

Reactions of Monofunctional Boranes with Hydridopolysilazane: Synthesis, Characterization, and Ceramic Conversion Reactions of New Processible Precursors to SiNCB Ceramic Materials

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Three new series of processible polymeric precursors (PIN-HPZ, BCP-HPZ, DEB-HPZ) to SiNCB ceramic materials have been synthesized by reaction of hydridopolysilazane (HPZ) with the monofunctional boranes, pinacolborane (PIN-H), 1,3-dimethyl-1,3-diaza-2-boracyclopentane (BCP-H), and 2,4-diethylborazine (DEB-H). Polymers can be prepared with a controllable range of boron contents from ~1 to 5%. Spectroscopic and chemical studies indicate the boranes are attached to the hydridopolysilazane backbone via B-N linkages that primarily result from dehydrocoupling reactions. The isolation of small amounts of trimethylsilane and Me₃SiNH-substituted borane side products (i.e., PIN-NHSiMe₃, BCP-NHSiMe₃, DEB-NHSiMe₃) from the polymer reactions, as well as from model reactions of the boranes with hexamethyldisilazane, also suggest borane reactions at the Si-N bonds of the HPZ backbone lead to some polymer chain cleavage. Consistent with these observations, combined molecular weight/infrared spectroscopy studies show that although the polymers are modified throughout the molecular weight distribution, the modified polymers have lower molecular weights than the starting HPZ, with the highest borane concentrations in the lower molecular weight fractions. The glass transition temperatures (*T*_g) of the PIN-HPZ and BCP-HPZ polymers are in the 100–120 °C range, while those of the DEB-HPZ polymers decreased to as low as 25 °C with increasing modification. The polymers each showed regions of thermal stability, thus allowing the formation of PIN-HPZ, BCP-HPZ, and DEB-HPZ polymer fibers by melt spinning. Pyrolysis of these fibers to 1200 °C then yielded SiNCB ceramic fibers. Studies of the polymer to ceramic conversion reactions showed the modified polymers yield SiNCB ceramics containing ~1–3% boron at 1400 °C, with the highest boron contents in the PIN-HPZ derived samples. At 1800 °C, the PIN-HPZ derived ceramic exhibited improved thermal stability with up to 23% nitrogen contents. In comparison, the ceramics obtained from unmodified HPZ, BCP-HPZ, and DEB-HPZ retained less than 4% nitrogen at this temperature. While the BCP-HPZ and DEB-HPZ derived ceramics showed crystallization properties similar to the ceramic obtained from unmodified HPZ, the PIN-HPZ derived ceramic was amorphous to 1600 °C and at 1800 °C showed only weak diffraction from β-SiC.

Introduction

Because of their lightweight and excellent thermal and oxidative stabilities, silicon carbide (SiC) and silicon nitride (Si₃N₄), as well as composite SiNC ceramics, are important structural materials.^{4,5} Recent work,^{6–21} has shown the addition of boron to these silicon-based

materials can result in greatly enhanced ceramic properties including reduced crystallinity and improved thermal and oxidative stabilities. These results have

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(4) See, for example: (a) Narula, C. K. In *Ceramic Precursor Technology and Its Applications*; Marcel Dekker: New York, 1995; (b) Messier, D. R.; Croft, W. J. In *Preparation and Properties of Solid State Materials*; Wilcox, W. R.; Ed.; Marcel Dekker: New York, 1982; Vol. 7, Chapter 2. (c) *Gmelin Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, Silicon Supplement B2, 1984; B3, 1986 and references therein.

intensified efforts directed at the design of new processible polyborosilazane precursors that could allow the formation of the SiNCB ceramics in technologically useful forms.

In general, two different approaches to the design of polyborosilazane SiNCB precursors have been explored. The most common strategy has involved the synthesis of copolymers with boron-containing units in the polymer backbone via the condensation of boron or borosilicon compounds with silazanes or amines. Examples include copolymers formed by the reaction of borazine with silazanes,^{12e,f} $\text{MeCl}_2\text{SiC}_2\text{H}_4\text{BR}_2$ with ammonia,^{15,16} or the condensation of $\text{Cl}_3\text{Si-NHBCl}_2$ with aliphatic amines.^{17,18} Backbone polyborosilazanes usually give excellent retention of boron in the pyrolysis products and allow the formation of ceramic materials with high boron-to-silicon ratios. However, because these polymers are formed by condensation polymerization, it is difficult to attain the high molecular weights and rheological properties that are desired for some applications.

The second approach to the formation of polyborosilazanes has been to start with a preformed polysilazane, then use dehydrocoupling or hydroboration reactions to attach a pendent boron-containing species to the silicon-

nitrogen backbone. This strategy is particularly useful for the formation of SiNCB materials containing lower boron-to-silicon ratios. Starting polymer frameworks have included polysilazanes^{6,7,10,11,12a-d,13,15,16} and polysilylcarbodiimides,^{15,16} which have then been modified with various boron sources including boranes, borates, BCl_3 , and borazine. An important advantage of this polymer-modification approach is the ability to start with a polysilazane polymer with relatively high molecular weights and tailored processing properties. However, one problem with pendent polyborosilazanes has been that further reaction of the pendent groups can introduce low-temperature cross-linking pathways which can then degrade the processibility of the new polyborosilazane.

Regardless of which approach is employed, the design of new second-generation polyborosilazane precursors that can produce SiNCB ceramics with the desired compositions, as well as have the chemical and thermal stabilities needed for polymer processing, continues to be a formidable challenge. In this paper we report the results of our studies, using the polymer-modification strategy, of the design, synthesis, and ceramic conversion reactions of three new types of processible pendent polyborosilazane precursors to SiNCB ceramic composite materials.

Experimental Section

All synthetic manipulations were carried out using standard high vacuum or inert atmosphere techniques as described by Shriver.²²

Materials. Hydridopolysilazane (HPZ) was obtained from the Advanced Ceramics Program at Dow Corning Corp. and stored in a desiccator until used. Pinacolborane, $(\text{Me}_2\text{CO})_2\text{BH}$ (PIN-H), was prepared as described in the literature²³ and purified by vacuum fractionation through a -20 , -30 , and -196 °C trap series, with only the material in the -30 °C trap used in the experiments. The 1,3-dimethyl-1,3-diaza-2-boracyclopentane, $(\text{H}_2\text{CNMe})_2\text{BH}$ (BCP-H), was prepared as reported²⁴ and purified by vacuum fractionation through a -40 , -78 , and -196 °C trap series with only the material in the -78 °C trap used in the experiments. The *B*-monoethylborazine, 2-Et- $\text{B}_3\text{N}_3\text{H}_5$ (MEB-H), and *B*-diethylborazine, 2,4-Et₂- $\text{B}_3\text{N}_3\text{H}_4$ (DEB-H), were prepared as described below. The purities of the boranes were shown by ¹H and ¹¹B NMR and GC/MS to be greater than 99%. Hexamethyldisilazane (HMD) was purchased from Aldrich Chemical Co. and distilled from CaH_2 before use.

Physical Measurements and Instrumentation. Diffuse-reflectance IR spectra (DRIFT) of the polymers and ceramics were obtained on Perkin-Elmer 1760 and 2000 Fourier transform spectrophotometers, respectively, equipped with diffuse-reflectance attachments. The ¹¹B NMR at 64.2 MHz and ¹H NMR at 200.1 MHz were carried out on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. All ¹¹B chemical shifts are referenced to $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All ¹H chemical shifts were measured relative to internal residual protons from the lock solvents and are referenced to Me_4Si (0.0 ppm). High-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. GC/MS analyses were performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 5970 Series mass-selective detector. The composition of each component was established

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both by its observed cutoff and by comparison of the calculated and observed isotope patterns in the parent and/or fragment envelopes.

Thermal mechanical analyses were carried out on a Dupont 940 thermal mechanical analyzer interfaced to an IBM computer. Thermogravimetric analyses were obtained on a Perkin-Elmer TGA 7 thermogravimetric analyzer using an argon gas purge. TGA/MS studies were performed on a Seiko Instruments Model 320 TG/DTA with a Fison Thermalab mass spectral analyzer. Powder X-ray diffraction spectra of the ceramic chars were obtained on a Rigaku Geigerflex powder X-ray diffractometer. Bulk polymer pyrolyses in alumina pyrolysis boats and tubes were carried out using a Lindberg 54000 series tube furnace with an Eurotherm 818P temperature control unit. Argon gas (99.999% pure), passed through a LabClear (No. DGP-250-R1) oxygen scavenger, was used as the purge gas. Bulk polymer pyrolyses using graphite furnaceware were carried out in an Astro graphite furnace. Scanning electron microscopy was performed on a JEOL 6300 electron microscope.

Elemental analyses were performed at the Nesmeyanov Institute of Organoelement Compounds (INEOS, Moscow, Russia) and reported as the average of the two determinations. Densities were measured by floatation in halogenated hydrocarbons.

Molecular Weight Analysis. Molecular weight distribution averages were determined by size-exclusion chromatography employing in-line viscometric detection (SEC/VISC). Chromatograms were obtained with a 150-CV SEC/VISC system (Waters Chromatography) operated at 35 °C.

A bank of four Ultrastaygel SEC columns (Millipore Co.) with mean permeabilities of 10⁵, 10⁴, 10³, and 10² Å was employed. UV-grade THF (Burdick and Jackson Co.) was used as the mobile phase. A flow rate setting of 1.0 mL/min was employed. The actual flow rate was determined gravimetrically before the start of the analysis. An injection volume of 400 µL was used.

Polymer solutions were prepared in a drybox to prevent hydrolysis. Concentrations of injected polymer solutions were typically 10 mg/mL. A universal calibration curve was generated from the DRI chromatograms of 16 nearly monodisperse ($M_w/M_n \leq 1.1$) polystyrene calibrants (Toya Soda Inc. and Polymer Laboratories Ltd.) ranging in molecular weight from 200 g/mol to 1.1 × 10⁶ g/mol. The Mark-Houwink relationship needed for the universal calibration was obtained by using the SEC/VISC system to determine an intrinsic viscosity, $[\eta]$, for each calibrant. The resulting Mark-Houwink relationship for polystyrene in THF at 35 °C was

$$[\eta] = 1.2175 \times 10^{-4} M^{0.712} \quad (1)$$

where M is the peak molecular weight of the calibrant.

