

Processible Precursor for Boron Nitride Coatings and Matrices

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An organic solvent soluble borazanyl oligomer, **1**, was formed by a reaction of B,B',B''-trichloroborazine with $\text{HN}(\text{SiMe}_3)_2$ at low temperatures in nonpolar solvents. High-purity BN powders, characterized by IR and X-ray diffraction spectra, were produced by bulk pyrolysis of **1** to 1000 °C in NH_3 . Thin $\sim 0.02\text{-}\mu\text{m}$ BN coatings were successfully applied to $\text{Al}_2\text{O}_3/\text{ZrO}_2$ and carbon fibers by dip coating fiber bundles in 5-10% (w/w) solutions of **1** followed by pyrolysis of the coated fibers in an ammonia atmosphere. The BN-coated carbon fibers were subjected to oxidation in air at 800 °C; scanning electron microscopy of the coated fibers and the BN sheaths remaining after oxidation confirmed the formation of BN coatings.

Introduction

Ceramic-coated fibers offer a number of advantages in advanced composite manufacture. Among these are increased fiber pullout, inhibition of crack propagation, and decrease if not elimination of chemical and physical interactions between the matrix and fibers at elevated temperatures.¹⁻⁴ Boron nitride coatings, in view of their non-oxide nature, provide a barrier to eutectic formation in oxide type ceramics together with oxidative resistance as compared to, e.g., carbon fibers. Thin films of h-BN are currently produced by chemical vapor deposition (CVD) using volatile boron compositions as exemplified by BCl_3 and B_2H_6 in the presence of NH_3 .^{5,6} Cost, scale-up problems, and deposition uniformity are some of the disadvantages inherent to this technique.

Utilization of processible BN precursors offers another avenue to coatings production. A number of BN preceramic compositions have been recently reported.⁷⁻¹⁴ In our investigations, we have identified several borazine-linked structures that were found to lead to BN ceramics.¹⁵⁻¹⁸

One of these was found to be specially suitable for coating applications. We report here studies involving this material.

Experimental Section

General Procedures. Operations were carried out either in an inert atmosphere enclosure (Vacuum/Atmospheres Model HE-93B), under nitrogen bypass, or in vacuo using standard high-vacuum techniques. Infrared spectra were recorded as double mulls (Kel-F oil No. 10 and Nujol); gases were in 10-cm cells on a Perkin-Elmer Model 1330 infrared spectrophotometer. Molecular weights were determined in benzene by using a Mechrolab Model 302 vapor pressure osmometer. Thermogravimetric (TGA) analyses were carried out in nitrogen from room temperature to 1000 °C at 10 °C/min with a Du Pont 990/951 system. ¹H NMR spectra were recorded on a Varian VXR-200 spectrometer; Me_4Si was used as an external standard. Scanning electron microscopy (SEM) was performed on a JEOL JSM-35 instrument. X-ray powder diffraction (XRD) spectra were obtained with $\text{Cu K}\alpha$ radiation using a Philips PW 1710 automated diffractometer equipped with a monochromator. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Materials. Ammonia (Matheson Gas Products) was purified by trap-to-trap distillation and dried over potassium. B,B',B''-trichloroborazine was prepared by a known procedure.¹⁹ $\text{HN}(\text{SiMe}_3)_2$ was purchased from Aldrich Chemical Co. The fibers, Du Pont PRD-166 Type I 254 ($\text{Al}_2\text{O}_3/\text{ZrO}_2$) and P-100-2K (C), received from Dr. Karl Prewo, United Technologies Research Center, were free of sizing. All solvents were rigorously dried and degassed before use.

