$\{B[C_2H_4Si(CH_3)NH]_2[C_2H_4Si(CH_3)N(SiH_2Ph)]\}_n$: The First Polyborosilazane Precursor for Silicoboron Carbonitride Stable to 2200 °C

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$\{B[C_2H_4Si(CH_3)NH]_2[C_2H_4Si(CH_3)N(SiH_2Ph)]\}_n$ was synthesized by base-catalyzed dehydrocoupling reaction of $\{B[C_2H_4Si(CH_3)NH]_3\}_n$ with phenylsilane. Pyrolysis of the new polyborosilazane precursor to 1050 °C gave an amorphous material $Si_{3.9}B_{1.0}C_{11}N_{3.2}$, which could resist thermal degradation to 2200 °C in argon.

Silicon nitride and silicon carbonitrides exhibit excellent chemical and mechanical properties at high temperatures but they normally decompose at 1400–1500 °C due to thermodynamic reasons.[1–3] Polyborosilazane $\{B[C_2H_4Si(CH_3)NH]_3\}_n$ **1** (where C_2H_4 = $CHCH_3$ or CH_2CH_2)[3] and its relatives $\{B[C_2H_4Si(CH_3)NH]_2[NH]_{0.5}\}_n$,[4] $\{B[C_2H_4Si(H)NH]_3\}_n$[5] and $\{B[C_2H_4\text{-}SiHCH_3\text{-}C_2H_4\text{-}Si(H)NH]_3\}_n$[6] have been shown to be excellent precursors for silicoboron carbonitrides thermally stable up to or near to 2000 °C in nitrogen-free environments. Here we report the synthesis of the first phenyl-containing polyborosilazane $\{B[C_2H_4Si(CH_3)NH]_2[C_2H_4Si(CH_3)N(SiH_2Ph)]\}_n$ **2** and its pyrolytic conversion into amorphous material $Si_{3.9}B_{1.0}C_{11}N_{3.2}$, which can resist thermal degradation up to 2200 °C in argon.

Polyborosilazane **2** was synthesized using a base-catalyzed dehydrocoupling reaction of **1** with phenylsilane, where a toluene solution of **1** and $PhSiH_3$ in a molar ratio up to $PhSiH_3$: $B[C_2H_4Si(CH_3)NH]_3$ = 3:1 was added into catalyst KH at room temperature and the reaction mixture was then heated to ~90 °C for 16 h, followed by quenching with CH_3I. The empirical formula $Si_{3.9}B_{1.0}C_{15}N_{3.1}H_{28}$ of **2** from elemental analysis is very close to its theoretical composition $Si_4B_1C_{15}N_3H_{30}$. This suggests that only one third of the N–H bonds in **1** attend the reaction. A spectroscopic comparison of **2** to **1** shows the appearance of new and strong FTIR absorption bands at 699, 734, 876 and 1116 cm^{-1} for δ (Ph) and at 2144 cm^{-1} for ν (Si–H) and significant decrease of the FTIR absorption band at 3370 cm^{-1} for ν (N–H) (Figure 1), as well as the presence of new ^1H NMR peaks at 4.9–5.8 ppm for the SiH_2Ph group. All these findings support the reaction (1):

$$\{B[C_2H_4Si(CH_3)NH]_3\}_n + n\,PhSiH_3 \rightarrow \{B[C_2H_4Si(CH_3)NH]_2[C_2H_4Si(CH_3)N(SiH_2Ph)]\}_n. \qquad (1)$$

Pyrolysis reaction of the polymer precursor **2** was carried out in 0.1 MPa Ar from room temperature to 1050 °C and at 1050 °C for 4 h, resulting in an amorphous material $Si_{3.9}B_{1.0}C_{11}N_{3.2}$ with 75 wt% yield. The similarity between the composition changes from **1** to $Si_{3.0}B_{1.0}C_{4.3}N_{2.0}$[3] and from **2** to $Si_{3.9}B_{1.0}C_{11}N_{3.2}$ suggests all the SiH_2Ph groups except hydrogen in **2** to be remained in $Si_{3.9}B_{1.0}C_{11}N_{3.2}$. XRD determinations show that this amorphous material can resist crystallization to 1700 °C in Ar.

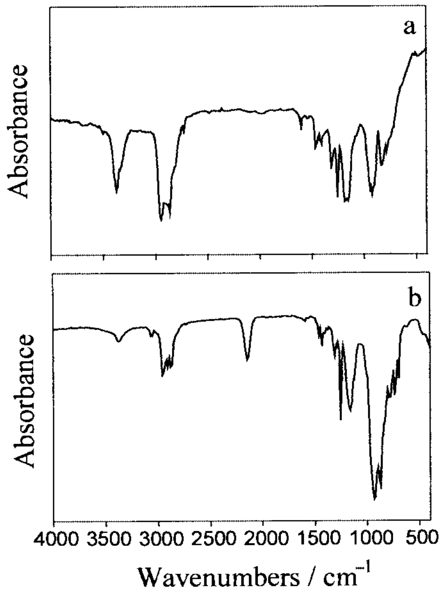

Figure 1. FTIR spectra of the polyborosilazanes (a) $\{B[C_2H_4Si(CH_3)NH]_3\}_n$ **1** and (b) $\{B[C_2H_4Si(CH_3)NH]_2[C_2H_4Si(CH_3)N(SiH_2Ph)]\}_n$ **2**.