A third-order polynomial was least-squares fitted to the log hydrodynamic volume versus retention volume data. From this universal calibration curve, hydrodynamic volume at each chromatographic data point, ϕ_i , was determined. Intrinsic viscosity at the corresponding data point, $[\eta]_i$, was calculated from the combined outputs of the VISC and DRI detectors following previously described²⁵ methodology. Prior to these calculations, DRI and VISC chromatograms were offset to account for the time delay between the two detectors. Offset times were obtained from the peak elution times of chromatograms for the polystyrene calibrants. A delay time of 5.2 s was found. Concentrations at each chromatographic data point, c_i , were obtained from the DRI peak height, h_i , and the mass of polymer injected, m :

$$c_i = m(h_i)/(v_i) \sum h_i \quad (2)$$

where v_i is the incremental volume corresponding to data point i .

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Molecular weight at each chromatographic point, M_i , was calculated from ϕ_i and $[\eta]_i$:

$$M_i = \phi_i/[\eta]_i \quad (3)$$

Molecular weight distribution averages, M_n , M_w and M_z , were obtained by the appropriate summations of M_i and c_i across a chromatogram. Reported molecular weight averages are mean values of two determinations.

Data acquisition and reduction were provided by either a micro pdp 11/23+ computer (Digital Equipment Co.) or a 486 desktop computer. Data acquisition performed with the 11/23+ computer employed a modified version of program MOLWT3 (Thermo Separations Inc.). Data acquisition performed by the 486 desktop computer employed the program TRISEC (Viskotec Corp.). Universal calibration and molecular weight calculations made with the MOLWT3-acquired data employed customized software. The same calculations performed with TRISEC-acquired data employed calculation modules in the TRISEC software package.

The variation of composition across a polymer molecular weight distribution was determined by infrared spectroscopic analysis of collected SEC fractions. The approach employed was previously described²⁶ for the characterization of copolymer compositional heterogeneity. Specific conditions used in the present study were as follows: A Model 100 LC-Transform (Lab Connections Inc.) was placed in-line with the SEC/VISC system and used to deposit eluting polymer fractions onto a Ge disk rotating at a constant angular speed of 10°/min. The deposition was performed by splitting off 15% of the eluting solution stream and devolatilizing the stream with a 20 psi flow of He heat to 51 °C. The fractions were deposited around the circumference of the Ge disk as a continuous polymer film. The chromatographic conditions used with the LC-Transform were identical with those used for SEC/VISC molecular weight analysis described above. The offset between VISC, IR, and DRI chromatograms was corrected by overlaying the Gramm-Schmidt reconstructed IR chromatogram and the corresponding VISC and DRI chromatograms for a monodisperse polystyrene standard ($M_p = 207\,000$ g/mol).

IR spectroscopy was conducted on a Magna 550 (Nicolet INST. Co.) spectrometer equipped with a DTGS detector, a KBr beam splitter, and optics for the Model 100 LC-transform. Each spectrum represented five co-added scans collected at a 4 cm⁻¹ resolution. Omnic Series software was used for data collection.

Synthesis of *B*-Monoethylborazine (MEB-H) and *B*-Diethylborazine (DEB-H). The *B*-mono- and *B*-diethylborazine were prepared by the metal-catalyzed hydroboration of ethylene by borazine, B₃N₃H₆, using a modification of the published procedure.²⁷ In a typical experiment, 34.3 g (0.43 mol) of B₃N₃H₆²⁸ was vacuum transferred into a 250 mL three-neck round-bottom flask, equipped with a gas inlet and stirbar, already containing 0.55 g (0.60 mmol, 0.14 mol %) of RhH(CO)(PPh₃)₃. The flask was maintained at 0 °C as a stream of ethylene was passed over the solution. When the ¹¹B NMR spectrum of the solution showed a 2:1 ratio of the *B*-ethyl (35.8 ppm) and *B*-H (31.0 ppm) resonances, the ethylene flow was stopped and the flask was backfilled with nitrogen. DEB-H was then separated from the mono- and triethylborazine by distillation (58 °C/18 mmHg), followed by fractionation through a -15, -25, and -196 °C trap series, with only the material in the -25 °C trap (16.1 g, 0.12 mol, 27.4%) used in the experiments. Smaller amounts of MEB-H were collected in the -196 °C trap.

Synthesis of Borane-Modified Hydridopolysilazanes (PIN-HPZ, BCP-HPZ, and DEB-HPZ). In a typical reaction, a HPZ sample was charged under an argon atmosphere into a 100 mL one-piece glass vessel equipped with a

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Table 1. Synthesis and Polymer Composition

| polymer | T_g (°C) | | composition | | |
|---|---|--------------------|---|------------|---|
| HPZ | 87.0 | | $\text{Si}_{1.00}\text{N}_{0.91}\text{C}_{1.14}\text{H}_{4.63}$ | | |
| HPZ with Pinacolborane (PIN-H) | | | | | |
| polymer | HPZ/PIN-H (g) | time (h) at 60 °C | yield (g) | T_g (°C) | composition |
| PIN-HPZ-1 | 7.99/7.98 | 2 | 8.39 | 120.9 | $\text{Si}_{1.00}\text{N}_{0.96}\text{C}_{1.00}\text{H}_{4.25}(\text{C}_6\text{H}_{12}\text{BO}_2)_{0.06}$ |
| PIN-HPZ-2 | 7.98/8.00 | 8 | 9.15 | 110.9 | $\text{Si}_{1.00}\text{N}_{0.87}\text{C}_{0.83}\text{H}_{4.01}(\text{C}_6\text{H}_{12}\text{BO}_2)_{0.13}$ |
| PIN-HPZ-3 | 8.00/7.99 | 24 | 9.71 | 102.3 | $\text{Si}_{1.00}\text{N}_{0.90}\text{C}_{0.86}\text{H}_{3.93}(\text{C}_6\text{H}_{12}\text{BO}_2)_{0.18}$ |
| HPZ with 1,3-Dimethylamino-2-borocyclopentane (BCP-H) | | | | | |
| polymer | HPZ/DBP-H (g) | time (h) at 100 °C | yield (g) | T_g (°C) | composition |
| BCP-HPZ-1 | 8.25/8.58 | 27 | 8.86 | 121.2 | $\text{Si}_{1.00}\text{N}_{0.87}\text{C}_{1.01}\text{H}_{4.18}(\text{C}_4\text{H}_{10}\text{BN}_2)_{0.05}$ |
| BCP-HPZ-2 | 8.04/8.29 | 70 | 8.60 | 123.6 | $\text{Si}_{1.00}\text{N}_{0.95}\text{C}_{1.07}\text{H}_{4.48}(\text{C}_4\text{H}_{10}\text{BN}_2)_{0.09}$ |
| BCP-HPZ-3 | 8.00/7.86 | 140 | 8.74 | 136.6 | $\text{Si}_{1.00}\text{N}_{0.95}\text{C}_{1.02}\text{H}_{4.50}(\text{C}_4\text{H}_{10}\text{BN}_2)_{0.10}$ |
| BCP-HPZ-4 | 5.98/23.27 | 29 days | 7.03 | | $\text{Si}_{1.00}\text{N}_{0.94}\text{C}_{1.02}\text{H}_{4.39}(\text{C}_4\text{H}_{10}\text{BN}_2)_{0.17}$ |
| HPZ with Diethylborazine (DEB-H) | | | | | |
| polymer | HPZ/DEB-H (g) | time (h) at 100 °C | yield (g) | T_g (°C) | composition |
| DEB-HPZ-1 | 6.60/6.67 | 8 | 6.55 | 78.4 | $\text{Si}_{1.00}\text{N}_{0.73}\text{C}_{1.04}\text{H}_{4.18}(\text{C}_4\text{H}_{13}\text{B}_3\text{N}_3)_{0.02}$ |
| DEB-HPZ-2 | 7.96/8.00 | 24 | 8.25 | 49.7 | $\text{Si}_{1.00}\text{N}_{0.84}\text{C}_{1.04}\text{H}_{4.25}(\text{C}_4\text{H}_{13}\text{B}_3\text{N}_3)_{0.06}$ |
| DEB-HPZ-3 | 7.50/7.63 | 70 | 8.77 | 23.0 | $\text{Si}_{1.00}\text{N}_{0.76}\text{C}_{0.94}\text{H}_{4.29}(\text{C}_4\text{H}_{13}\text{B}_3\text{N}_3)_{0.12}$ |
| HPZ with Pinacolborane (PIN-H) in C_6H_{12} | | | | | |
| polymer | HPZ/PIN-H/ C_6H_{12} (g/g/mL) | time (h) at 75 °C | yield (g) | T_g (°C) | composition |
| PIN-HPZ-4 | 8.02/1.48/8.0 | 96 | 8.36 | 96.3 | $\text{Si}_{1.00}\text{N}_{0.94}\text{C}_{1.00}\text{H}_{4.64}(\text{C}_6\text{H}_{12}\text{BO}_2)_{0.07}$ |
| PIN-HPZ-5 | 5.28/2.26/5.3 | 96 | 5.96 | 83.3 | $\text{Si}_{1.00}\text{N}_{0.92}\text{C}_{1.01}\text{H}_{4.27}(\text{C}_6\text{H}_{12}\text{BO}_2)_{0.16}$ |
| PIN-HPZ-6 | 4.50/2.89/4.5 | 96 | 5.53 | 76.5 | $\text{Si}_{1.00}\text{N}_{0.97}\text{C}_{0.97}\text{H}_{4.31}(\text{C}_6\text{H}_{12}\text{BO}_2)_{0.22}$ |