Preparation of 1. Under nitrogen bypass to a stirred solution of hexamethyldisilazane (11.3 g, 70.0 mmol) in heptane (120 mL) was added at -50 to -40 °C a solution of B,B',B''-trichloroborazine (2.5 g, 13.6 mmol) in 1:1 benzene/heptane (25 mL) over 1.5 h. Following the addition, the solution was stirred at -35 °C for 1.5 h, and then the reaction mixture was allowed to warm slowly to room temperature. The precipitate that formed, 0.6 g, was filtered off, and on evaporation of the filtrate **1** (2.3 g, 79.4% yield) was obtained. Anal. Calcd for $\text{C}_{21}\text{H}_{89}\text{B}_{15}\text{N}_{26}\text{Si}_7$: C, 23.69; H, 8.42;

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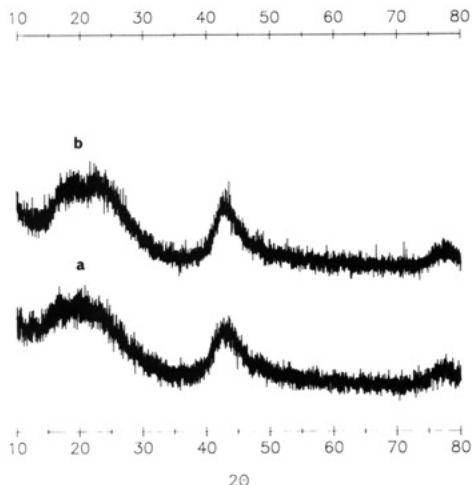


Figure 1. X-ray powder diffraction spectra of BN powders prepared from pyrolysis of 1 in NH₃ at 1000 °C/8 h/8 h (a) without further heat treatment and (b) followed by exposure to 1600 °C/4 h/4 h in N₂.

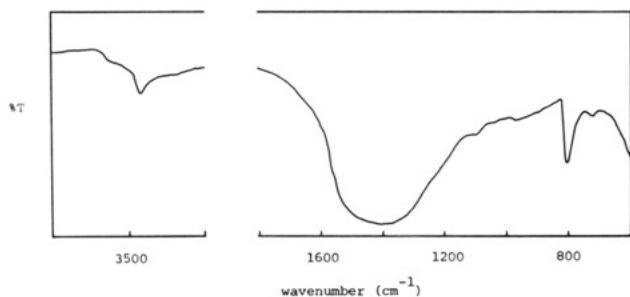


Figure 2. Infrared spectrum of BN powder prepared by pyrolysis of 1 at 1000 °C in NH₃.

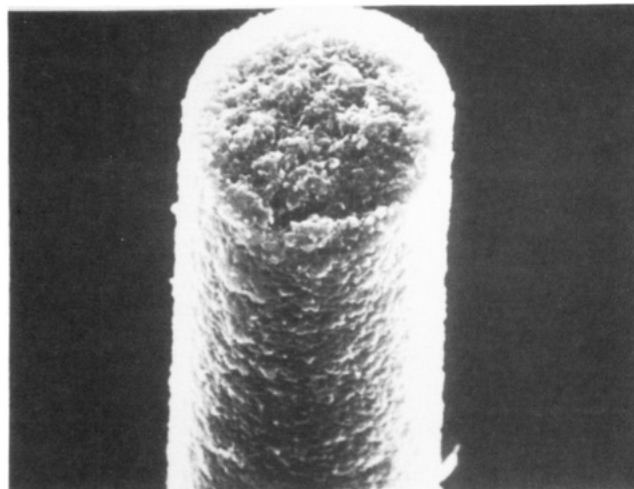
B, 15.23; N, 34.20; Si, 18.46; MW, 1064.89. Found: C, 23.99; H, 8.20; B, 14.88; N, 35.39; MW, 1150 (by osmometry in benzene, 3.5 wt %). IR (cm⁻¹, NaCl plates) 3440 (m), 3400 (s), 2948 (s), 2895 (m), 1600 (w), 1470 (s, br), 1400 (s, br), 1300 (m, br), 1261 (m), 1250 (s), 1196 (m), 1110 (s), 965 (s), 940 (w), 869 (m), 838 (s), 752 (m), 720 (s, br), 620 (m); ¹H NMR (C₆D₆) δ 0.07 (s), 0.11 (s), 0.16 (s), 0.20 (s, SiCH₃), 0.9 (br), 1.3 (br), 3.5 (v br, NH). Ratio of the methyl protons to NH protons, 2.9:1; theory 2.4:1 (63:26). TGA (N₂, 10 °C/min to 1000 °C): black residue, weight loss 52.5% (calcd C₂₁H₈₉B₁₅N₂₆Si₇ → 15BN, 65.04% weight loss), onset 100 °C; weight loss complete at 700 °C.