Thermogravimetric analysis of $Si_{3.9}B_{1.0}C_{11}N_{3.2}$ was carried out in 0.1 MPa Ar with Netzsch STA 501 equipment in graphite crucibles from room temperature to 2200 °C and at 2200 °C for 30 min, resulting in a crystalline material $Si_{3.8}B_{1.0}C_{11}N_{2.8}$. Here the continuous mass loss was very low [3.9 wt% between 1400 and 2200 °C (Figure 2a) and 1.2 wt% at 2200 °C for 30 min (Figure 2b)] and the composition change from $Si_{3.9}B_{1.0}C_{11}N_{3.2}$ to $Si_{3.8}B_{1.0}C_{11}N_{2.8}$ was negligible. Moreover, this crystalline sample contains a large amount of β-Si_3N_4 phase (Figure 3). All these results indicate that the material $Si_{3.9}B_{1.0}C_{11}N_{3.2}$ can resist thermal degradation up to 2200 °C in nitrogen-free environments.

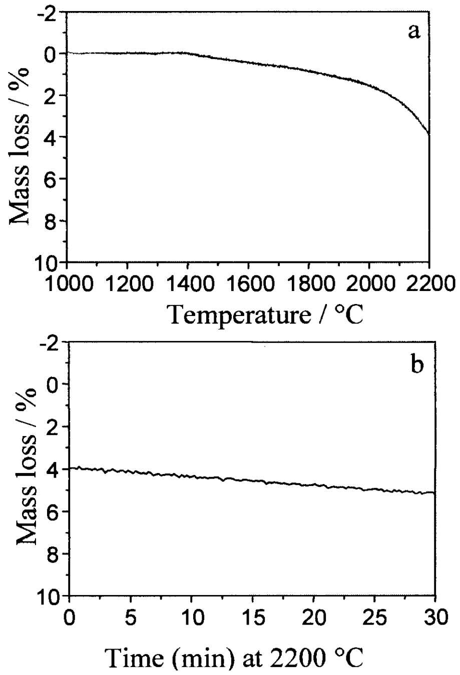

Figure 2. Thermogravimetric analysis for the amorphous material $Si_{3.9}B_{1.0}C_{11}N_{3.2}$ in 0.1 MPa Ar: (a) continuous mass loss as a function of temperature between 1000 and 2200 °C; and (b) continuous mass loss as a function of time at 2200 °C for 30 min. Heating rate: 10 °C min^{-1} at $T \leq 1050$ °C and 2 °C min^{-1} at $T > 1050$ °C.

Silicoboron carbonitrides normally contain excess carbon[3–7] and thus have a thermodynamic equilibrium nitrogen pressure high up to ≥15 MPa (0.15 kbar) at 2200 °C due to the crystallization and decomposition as already discussed[3]:

$$4\ Si_xB_{1.0}C_yN_z \rightarrow 4\ BN + (z-1)\ \beta\text{-}Si_3N_4 + (4x+3-3z)\ \beta\text{-}SiC + (4y+3z-4x-3)\ C, \quad (2)$$

$$\beta\text{-}Si_3N_4(s) + 3\ C(s) \rightarrow 3\ \beta\text{-}SiC(s) + 2\ N_2(g). \quad (3)$$

It is known[7] that N–H and Si–CH_3 bonds in polyborosilazane **1** are eliminated at ~400 °C, cross-linking to form Si–N network, before the formation of amorphous silicoboron carbonitride. While this study shows that all the N–SiH_2Ph units except hydrogen in polyborosilazane **2** are remained in the amorphous material $Si_{3.9}B_{1.0}C_{11}N_{3.2}$. The remained SiC_6 units may increase activation free energies for the solid-state cross-linking, crystallization (2) and decomposition (3) and thus the material $Si_{3.9}B_{1.0}C_{11}N_{3.2}$ can kinetically exhibit ultrahigh-temperature stability. If this simple argument is true, polyborosilazane **2** may comprise one member of a new class of polymer precursors for silicoboron carbonitrides resistant to thermal degradation to 2200 °C.

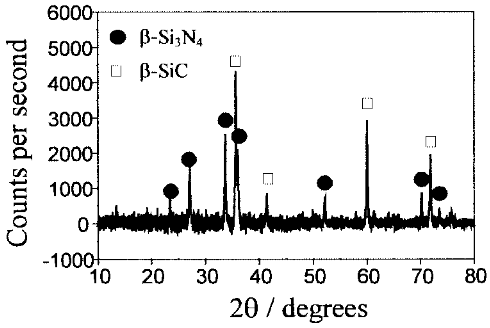

Figure 3. X-ray diffraction pattern of the crystalline material $Si_{3.8}B_{1.0}C_{11}N_{2.8}$ obtained after heating at 2200 °C for 30 min in 0.1 MPa Ar.

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Reference and Notes

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