stirbar and high-vacuum stopcock. The borane was added via syringe under argon to form a clear, colorless solution. The vessel was then evacuated and sealed. The different mixtures were heated in an oil bath as summarized in Table 1. Periodically (~every 2 days) the vessel was removed to the vacuum line, where it was frozen at -196 °C, and any evolved hydrogen was measured by expansion into a known volume. After the reaction, the vessel was opened to the vacuum line and any volatile materials were vacuum distilled at 95 °C for 6 h. The modified polymers were removed from the reaction vessel under an inert atmosphere and isolated as clear, colorless solids. Anal. Found. HPZ, C, 22.69%; H, 7.36%; B, <0.5%; N, 21.12%; Si, 46.74%; PIN-HPZ-1, C, 24.78%; H, 7.62%; B, 0.96%; N, 20.58%; Si, 42.92%; PIN-HPZ-2, C, 26.26%; H, 7.67%; B, 1.88%; N, 16.74%; Si, 38.68%; PIN-HPZ-3, C, 29.23%; H, 7.66%; B, 2.45%; N, 15.66%; Si, 34.85%; BCP-HPZ-1, C, 22.69%; H, 7.36%; B, 0.88%; N, 21.12%; Si, 43.60%; BCP-HPZ-2, C, 25.22%; H, 8.01%; B, 1.39%; N, 23.37%; Si, 41.80%; BCP-HPZ-3, C, 25.24%; H, 8.15%; B, 1.64%; N, 23.44%; Si, 40.65%; BCP-HPZ-4, C, 27.25%; H, 8.17%; B, 2.46%; N, 23.85%; Si, 37.38%; DEB-HPZ-1, C, 21.63%; H, 7.22%; B, 1.21%; N, 17.95%; Si, 44.83%; DEB-HPZ-2, C, 23.03%; H, 7.58%; B, 2.84%; N, 21.24%; Si, 42.11%; DEB-HPZ-3, C, 22.83%; H, 7.90%; B, 5.14%; N, 21.06%; Si, 37.82%. NMR data for polymer PIN-HPZ-3: ^{11}B NMR (64.2 MHz, C_6D_6), 24.8 (s); ^1H NMR (200 MHz, C_6D_6), 5.3 (br, SiH), 1.2 (br, CH_3), 0.3 (br, SiCH_3). IR data for PIN-HPZ-3: 3365 (s, N-H), 2965 (s, C-H), 2945 (s, C-H), 2880 (m, C-H), 2410 (w), 2140 (s, Si-H), 1465 (s), 1440 (s), 1360 (s), 1320 (s), 1300 (s), 1230 (s), 1145 (s), 890 (s), 745 (m, sh), 660 (s) cm^{-1} . NMR data for polymer BCP-HPZ-3: ^{11}B NMR (64.2 MHz, C_6D_6), 26.1 (s); ^1H NMR (200 MHz, C_6D_6), 5.3 (br, SiH), 2.8 (br, CH_2 and CH_3), 0.3 (br, SiCH_3). IR data for BCP-HPZ-3: 3370 (s, N-H), 2940 (s, C-H), 2880 (s, C-H), 2845 (s, C-H), 2783 (s, C-H), 2140 (Si-H), 1675 (w), 1480 (s), 1460 (s), 1400 (s), 1380 (s), 1295 (s), 1275 (s), 1235 (s), 1145 (s), 890 (vs), 745 (m, sh), 660 (s) cm^{-1} . NMR data for polymer DEB-HPZ-3: ^{11}B NMR (64.2 MHz, C_6D_6), 35.4 (s, 2, BEt), 26.5 (s, 1, BN); ^1H NMR (200 MHz, C_6D_6), 5.3 (br, SiH), 4.3 (br, NH), 1.0 (m, CH_2 , CH_3), 0.3 (br, SiCH_3). IR data for DEB-HPZ-3: 3480 (m, N-H, borazine), 3380 (s, N-H, HPZ), 2970 (s, C-H), 2870 (s, C-H), 2150 (s, Si-H), 1470 (s, BN), 1230 (s), 1145 (s), 915 (s), 830 (s), 745 (m, sh), 670 (m) cm^{-1} . Similar NMR and IR spectra were recorded for each of the polymers prepared with the same borane with the intensities of the peaks varying according to

Table 2. Polymer Molecular Weights

| polymer | M_n | M_w | M_z | M_w/M_n |
|---|-------|--------|-----------|-----------|
| HPZ | 25800 | 149200 | 1011592 | 5.78 |
| Pinacolborane/HPZ Polymers | | | | |
| polymer | M_n | M_w | M_z | M_w/M_n |
| PIN-HPZ-1 | 6110 | 84 950 | 505 300 | 13.9 |
| PIN-HPZ-2 | 2655 | 39 500 | 271 750 | 14.88 |
| PIN-HPZ-3 | 2205 | 26 350 | 223 450 | 11.95 |
| PIN-HPZ-4 | 5265 | 71 150 | 426 600 | 13.51 |
| PIN-HPZ-5 | 4080 | 32 550 | 149 950 | 7.98 |
| PIN-HPZ-6 | 3935 | 41 650 | 228 350 | 10.58 |
| 1,3-Dimethylamino-2-borocyclopentane/HPZ Polymers | | | | |
| polymer | M_n | M_w | M_z | M_w/M_n |
| BCP-HPZ-1 | 5000 | 78 600 | 465 700 | 17.72 |
| BCP-HPZ-2 | 1790 | 33 600 | 210 500 | 18.8 |
| BCP-HPZ-3 | 1180 | 61 20 | 31 200 | 5.19 |
| 2,4-Diethylborazine/HPZ Polymers | | | | |
| polymer | M_n | M_w | M_z | M_w/M_n |
| DEB-HPZ-1 | 3710 | 69 100 | 1 098 500 | 18.6 |
| DEB-HPZ-2 | 3260 | 36 050 | 241 400 | 11.1 |
| DEB-HPZ-3 | 2730 | 28 500 | 190 650 | 10.4 |

the borane content. All three polymer systems were meltable and soluble in common organic solvents, including ethers and hydrocarbons. Additional properties of the modified polymers are listed in Table 1. Polymer molecular weights are displayed in Table 2.

The volatile products distilled from each of the reaction mixtures were separated by vacuum fractionation through a -20 (PIN products), -30 (BCP products), 0 (DEB products), -78 and -196 °C trap series, yielding $(\text{SiMe}_3)\text{HN}$ -substituted boranes (highest temperature trap) and unreacted borane (-78 °C trap). In addition, small (~ 50 mg) quantities of trimethylsilane were also isolated (-196 °C trap) which were identified by comparison of their gas-phase IR and mass spectra with an authentic sample. The identities of the $(\text{SiMe}_3)\text{HN}$ -substituted boranes were confirmed by ^{11}B and ^1H NMR, and GC/MS. PIN-NH(SiMe_3) (-20 °C trap): ^{11}B NMR (64.2 MHz, C_6D_6), 24.6 (s); ^1H NMR (200 MHz, C_6D_6), 1.09 (s, CH_3), 0.17 (s, $-\text{SiMe}_3$); cutoff m/e 201 (100%, $\text{P}-\text{CH}_3$). BCP-NH(SiMe_3)

Table 3. Polymer Ceramic Conversion and Composition to 1400 °C

| polymer | ceramic yield (wt %) | composition | <i>d</i> (g/cm ³) |
|-----------|----------------------|---|-------------------------------|
| HPZ | 59.6 | Si _{1.00} N _{1.02} C _{0.44} | 2.37 |
| polymer | ceramic yield (wt %) | composition | <i>d</i> (g/cm ³) |
| PIN-HPZ-1 | 62.5 | Si _{1.00} B _{0.04} N _{0.99} C _{0.50} (O _{0.05}) ³⁷ | 2.36 |
| PIN-HPZ-2 | 60.0 | Si _{1.00} B _{0.10} N _{0.95} C _{0.51} (O _{0.12}) ³⁷ | 2.26 |
| PIN-HPZ-3 | 60.0 | Si _{1.00} B _{0.14} N _{0.98} C _{0.55} (O _{0.27}) ³⁷ | 2.18 |
| PIN-HPZ-4 | 54.9 | Si _{1.00} B _{0.06} N _{0.98} C _{0.47} (O _{0.15}) ³⁷ | 2.34 |
| PIN-HPZ-5 | 55.7 | Si _{1.00} B _{0.12} N _{1.07} C _{0.54} (O _{0.21}) ³⁷ | 2.35 |
| PIN-HPZ-6 | 52.8 | Si _{1.00} B _{0.18} N _{1.04} C _{0.56} (O _{0.35}) ³⁷ | 2.43 |
| polymer | ceramic yield (wt %) | composition | <i>d</i> (g/cm ³) |
| BCP-HPZ-1 | 60.4 | Si _{1.00} B _{0.03} N _{1.07} C _{0.49} | 2.40 |
| BCP-HPZ-2 | 57.7 | Si _{1.00} B _{0.04} N _{1.10} C _{0.50} | 2.35 |
| BCP-HPZ-3 | 60.4 | Si _{1.00} B _{0.05} N _{1.12} C _{0.52} | 2.37 |
| BCP-HPZ-4 | 58.0 | Si _{1.00} B _{0.10} N _{1.13} C _{0.52} | 2.32 |
| polymer | ceramic yield (wt %) | composition | <i>d</i> (g/cm ³) |
| DEB-HPZ-1 | 59.8 | Si _{1.00} B _{0.02} N _{0.99} C _{0.43} | 2.32 |
| DEB-HPZ-2 | 57.4 | Si _{1.00} B _{0.08} N _{1.08} C _{0.53} | 2.38 |
| DEB-HPZ-3 | 52.9 | Si _{1.00} B _{0.11} N _{1.14} C _{0.44} | 2.38 |

(−25 °C trap): ¹¹B NMR (64.2 MHz, C₆D₆), 25.7 (s); ¹H NMR (200 MHz, C₆D₆), 2.95 (s, CH₂), 2.52 (s, CH₃), 0.20 (s, SiMe₃); cutoff *m/e* 184 (70%), 170 (100%). DEB-NH(SiMe₃) (0 °C trap): ¹¹B NMR (64.2 MHz, C₆D₆), 35.8 (s, 2), 25.9 (s, 1); ¹H NMR (200 MHz, C₆D₆), 4.30 (s, NH), 3.85 (s, NH), 0.99 (m, CH₃), 0.83 (m, CH₂), 0.13 (s, SiMe₃); cutoff *m/e* 224 (4%), 209 (100%, P-CH₃).