Bulk Pyrolysis of 1 in Ammonia in a Static System. 1, 102.5 mg, was heated in a platinum cup inserted into a quartz tube under 500 mmHg of ammonia from 25 to 990 °C over 7 h. White residue, 37.6 mg (63.32% weight loss), was obtained (calcd for C₂₁H₈₉B₁₅N₂₆Si₇ → 15BN weight loss, 65.04%). The residue was completely colorless. Its TGA, performed in air to 1000 °C, showed a total weight loss of 0.5% with an onset at 850 °C.

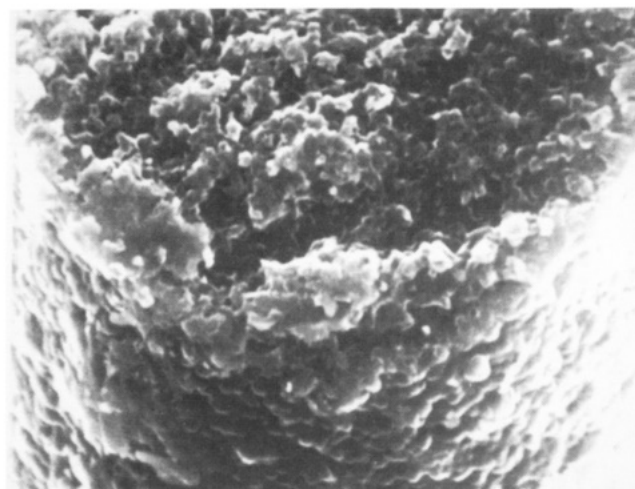
Bulk Pyrolysis of 1 in Ammonia under Dynamic Conditions. 1 was pyrolyzed to 1000 °C under NH₃ flowing at 0.4 standard cubic feet per hour (SCFH). The temperature was ramped from ambient to 1000 °C in 8 h, held at 1000 °C for 8 h, and then returned to ambient.

A portion of the pyrolyzed sample was annealed to 1600 °C under N₂ flowing at 0.4 SCFH. The temperature was ramped from ambient to 1600 °C in 4 h, held at 1600 °C for 4 h, and then returned to ambient.

Fiber Coating. Alumina (Al₂O₃/ZrO₂) and carbon (P-100-2K) fibers were coated by dipping bundles of fibers into a 5.9% (by weight) solution of 1 in 1:1 benzene/hexane. Carbon fibers were also coated by using a 10.4% solution of 1 in benzene/hexane. The fibers were then transferred into a quartz tube that was evacuated, filled with 500 mmHg of NH₃, and followed by heating from 35 to 1000 °C over 2.5 h and exposure at 1000 °C for 1 h. Subsequently, the tube was evacuated while still at 1000 °C and allowed to cool in vacuo.



(a)



(b)

Figure 3. SEM of freshly fractured PRD-166 (Al₂O₃/ZrO₂) fibers dip-coated in 5.9% w/w solution of 1 and pyrolyzed in NH₃ to 1000 °C: (a) ×2000; (b) ×6600.

