Summary

Novel Si−B−C−N−H polymers for the synthesis of precursor derived Si−B−C−N ceramics were successfully prepared starting from dichlorodivinylsilane or chlorotrivinylsilane. Reaction of $Cl_2Si(CH{=}CH_2)_2$ with ammonia lead to the formation of tri- and tetrameric silazanes $[Si(CH{=}CH_2)_2NH]_n$ (n = 3, 4), whereas $ClSi(CH{=}CH_2)_3$ formed a mixture of trivinylsilylamin and the corresponding di- and trisilazane $[H_xN\{Si(CH{=}CH_2)_3\}_{3-x}]$ (x = 0, 1, 2)] in the presence of ammonia. $Cl_2Si(CH{=}CH_2)_2$ and $ClSi(CH{=}CH_2)_3$ were also reacted with cyanamide, H_2NCN, to yield the polymer $[SiVi_2{-}N{=}C{=}N]_n$ and the monomer $[Vi_3SiN{=}C{=}NSiVi_3]$ (Vi:$CH{=}CH_2$), respectively. The vinyl groups in these liquid Si−C−N−H compounds were hydroborated with stoichiometric amounts of borane dimethyl sulfide to produce solid colorless polymers in almost quantitative yield (>95%). IR spectroscopy indicated the presence of residual vinyl and H−B groups in polyborosilazanes which was due to incomplete H−B addition. With ongoing hydroboration, cross-linking proceeds leading to an increased rigidity of the polymer network with the reaction centers probably far apart. Reactions are furthermore hindered by increasing viscosity of the reaction mixture. The respective absorptions (ν H−B and ν ═CH) were absent in the IR spectra of polyborosilylcarbodiimides. This finding suggests that the larger carbodiimide groups act efficiently as spacer groups between reaction centers during hydroboration which may cause the polymer network to be more flexible or relaxed.

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The compositions of the boron-containing polymers synthesized in this study are characterized by atomic ratios B/N between 1:3 and 1:0.5. On the basis of the assumption that these ratios remain roughly constant during thermolysis, the compositions of the obtained ceramics will lie in four different phase fields, namely, BN + Si_3N_4 + SiC + C, BN + Si_3N_4 + C, BN + SiC + C, and BN + $B_{4+\delta}C$ + SiC + C. Therefore, the properties and microstructures of the materials should be very different. The successful polymer-to-ceramic transformation by thermolysis will be discussed in the second part of this study[33] where investigations concerning mass and compositional changes during ceramization as well as the high-temperature behavior of the obtained ceramic materials will be described.

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