Reactions of Hydridopolysilazane (HPZ) with Pinacolborane (PIN-H) in Cyclohexane, C₆H₁₂. In a typical reaction, a HPZ sample was charged under an argon atmosphere into a 100 mL one-piece glass vessel equipped with a high-vacuum stopcock and stirbar. Both PIN-H and C₆H₁₂ were then added by vacuum transfer. The flask was sealed, and upon warming to 25 °C, a clear, colorless solution was formed. The solution was then heated in an oil bath as summarized in Table 3. Periodically (~every 2 days), the vessel was removed to the vacuum line, frozen at −196 °C, and the evolved hydrogen measured by expansion into a known volume. At the completion of the reaction, the volatile products were vacuum evaporated and the remaining clear solid polymer product was removed under an inert atmosphere. Anal. Found: PIN-HPZ-4, C, 24.75%; H, 8.06%; B, 1.11%; N, 19.34%; Si, 40.94%; PIN-HPZ-5, C, 30.13%; H, 7.98%; B, 2.19%; N, 16.49%; Si, 36.07%; PIN-HPZ-6, C, 32.22%; H, 8.17%; B, 2.80%; N, 15.73%; Si, 32.61%. The NMR and IR spectra for the PIN-HPZ-4, PIN-HPZ-5, and PIN-HPZ-6 polymers were similar to those of PIN-HPZ-3, with the relative intensities of the peaks varying with borane content. The modified polymers were melttable and soluble in common organic solvents, including ethers and hydrocarbons. Additional properties of the modified polymers are listed in Table 1. Polymer molecular weights are given in Table 2.

Reaction of Hexamethyldisilazane (HMD) with Boranes. Samples of HMD and each borane were charged under an argon atmosphere into 100 mL one-piece glass vessels equipped with high-vacuum stopcocks and stirbars. The vessels were then evacuated, sealed, and heated at temperatures between 60 and 100 °C. Analysis of the reaction mixtures by ¹H and ¹¹B NMR, and GC/MS showed mostly unreacted borane and HMD. Evaporation of the volatile reactants left <100 mg mixtures of the (SiMe₃)₂NH- and (SiMe₃)₂N-substituted boranes, with the relative amounts depending on reaction times and conditions: PIN-N(SiMe₃)₂: ¹¹B NMR (64.2 MHz, C₆D₆), 24.8 (s); ¹H NMR (200 MHz, C₆D₆), 1.02 (s, CH₃), 0.36 (s, −SiMe₃); (cutoff *m/e* 272, P-CH₃). BCP-N(SiMe₃)₂: ¹¹B NMR (64.2 MHz, C₆D₆), 27.9 (s); ¹H NMR (200 MHz, C₆D₆), 2.95 (s, CH₂), 2.51 (s, CH₃), 0.19 (s, −SiMe₃); (cutoff *m/e* 257). DEB-N(SiMe₃)₂: ¹¹B NMR (64.2 MHz, C₆D₆), 36.6 (s, 2), 24.0 (s, 1); ¹H NMR (200 MHz, C₆D₆), 4.20 (t, NH), 0.99 (m, CH₃), 0.84 (m, CH₂), 0.22 (s, SiMe₃); (cutoff *m/e* 296).

Thermolysis of PIN-HPZ-3. A 0.89 g sample of PIN-HPZ-3 was heated in vacuo at a rate of 2 °C/min to 180 °C in a one-piece glass vessel open to a −196 °C trap. Volatile materials (0.02 g) that evolved from the polymer were collected in the −196 °C trap and determined by ¹H NMR to be a 1:2 mixture of PIN-H and PIN-NH(SiMe₃). Analysis of the white solid polymeric residue (0.87 g) removed from the flask under an inert atmosphere (Anal. Found: PIN-HPZ-3Δ, C, 29.50%; H, 7.89%; B, 2.30%; N, 11.97%; Si, 37.04%) consistent with a Si_{1.00}N_{0.65}C_{0.89}H_{4.00}(PIN)_{0.16} composition. The ¹H and ¹¹B NMR and IR spectra of the material are similar to that for PIN-HPZ-3.

Reaction of Hydridopolysilazane (HPZ) with Monoethylborazine (MEB-H). A 4.56 g sample of HPZ was charged under an argon atmosphere into a 100 mL one-piece glass vessel equipped with a stirbar and high-vacuum stopcock. MEB-H (4.30 g) was added to the vessel under argon, forming a clear, colorless solution. The vessel was then evacuated at −196 °C and sealed. The mixture was heated in an oil bath at 85 °C for 32 h. After the reaction, the vessel was opened to the vacuum line and any volatile materials were vacuum distilled away at 95 °C for 6 h. The modified polymer was removed from the reaction vessel under an inert atmosphere and isolated as a clear, colorless solid (5.11 g) that was sparingly soluble in benzene and THF. The elemental analysis (Anal. Found: MEB-HPZ-1, C, 21.27%; H, 7.68%; B, 7.67%; N, 24.81%; Si, 36.08%) is consistent with a Si_{1.00}N_{0.83}C_{1.01}H_{4.27}(MEB)_{0.18} composition. NMR data for the soluble portion of polymer MEB-HPZ-1: ¹¹B NMR (64.2 MHz, C₆D₆), 36.0 (s, BEt), 30.3 (br d, B-H), 25.6 (br, B-N); ¹H NMR (200 MHz, C₆D₆), 5.3 (br s, SiH), 4.3 (br, NH), 1.0 (m, CH₂, CH₃), 0.3 (br, SiCH₃). Molecular weights for the soluble portion of MEB-HPZ-1 could not be accurately determined.

Reaction of DEB-HPZ-3 with Monoethylborazine (MEB-H). A 1.10 g sample of DEB-HPZ-3 was charged under an argon atmosphere into a 100 mL one-piece glass vessel equipped with a high-vacuum stopcock and stirbar. The flask was evacuated and 1.83 g of MEB-H was vacuum transferred into the flask at −196 °C. The flask was then sealed and brought to room temperature to form a clear, colorless solution. The reaction was heated at 75 °C for 16 h. Any volatile materials were then distilled from the reaction mixture at 95 °C for 6 h. The white polymeric solid (0.76 g) was removed from the flask under an inert atmosphere and was found to be soluble in ethers or hydrocarbons. The elemental analysis (Anal. Found: DEB-HPZ-3.2, C, 20.69%; H, 7.93%; B, 10.07%; N, 23.56%; Si, 31.57%) is consistent with a Si_{1.00}N_{0.73}C_{0.92}H_{4.11}(DEB)_{0.12}(MEB)_{0.02} composition. NMR data for polymer DEB-HPZ-3.2: ¹¹B NMR (64.2 MHz, C₆D₆), 35.6 (s, BEt), 30.2 (d, B-H), 25.6 (s, BN); ¹H NMR (200 MHz, C₆D₆),

5.3 (vbr s, SiH), 4.7–4.1 (br, NH), 1.0 (m, CH₂, CH₃), 0.3 (br, SiCH₃).

Crystallographic Data. A single crystal of SiMe₃-NH-PIN (1) C₉H₁₆BN₂O₂Si was mounted inside a capillary tube which was then sealed with glue and mounted on the diffractometer.

Collection and Refinement of the Data. X-ray intensity data were collected on an MSC/RAXIS IIC area detector employing graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at a temperature of 195 K. Indexing was performed from a series of 1° oscillation images with exposures of 8 min/frame. A hemisphere of data was collected using 10° oscillation angles with exposures of 8 min/frame and a crystal-to-detector distance of 82 mm.

Solution and Refinement of the Structure. The oscillation images were processed using biotex,²⁹ producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the teXsan³⁰ program package for further processing, structure solution, and refinement on a Silicon Graphics Indigo R4000 computer. The intensity data were corrected for Lorentz and polarization effects, but not for absorption. The structure was solved by direct methods (SIR92). Refinement was by full-matrix least-squares techniques based on F to minimize the quantity $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically.

Supplementary Table S.1 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Table S.2. Anisotropic thermal parameters are in Table S.3. Tables S.4 and S.5 list bond distances and bond angles.

Fiber Spinning. Polymer fibers were formed by extruding polymer melts from a crude ram extruder built from a 2 mL Micro-Mate luerlock glass syringe with a 21 G needle. The syringe was charged with ~1 g polymer powder under an inert atmosphere and then loaded into an aluminum heating block. The heating block was warmed at 100–120 °C while pressure was applied to the piston. Fiber draw-down and takeup onto a polyethylene drum 10 cm in diameter were achieved with a variable-speed motor controlled by a Variac. Take-up rates of ~30 m/min produced continuous polymer fibers ~30–40 μ m in diameter. After a brief cure with HSiCl₃, followed by moist air, the fibers were pyrolyzed to 1200 °C under an inert atmosphere to produce intact black ceramic fibers 30 μ m in diameter.