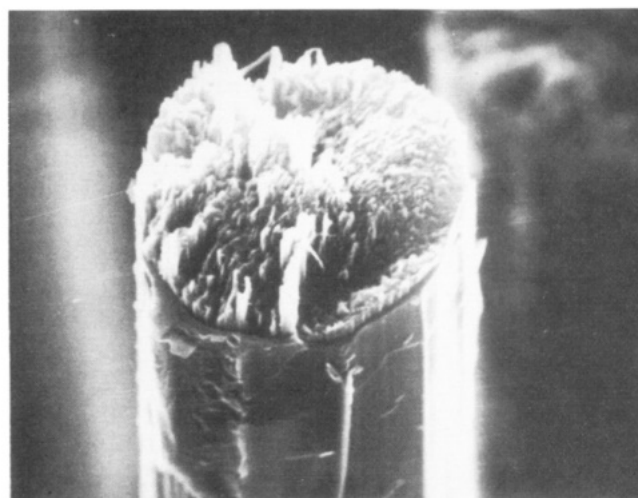


Figure 4. SEM of freshly fractured P-100-2K carbon fiber dip-coated in 10.4% (w/w) solution of 1 and pyrolyzed in NH₃ to 1000 °C (×5400).

Oxidation of Carbon Fibers. A portion of carbon fibers that were coated with the 5.9% solution was heated in air in a quartz tube from 35 to 780 °C; the oxidation was interrupted prior to completion. A portion of the fibers coated with the 10.4% solution

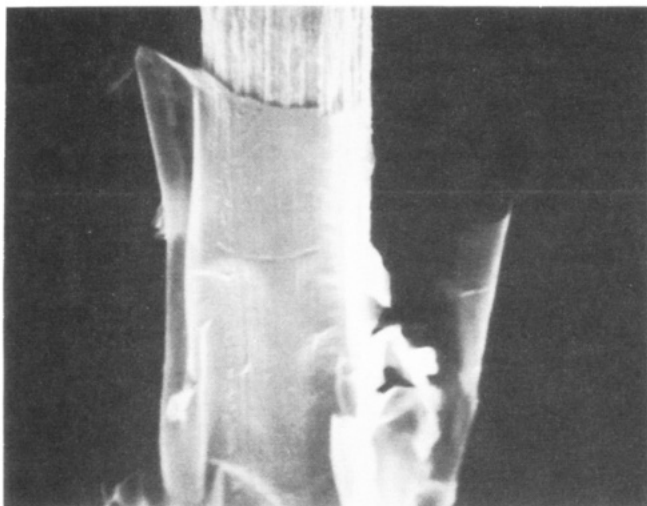


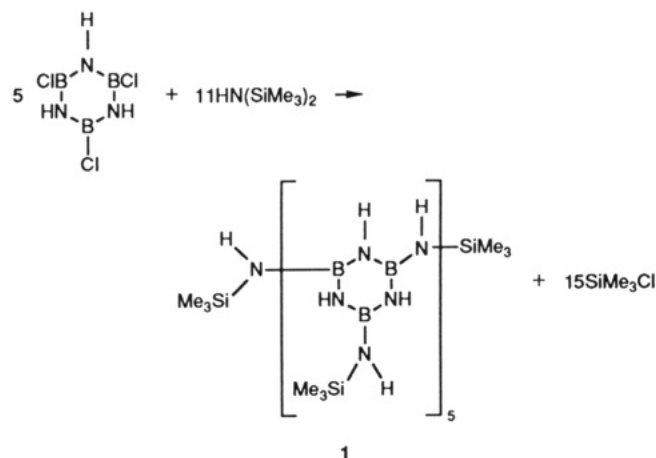
Figure 5. SEM of BN-coated P-100-2K carbon fiber dip-coated in 5.9% w/w solution of **1** and pyrolyzed in NH_3 to $1000\text{ }^\circ\text{C}$ following partial carbon removal by exposure to air at $780\text{ }^\circ\text{C}$ ($\times 4400$).

was heated in air in a quartz tube at $800\text{ }^\circ\text{C}$ for 10 h; prior to oxidation, the ends were cut to ensure air access. The oxidation of carbon was complete as shown by appearance of transparent sheaths and by the quantity of carbon dioxide produced. Weight of coated fibers used, 6.0 mg; CO_2 collected, 20.5 mg; neglecting the weight of coating calcd CO_2 , 22.0 mg.