Ceramic Conversion Reactions. 1400 °C pyrolyses (Al₂O₃ tube furnace). Alumina tubes were dried by heating to 1400 °C and cooled under argon. Polymer samples of 1–2 g were weighed under argon, transferred into alumina boats, and placed in the pyrolysis tube. After purging the system with argon for 30 min, the samples were heated at 10 °C/min to the final temperature and then held for 1 h before cooling to room temperature. After pyrolyses, all manipulations of ceramics were carried out in air. Anal. Found: HPZ, C, 10.92%; N, 29.67%; Si, 58.31%; PIN-HPZ-1, C, 12.26%; B, 0.95%; N, 28.07%; Si, 57.11%; PIN-HPZ-2, C, 12.14%; B, 2.08%; N, 26.35%; Si, 55.56%; PIN-HPZ-3, C, 12.15%; B, 2.76%; N, 25.23%; Si, 51.86%; PIN-HPZ-4, C, 11.14%; B, 1.19%; N, 27.18%; Si, 55.73%; PIN-HPZ-5, C, 11.92%; B, 2.42%; N, 27.63%; Si, 51.81%; PIN-HPZ-6, C, 11.83%; B, 3.42%; N, 25.52%; Si, 49.31%; BCP-HPZ-1, C, 12.01%; B, 0.65%; N, 30.67%; Si, 57.62%; BCP-HPZ-2, C, 12.20%; B, 0.97%; N, 30.94%; Si, 56.82%; BCP-HPZ-3, C, 12.54%; B, 1.08%; N, 31.33%; Si, 56.05%; BCP-HPZ-4, C, 11.77%; B, 2.11%; N, 29.60%; Si, 52.72%; DEB-HPZ-1, C, 10.66%; B, 0.53%; N, 28.51%; Si, 57.58%; DEB-HPZ-2, C, 12.68%; B, 1.62%; N, 29.89%; Si, 55.68%; DEB-HPZ-3, C, 10.46%; B, 2.31%; N, 31.29%; Si, 55.21%. All ceramics pyrolyzed to 1400

Table 4. High-Temperature Ceramic Compositions

| temp (°C) | ceramic yield (wt %) | composition | d (g/cm ³) |
|-----------|----------------------|---|--------------------------|
| HPZ | | | |
| 1400 | 62.0 | Si _{1.00} N _{1.00} C _{0.44} | 2.36 |
| 1600 | 55.5 | Si _{1.00} N _{0.92} C _{0.53} | 2.45 |
| 1800 | 51.5 | Si _{1.00} C _{0.94} N _{0.03} | 2.32 |
| PIN-HPZ-3 | | | |
| 1400 | 59.1 | Si _{1.00} B _{0.15} N _{1.02} C _{0.67} (O _{0.26}) ³⁷ | 2.30 |
| 1600 | 58.6 | Si _{1.00} B _{0.16} N _{1.01} C _{0.67} (O _{0.24}) ³⁷ | 2.26 |
| 1800 | 53.7 | Si _{1.00} B _{0.18} N _{0.91} C _{0.68} (O _{0.28}) ³⁷ | 2.45 |
| BCP-HPZ-4 | | | |
| 1400 | 61.3 | Si _{1.00} B _{0.09} N _{1.10} C _{0.65} | 2.38 |
| 1600 | 57.9 | Si _{1.00} B _{0.09} N _{1.15} C _{0.63} | 2.36 |
| 1800 | 34.8 | Si _{1.00} B _{0.12} N _{0.19} C _{1.30} | 2.32 |
| DEB-HPZ-1 | | | |
| 1400 | 61.0 | Si _{1.00} B _{0.06} N _{0.81} C _{0.61} | 2.45 |
| 1600 | 57.9 | Si _{1.00} B _{0.07} N _{0.92} C _{0.61} | 2.20 |
| 1800 | 45.8 | Si _{1.00} B _{0.04} N _{0.05} C _{0.86} | 2.30 |

°C were black and glassy. Additional properties of these ceramics are presented in Table 3.

High-Temperature Pyrolyses (Graphite Furnace). For bulk conversions in graphitic environments, aliquots of the polymer were weighed into a graphite crucible and placed into an Astro graphite furnace. The furnace was then evacuated to less than 10⁻⁶ Torr and refilled with argon. The samples were heated at a rate of 10 °C/minute to the final temperature and held 1 h before cooling. Anal. Found: 1400 °C: HPZ, C, 10.99%; N, 29.10%; Si, 58.16%; PIN-HPZ-3, C, 14.37%; B, 2.83%; N, 25.42%; Si, 49.92%; BCP-HPZ-4, C, 14.01%; B, 1.85%; N, 27.63%; Si, 50.58%; DEB-HPZ-1, C, 15.02%; B, 1.35%; N, 23.44%; Si, 57.67%. 1600 °C: HPZ, C, 13.01%; N, 26.22%; Si, 56.94%; PIN-HPZ-3, C, 14.41%; B, 3.12%; N, 25.40%; Si, 50.26%; BCP-HPZ-4, C, 14.37%; B, 1.77%; N, 30.27%; Si, 52.96%; DEB-HPZ-1, C, 14.44%; B, 1.41%; N, 25.27%; Si, 55.28%. 1800 °C: HPZ, C, 28.81%; N, 1.0%; Si, 71.66%; PIN-HPZ-3, C, 14.81%; B, 3.58%; N, 22.97%; Si, 50.62%; BCP-HPZ-4, C, 28.40%; B, 2.29%; N, 4.78%; Si, 50.92%; DEB-HPZ-1, C, 24.44%; B, 1.10%; N, 1.50%; Si, 66.73%. The ceramics derived from the modified polymers were black and glassy up to 1600 °C, and gray-green at 1800 °C. The ceramics derived from unmodified HPZ became yellowish-green above 1400 °C. Additional properties of these ceramics are presented in Table 4.

Results and Discussion

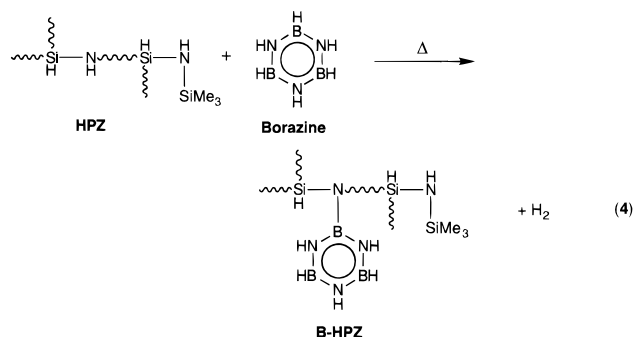
Polymer Synthesis and Spectroscopic Characterization. Hydridopolysilazane (HPZ) is a well-established³¹ polymeric precursor to SiC/Si₃N₄ ceramic materials, including ceramic fibers, and is an ideal starting material for the formation of new processible polyborosilazane precursors to SiNCB materials. The polymer is prepared by the reaction of Cl₃SiH with (Me₃Si)₂NH and is obtained as a clear, colorless solid. Molecular weights of the lot used in these studies ($M_n = 25,800$; $M_w = 149,200$; $M_z = 1,011,592$) are typical of other HPZ lots. The polymer has a general composition of (HSi)_{0.33}(Me₃Si)_{0.17}(NH)_{0.33}N_{0.17}, consistent with approximately 11 mmol/g of N-H sites on the polymer backbone, thus providing a significant number of potentially reactive sites for the attachment of pendent groups. HPZ is soluble in both polar and nonpolar organic solvents and shows no appreciable reactivity to dry air at ambient temperature. Exposure of the polymer to moisture does result in an increase in molecular weight concomitant with the liberation of ammonia.

(29) Chen, D.; Day, C. L.; Ferrara, J. D.; Higashi, T. L.; Pflugrath, J. W.; Santarsiero, B. D.; Swepston, P. N.; Troup, J. M.; Vincent, B. R.; Xiong, L. *biotex: A Suite of Programs for the Collection, Reduction and Interpretation of Imaging Plate Data*; Molecular Structure Corp.: The Woodlands, TX 77381, 1995.

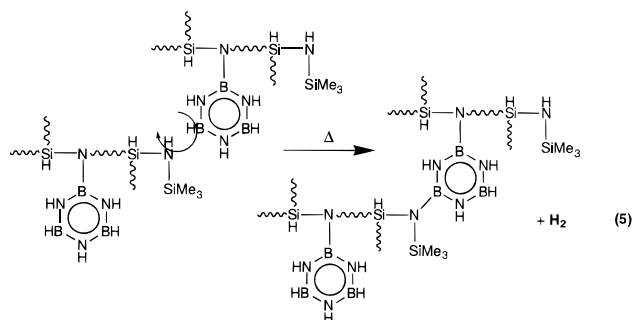
(30) *teXsan: Single-Crystal Structure Analysis Software*, Version 1.7, Molecular Structure Corporation, The Woodlands, TX 77381, 1995.

(31) Legrow, G. E.; Lim, T. F.; Lipowitz, J.; Reaach, R. S. *Am. Ceram. Soc. Bull.* **1987**, *66*, 363–367.

We have already demonstrated^{12a-d} HPZ can be readily modified by reaction with borazine, B₃N₃H₆, to produce new hybrid (B-HPZ) polymers in which pendent borazine rings are bonded to the polysilazane backbone via B-N linkages. The borazine-modified hydridopolysilazanes can be prepared with relatively high molecular weights ($M_n = 5\,000-24\,000$), and controllable boron contents (2-17%):



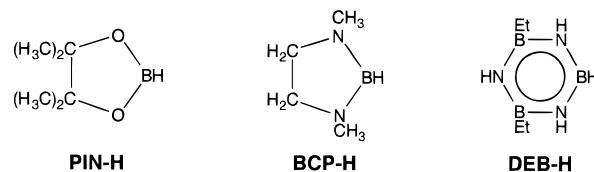
The B-HPZ polymers are excellent precursors to SiNCB materials and have properties suitable for their use in the formation of ceramic matrix materials and/or coatings. However, due to the latent reactivity of the B-H groups on the pendent borazinyl rings, the B-HPZ polymers continue to react and build molecular weight during melt processing, as shown in eq 5. Therefore, the B-HPZ polymers are not suitable for processes that require stable melt viscosities, as, for example, in the generation of polymer fibers by melt-spinning.



The key to utilizing modified-HPZ polymers for such demanding applications as melt-spinning is to eliminate, or inhibit, any polymer cross-linking reactions involving the pendent groups. One way to control the dehydrocoupling reactions that result in cross-linking is to remove any B-H groups on the pendent borane units. With this goal in mind the design and synthesis of second-generation HPZ polymers derived from *monofunctional* boranes were investigated. There are a number of monofunctional boranes that could potentially be useful for the functionalization of HPZ; however, the ideal pendants must be stable to the required processing conditions and should be relatively easy to prepare, handle, and purify.

While a number of monofunctional boranes were investigated, the three-ring systems shown below, pinacolborane (PIN-H), 1,3-dimethyl-1,3-diaza-2-boracyclopentane (BCP-H), and 2,4-diethylborazine (DEB-H), provided the best balance of the required properties:

All three boranes may be readily synthesized. PIN-H¹⁹ and BCP-H²⁰ may be prepared by reacting BH₃-THF with pinacol or *N,N*-dimethylethylenediamine,



respectively. DEB-H may be synthesized by the catalyzed hydroboration of borazine, B₃N₃H₆, with ethylene, as described in the Experimental Section. Many monofunctional boranes are unstable toward disproportionation, redistribution, isomerization, or elimination reactions,^{32,33} but the PIN-HPZ, BCP-HPZ, and DEB-HPZ do not decompose under the conditions required for polymer modification or subsequent polymer processing.

The three boron-modified polymers, PIN-HPZ, BCP-HPZ, and DEB-HPZ, were readily prepared by heating solutions of HPZ dissolved in each borane at 60-100 °C. For example, in a typical preparation of PIN-HPZ-3, an 8.00 g (90.4 mmol of N-H sites) sample of HPZ dissolved in 7.99 g (62.5 mmol) of PIN-H was heated at 60 °C for 24 h. After vacuum evaporation of the volatile materials, the modified polymer was removed from the reaction vessel under an inert atmosphere and isolated as a clear, colorless solid. Elemental analysis of PIN-HPZ-3 is consistent with a (HSi)_{0.33}(Me₃Si)_{0.15}(NH)_{0.24}N_{0.13}(PIN)_{0.09} composition. The BCP-HPZ and DEB-HPZ polymers were prepared in a similar fashion, but required longer reaction times (up to 29 days), and higher temperatures (100 °C), as summarized in Table 1. All three polymer systems were soluble in common organic solvents, including ethers and hydrocarbons.

As seen in Table 1, the degree of modification could be easily controlled by the duration of the reaction, with typical boron contents of ~1-3%. The higher reactivity of pinacolborane allowed the preparation of PIN-HPZ polymers by reacting PIN-H with 1 g/mL solutions of HPZ in cyclohexane, yielding polymers PIN-HPZ-4, PIN-HPZ-5, PIN-HPZ-6. As outlined in Table 1, the boron contents of 1-3% could be controlled by varying the amount of the PIN-H added to polymer solution.

In all three polymer systems, increases in the boron content were accompanied by stoichiometric increases in the carbon and hydrogen contents owing to the alkyl groups on the borane rings. In addition, the DEB-HPZ polymers showed the expected increase in nitrogen content owing to the borane ring nitrogens. Oxygen content, as determined by difference, paralleled changes in boron content in the PIN-HPZ polymers.

In each system, hydrogen was evolved in an almost 1:1 molar ratio with the amount of incorporated borane suggesting dehydrocoupling is the dominant means of modification. Spectroscopic studies indicate, as was proposed^{12a-d} for the B-HPZ polymer, that borane

(32) See, for example: (a) Hughes, R. L.; Smith I. C. Lawless, E. W. In *Production of the Boranes and Related Research*; Holzmann, R. T., Ed.; Academic Press: New York, 1967, Ch. 3. (b) Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*. Academic Press: New York, 1988, Part 3. (c) Pasto, D. J.; Balasubramanian, V.; Wojtkowski, P. W. *Inorg. Chem.* **1969**, *8*, 594-598.

(33) Indeed, several other common monofunctional boranes, including catecholborane, 1,3-diaza-2-boracyclohexane and 9-BBN were found to undergo such side reactions during the modification of HPZ. However, a number of new, thermally stable dioxaborinanes and dioxoboralanes have been recently reported. See: Lang, A.; Nöth, H.; Thomann-Albach, M. *Chem. Ber.* **1997**, *130*, 363-369.

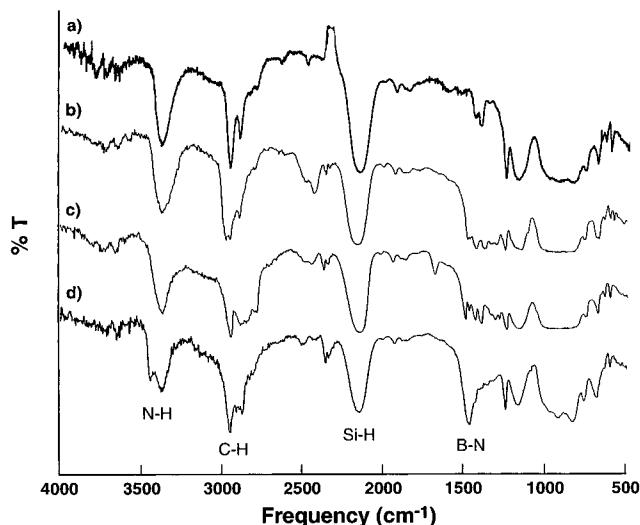
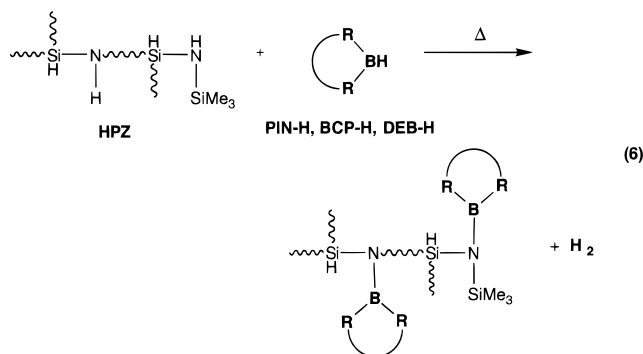


Figure 1. Infrared spectra of (a) HPZ, (b) PIN-HPZ-3, (c) BCP-HPZ-3, and (d) DEB-HPZ-3.

modification of the polymer occurs via the creation of B-N linkages:



Consistent with the proposed means of polymer modification, no B-H stretching absorptions were observed in the IR spectra (Figure 1) of the modified polymers. A decrease in the polymer N-H (3480 cm^{-1}) stretch was observed with increasing boron content in each system, due to the dehydrocoupling reaction given in eq 6. In addition, the borazine B-N (1410 cm^{-1}) and N-H stretches (3500 cm^{-1}), increased upon modification in the DEB-HPZ. Changes in the structure of the C-H peak were also noted upon modification with each borane.

The ^{11}B NMR spectra of the polymers (Figure 2a) show singlet resonances in place of the doublet resonances (B-H group, $J_{\text{B-H}} \sim 100\text{ Hz}$) observed in the starting boranes (Figure 2c). Furthermore, these resonances are shifted upfield $\sim 3\text{ ppm}$, from the 28–31 ppm range found in the unreacted boranes to 25–27 ppm in the modified polymers consistent with amino substitution at the boron.³⁴ Similar shifts in the ^{11}B resonances relative to the unreacted boranes were observed in the $(\text{SiMe}_3)\text{NH}$ -substituted boranes (Figure 2b) and $(\text{SiMe}_3)_2\text{N}$ -substituted boranes (Experimental Section), as well as for the resonances of the polymer bound boron atoms in the B-HPZ polymers.^{12a-d} The ^1H NMR

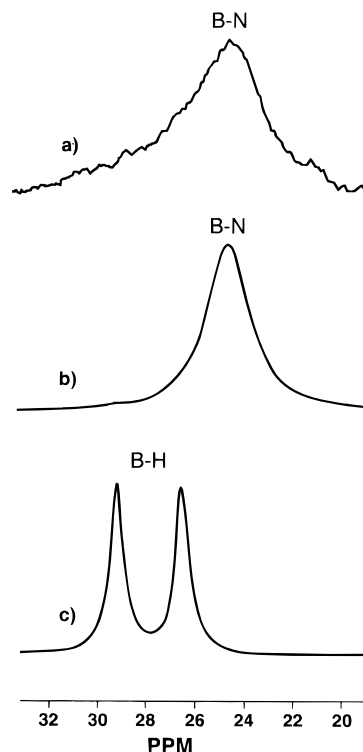
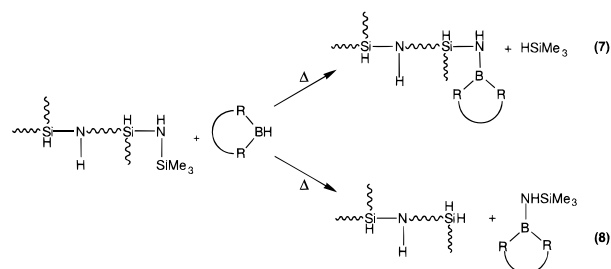


Figure 2. ^{11}B NMR spectra of (a) PIN-HPZ-3, (b) PIN-NH(SiMe_3), and (c) PIN-H (pinacolborane).

spectra of the modified polymers show broad borane-alkyl resonances, as well as the broad peaks characteristic of HPZ (5.3 and 0.3 ppm). Consistent with the singlets observed in the ^{11}B NMR spectra, no B-H resonances were observed in the ^1H NMR spectra.

Small amounts of trimethylsilane ($\sim 50\text{ mg}/8\text{ g}$ of HPZ used in the reaction) and $(\text{SiMe}_3)\text{NH}$ -substituted boranes were isolated (see Experimental Section) as byproducts of the reactions of HPZ with each borane. This suggests an alternate route for forming borane-HPZ linkages via Si-N cleavage of pendent $-\text{SiMe}_3$ groups (eqs 7 and 8).



Although BCP-NHSiMe₃ and DEB-NHSiMe₃ are liquids at room temperature, PIN-NHSiMe₃ (1) is a crystalline solid with a melting point of $\sim 25\text{ }^\circ\text{C}$, enabling the determination of its structure (Figure 3) by low-temperature single-crystal X-ray diffraction. This compound serves as a model for the polymer-bound PIN. The chemical shifts of the singlet ^{11}B resonances observed in the NMR spectra of the $(\text{SiMe}_3)\text{NH}$ -substituted boranes (Figure 2b) range from 24 to 26 ppm and are similar to those observed in the modified polymer, again suggesting amino substitution of each borane upon polymer modification.

Molecular Weight Studies. SEC/VISC chromatograms for HPZ and modified-HPZ were typically mul-

(34) (a) Gaines, D. F.; Borlin, J. In *Boron Hydride Chemistry*; Muettterties, E. L., Ed.; Academic Press: New York, 1975; pp 245–246. (b) Nöth, H.; Wrackmeyer, B. In *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: New York, 1978; pp 188–196.