Results and Discussion

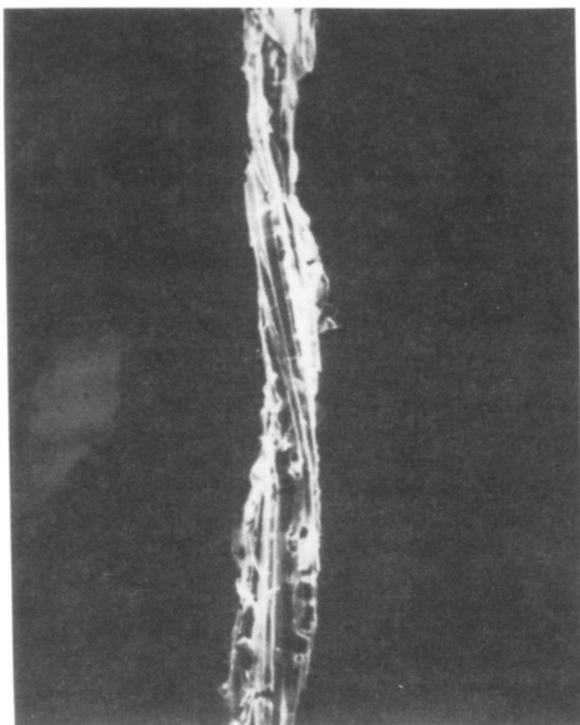
Paine and co-workers prepared preceramic BN gels by reaction of B,B',B''-trichloroborazine with hexamethyldisilazane in diethyl ether at low temperatures.^{8-10,14} These materials, according to the researchers, are essentially free of trimethylsilyl groups and are believed to consist of a cross-linked, via NH groups, borazine ring matrix. By conducting the reaction of B,B',B''-trichloroborazine with

hexamethyldisilazane in benzene/heptane or benzene/hexane and by adding the chloroborazine into the hexamethyldisilazane solution at $\sim -35\text{ }^\circ\text{C}$, we were able to isolate a (trimethylsilyl)amino-substituted oligomer **1**, i.e.

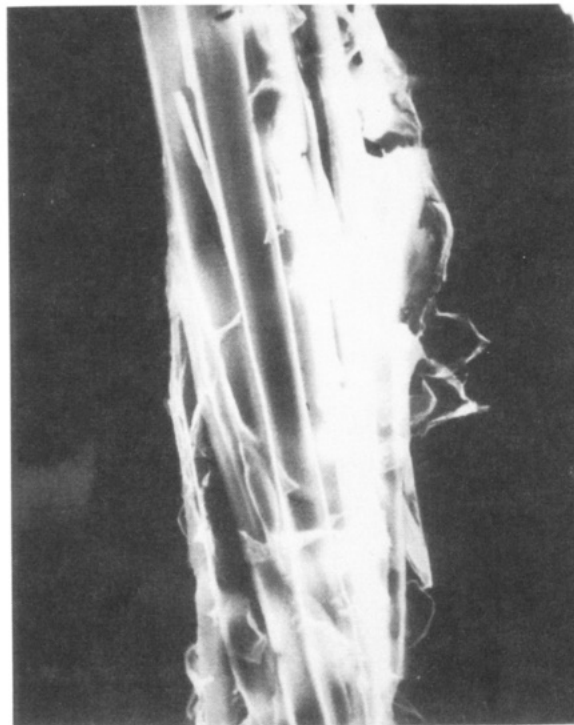


Apparently the reaction conditions, solvent temperature, and the mode of addition control the nature of the products formed. As an example, a mixture of chloroborazine and hexamethyldisilazane in hexane, prepared at $-196\text{ }^\circ\text{C}$, after warming to $-10\text{ }^\circ\text{C}$ gave only insoluble material that failed to dissolve in hot benzene. The best yields of **1** were obtained conducting the process at $\sim -35\text{ }^\circ\text{C}$. As noted in the Experimental Section even under the above conditions $\sim 20\%$ of insoluble material resulted. It is of interest that on standing in solution at room temperature for several days, **1** formed a gel most likely due to cross-linking analogous to that described by Narula et al.⁹

The infrared spectrum of **1** supports the postulated structure. The two bands in the NH stretching region point to two types of NH linkages, whereas the band at 1110 cm^{-1} confirms the presence of NHSiMe_3 groups.²⁰



(a)



(b)

Figure 6. SEM of BN sheaths remaining after complete carbon removal in air at $800\text{ }^\circ\text{C}$ from BN coated P-100-2K carbon fibers dip-coated in 10.4% w/w solution of **1**, pyrolyzed in NH_3 to $1000\text{ }^\circ\text{C}$: (a) $\times 160$; (b) $\times 660$.