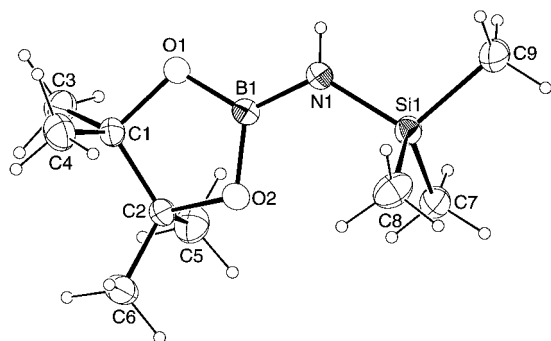


Figure 3. ORTEP drawing of the molecular structure of PIN-NH(SiMe₃).

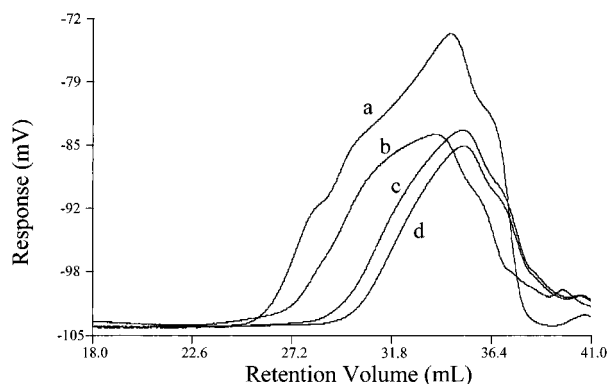


Figure 4. DRI chromatograms of (a) HPZ, (b) PIN-HPZ-1, (c) PIN-HPZ-2, and (d) PIN-HPZ-3.

timodal, indicating heterogeneous chain/cage structures and/or compositional heterogeneity. As summarized in Table 2, increasing functionalization decreased polymer weight, suggesting chain degradations. The nature of the chain degradation was investigated with the aid of the representative peak-normalized DRI chromatograms shown in Figure 4. The high molecular weight region of HPZ, corresponding to retention times between 27 and 35 min, was severely reduced in intensity relative to later eluting, lower molecular weights following functionalization, supporting the proposed side reactions of Si-N bond cleavage leading to chain degradation, as shown in eqs 7 and 8. It is also possible that the lower molecular weight, less branched/caged HPZ chains have a higher reactivity toward PIN-H.

Further insight into the reactions of the boranes with HPZ during modification was provided by recording IR spectra across the size-exclusion chromatograms of the polymers. Prior to IR analysis of functionalized HPZ polymers, the IR spectra shown in Figure 5, were obtained for the HPZ parent polymer at the representative elution times indicated in Figure 6. These retention times corresponded to a range in molecular weight from 680 800 to 4900. Little qualitative variation is observed in the relative intensities of the characteristic $\nu_{\text{N-H}}$, $\nu_{\text{C-H}}$, and $\nu_{\text{Si-H}}$ vibrational bands, suggesting compositional homogeneity over this molecular weight range. Measured intensity ratios of $\nu_{\text{Si-H}}$ to $\nu_{\text{N-H}}$ ($\nu_{\text{Si-H}}/\nu_{\text{N-H}}$) at representative retention times were nearly constant (2.88 ± 0.04). This small variation in the intensity ratio is consistent with little or no compositional variation across the polymer molecular weight distribution.

It was also noted that, unlike the higher frequency functional group absorption bands, subtle intensity changes in the fingerprint region of the IR below 1000

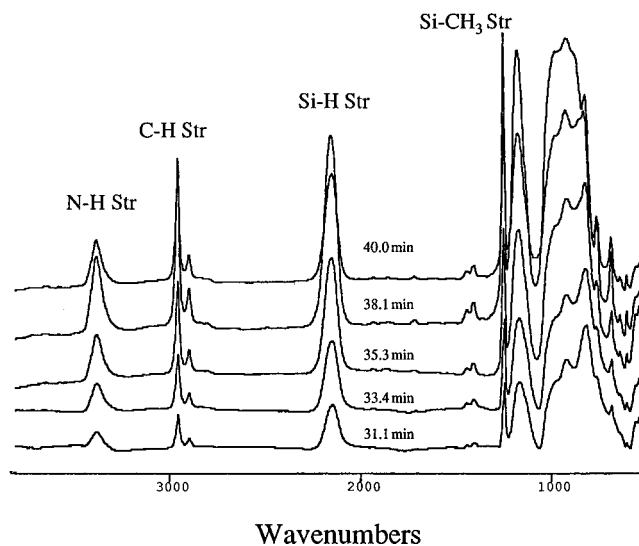


Figure 5. Stacked IR spectra for HPZ at the retention times marked with arrows in Figure 6.

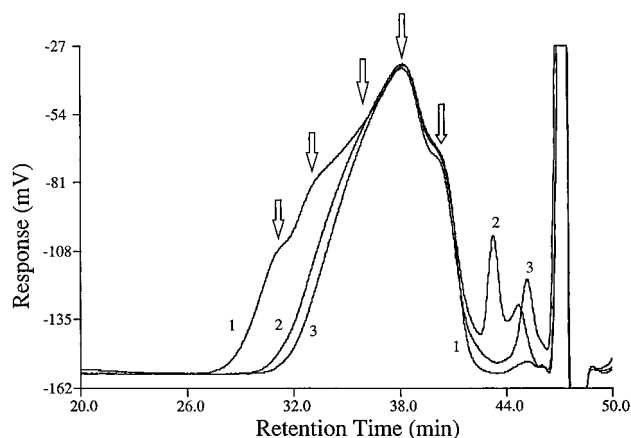


Figure 6. Overlaid peak normalized DRI chromatograms for (1) HPZ, (2) PIN-HPZ-3, and (3) DEB-HPZ-3. Arrows indicate retention times at which IR spectra were recorded. The indicated positions correspond to retentions of 31.1, 33.4, 35.3, 38.1, and 40 min.

cm^{-1} were observed (see Figure 5). A complete assignment of this region was beyond the scope of this study, but it is plausible to interpret the observed variability as the result of structural changes, possibly branching of the polymer backbone.

The corresponding IR spectra as a function of retention time for representative polymer PIN-HPZ-3 are shown in Figure 7. The computed molecular weight range covered by the selected retention times was 144 900 to 3200. Evidence of PIN addition was confirmed by $\nu_{\text{Si-H}}/\nu_{\text{N-H}}$ over this range. Its value averaged for the representative retention times was 3.24 with a standard deviation of 0.08. The increase of this value relative to the ratio of 2.28 for HPZ supported the observations by bulk IR that the N-H stretch decreased upon functionalization.

It was also found that the average $\nu_{\text{Si-H}}/\nu_{\text{N-H}}$ for PIN-HPZ-3 had a larger standard deviation (0.08) than the corresponding value (0.04) for HPZ, suggesting more compositional variation across its molecular weight distribution than its parent HPZ. However, no clear trend in $\nu_{\text{Si-H}}/\nu_{\text{N-H}}$ as a function of retention time was noted. A better indication of a trend in compositional heterogeneity was found in a qualitative inspection of

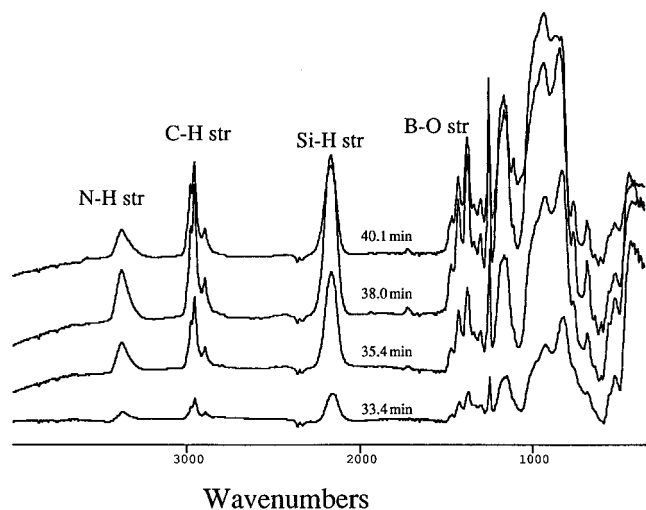


Figure 7. Stacked IR spectra for PIN-HPZ-3 at indicated retention times.

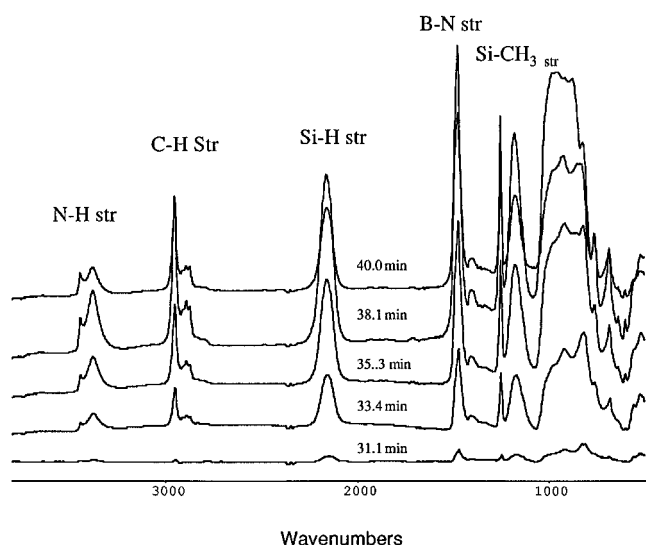


Figure 8. Stacked IR spectra for DEB-HPZ-3 at indicated retention times.

$\nu_{\text{B-O}}/\nu_{\text{Si-H}}$. The variation in this intensity ratio indicated an enrichment of PIN content in the lower molecular weight region of the size-exclusion chromatogram. This finding is consistent with modification of the polymer via Si-N bond formation with chain cleavage producing a smaller polymer fragment with a terminal borane.

The analysis of IR spectra for DEB-HPZ-3 in Figure 8 provided similar trends as observed for PIN-HPZ-3. A molecular weight range of 415 000 to 2600 was encompassed by the selected retention time points. The $\nu_{\text{Si-H}}/\nu_{\text{N-H}}$ values was 3.38 ± 0.19 , indicating functionalization over this molecular weight range. The ratio's standard deviation value of 0.19 relative to the 0.04 value of the parent HPZ suggests greater compositional heterogeneity than in the HPZ or PIN-HPZ polymers. The overlapping of N-H absorbances from the DEB ring (3500 cm^{-1}) and HPZ (3480 cm^{-1}) interfered with quantization of the $\nu_{\text{Si-H}}/\nu_{\text{N-H}}$ as a function of molecular weight. Qualitatively, however, borane enrichment could be observed in the lower molecular weight chains of the polymer.