The ^1H NMR data support the above structure. The ratio of the methyl protons to the NH protons is in agreement with the theory. On the basis of the relative ratios and positions, it is believed that the broad resonance centered at 3.5 ppm is due to the bridging and ring NH protons, whereas the 1.3 and 0.9 ppm resonances are due to the protons on the pendant NHSiMe_3 groups. The ratio of bridging plus ring NH to pendant NH of 2.3:1 is close to the theoretical value of 2.7:1. **1** was found to be infusible and thus not amenable to melt fiber spinning. However, due to its ready solubility in solvents such as benzene, it offers a candidate system for coating applications. The lack of melting, prior to BN formation, is of great advantage in the transformation process, since the temperature can be raised rapidly without any danger of material loss by dripping and resultant variable film thickness production.

Bulk pyrolysis in vacuo and inert atmospheres led to carbon and silicon retention; however, when the pyrolysis was carried out in ammonia, no silicon or carbon remained in the ceramic. The volatility of the leaving compounds H_2NSiMe_3 and $\text{HN}(\text{SiMe}_3)_2$ avoided any solid deposition in the cooler portions of the apparatus. The X-ray diffraction spectrum (XRD) of the bulk sample pyrolyzed by ammonia at 1000 °C (Figure 1) shows clearly turbostratic BN.^{12,21} Annealing to 1600 °C did not change significantly the diffractogram, although the peaks have sharpened slightly (Figure 1). This result is consistent with the observations of Thomas et al.,²¹ who reported that samples of turbostratic BN of substantial purity (>54% N), which have been heated to about 2000 °C under nitrogen stream, show essentially unchanged diffractograms. Apparently the presence of boron oxide enhances the transformation into the highly ordered structure.

The IR (Figure 2) spectrum of the material heated to 1000 °C in ammonia exhibited the characteristic BN absorptions²² (2550–1400, 800 cm^{-1}), but in addition, a weak

absorption was observed in the NH stretching region, indicating the presence of residual NH moieties. Beck et al.¹² also reported the presence of NH in their BN materials.

In the coating evaluations of the BN preceramic material, two concentrations were studied, 5.9 and 10.4%. The higher loading permitted a better resolution of the BN coating by SEM, in particular on the carbon fibers. The coating is clearly evident in the SEM of the PRD-166 fibers shown in Figure 3. Using the 5.9% w/w solution of **1** on carbon fiber failed to give a discernible film; however, a higher loading afforded an SEM-visible BN coating (Figure 4). Since the carbon fibers are 10–12 μm in diameter, the film is $\sim 0.02 \mu\text{m}$ thick.

The oxidation resistance of BN is well-known, and the recently reported studies¹² show that the turbostratic material is oxidatively stable at least to 820 °C. To discern the BN film on the carbon fibers coated from the 5.9% w/w solution and to see whether the film was continuous, the BN-coated fibers were partially oxidized in air at 780 °C. The presence of the film is clearly evident from the SEM (Figure 5). The film appeared transparent and continuous. Conducting the oxidation at 800 °C over a prolonged period of time resulted in the production of transparent sheaths (Figure 6). These results show clearly the suitability of **1** to BN coatings production and demonstrate the oxidative resistance of the BN film thus produced. The ease of the precursor film production, the relatively high chemical BN yield, and the volatility of the leaving moieties render this system of definite potential in practical BN coatings applications.

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Registry No. **1**, 112307-72-9; Bn, 10043-11-5; hexamethyldisilazane, 999-97-3; *B,B',B''*-trichloroborazine, 933-18-6.

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