Melt Spinning Studies. Thermal mechanical analyses (TMA) were used to determine changes in polymer

rheology following modification and evaluate the three different polymer systems for melt-spinnability. With a glass transition temperature (T_g) of 87°C , and an onset of weight loss at $\sim 200^\circ\text{C}$, the HPZ polymer has excellent rheology for melt-spinning. Slight increases in the T_g with modification were observed in the PIN-HPZ and BCP-HPZ. In the case of BCP-HPZ-4, the prolonged reaction times and/or more extensive modification led to a complex softening profile and indiscreet glass transition temperature.

In DEB-HPZ samples, large decreases in the T_g were observed upon increasing modification such that DEB-HPZ-3 was a fluid at room temperature. Although this may be due to the decrease in molecular weight, the TMA spectra of the polymers also support the presence of molecular species which can lower the T_g of polymers.³⁵ It is also possible that the ethyl groups on the borazine ring serve as plasticizers for the polymer.³⁶

With the controlled cross-linking properties of the monofunctional boranes, each series of modified polymers was found to be melt-spinnable. Without optimizing the conditions and using only a glass syringe with a 21 G luerlock stainless steel needle, continuous fibers several hundred meters in length were extruded in air. The polymer fibers were clear, colorless and flexible, but owing to reaction of the polymer with moisture, uncured fibers became brittle upon prolonged exposure to air. Because of the stability of the T_g in the PIN-HPZ samples, as well as the relatively high boron contents achieved under mild reaction conditions, the fibers derived from PIN-HPZ polymers were selected for further study.

Scanning electron micrographs (Figure 9b) show the PIN-HPZ polymer fibers are smooth, uniform, and free of voids, despite the relatively crude apparatus used for spinning. Typical polymer fibers were $35 \mu\text{m}$ in diameter. The fibers were then cured by brief exposure to HSiCl_3 followed by moist air to produce a surface SiO_2 layer.³¹ Pyrolysis under an argon atmosphere at a rate of $5^\circ\text{C}/\text{min}$ to 1200°C produced black ceramic fibers (Figure 9c). The ceramic fibers were dense and relatively uniform, but due to the size of the fibers and defects induced by the crude conditions used in the spinning, the fibers were found to be too weak for mechanical testing. Because strengths are strongly dependent on the fiber diameter and processing parameters, significant increases in ceramic fiber strengths are expected with the use of a more sophisticated spinning apparatus and curing procedures.

Ceramic Conversion Reactions. HPZ is an excellent precursor to SiNC and SiC ceramics.³¹ Pyrolysis of HPZ to 1400°C under inert atmosphere produces black ceramics in $\sim 60\%$ yield with typical compositions of $\text{Si}_{1.00}\text{N}_{1.02}\text{C}_{0.44}$ and densities of $2.4 \text{ g}/\text{cm}^3$.^{12a-d} Initial crystallization of $\alpha\text{-Si}_3\text{N}_4$ in these ceramics is usually observed near 1400°C . Above 1600°C , HPZ ceramics begin to decompose with loss of nitrogen, and both $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-SiC}$ crystallize. By 1800°C , nitrogen loss is complete and only crystalline $\beta\text{-SiC}$ is observed by XRD (Figure 10). On the other hand, studies of the

(35) Mark, J. E.; Eisenberg, A.; Graessley, W. W.; Mandelkern, L.; Samulski, E. T.; Koenig, J. L.; Wignall, G. D. *Physical Properties of Polymers*, 2nd ed.; American Chemical Society: 1993; pp 83-85.

(36) Stevens, M. P. *Polymer Chemistry: An Introduction*, 2nd ed.; Oxford University Press: New York, 1990; pp 82-83.

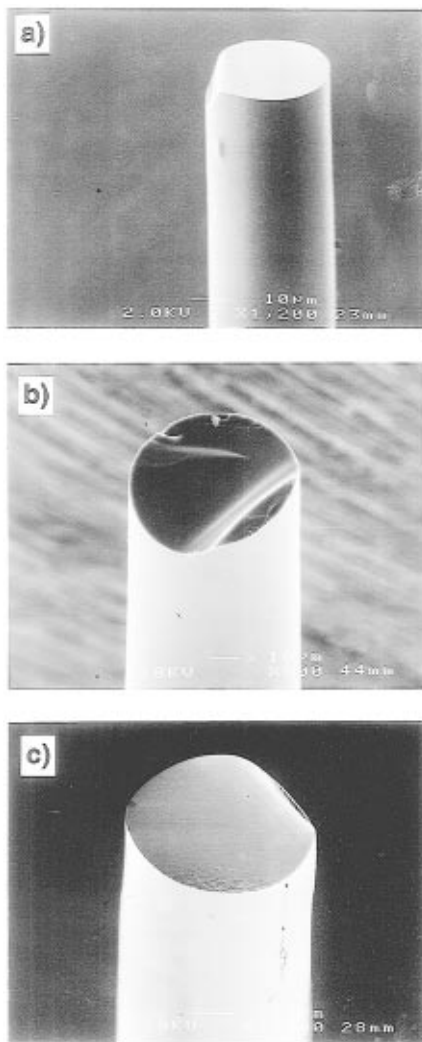


Figure 9. Scanning electron micrographs of (a) polymer fiber derived from DEB-HPZ-1, (b) polymer fiber derived from PIN-HPZ-3, and (c) ceramic fiber derived from PIN-HPZ-3 at 1200 °C.

B-HPZ derived ceramics,^{12a-d} as well as other SiNCB systems,⁶⁻²⁰ have demonstrated that as little as ~2% boron inhibit their decomposition and change their crystallization behavior. Thus, the B-HPZ derived SiNCB ceramics are largely amorphous to 1600 °C. At 1800 °C there is still significant retention of nitrogen with the XRD spectra showing the presence of α -Si₃N₄, β -Si₃N₄ and β -SiC.^{12a-d}

While B-HPZ polymers show initial weight losses due to cross-linking below 80 °C,^{12a-d} TGA studies (Figure 11) of the PIN-HPZ, BCP-HPZ, and DEB-HPZ samples showed a broad weight loss over the 200–800 °C temperature range, very similar to that of the parent HPZ. Ceramic yields were also similar to HPZ (52–63%) with little variation with the boron content. TGA/MS analyses of the volatiles evolved during pyrolysis showed no differences between the modified and unmodified polymers. Clearly, the cross-linking reaction that results in the low-temperature weight loss in the B-HPZ polymers has been suppressed in the PIN-HPZ, BCP-HPZ, and DEB-HPZ polymers.

Bulk Ceramic Conversions to 1400 °C. Bulk pyrolyses in either alumina or graphite furnaces under argon of 1–2 g samples of the modified polymers to 1400 °C afforded glassy black ceramics in 52–62% ceramic

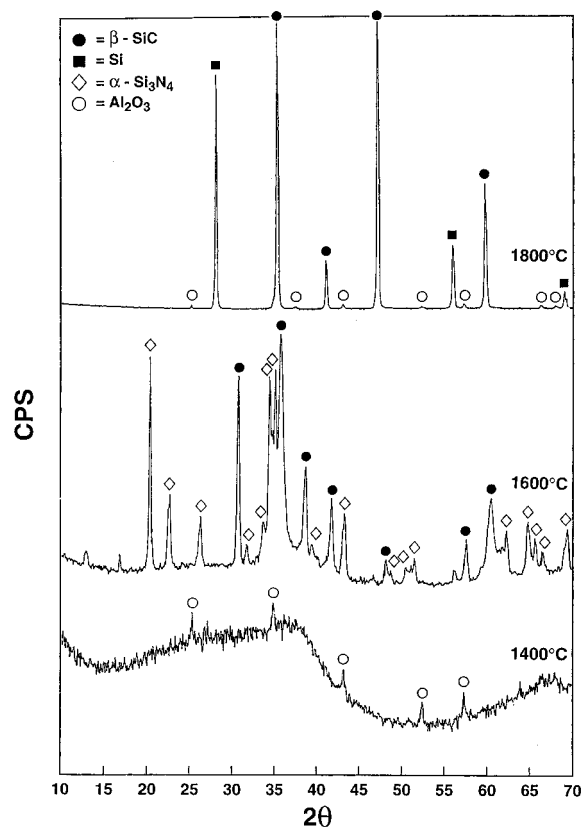


Figure 10. Powder XRD spectra of HPZ pyrolyzed to (a) 1400, (b) 1600, and (c) 1800 °C. (The Al₂O₃ impurity comes from the mortar and pestle used to grind the sample.) See the Experimental Section for details of the pyrolyses conditions.

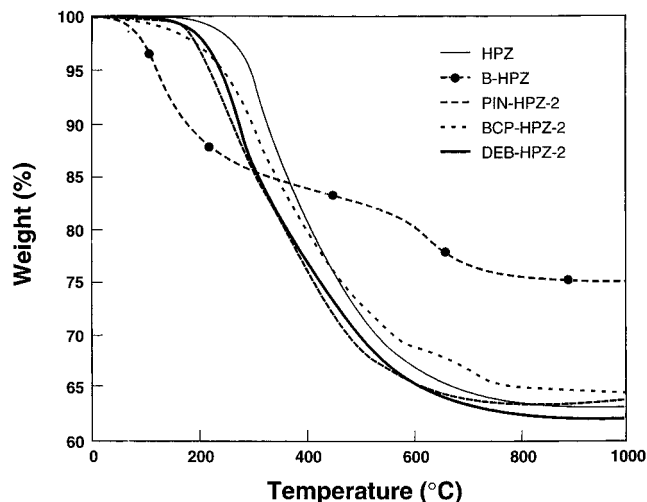


Figure 11. TGA of HPZ, B-HPZ, PIN-HPZ-2, BCP-HPZ-2, and DEB-HPZ-2. (10 °C/min, heating rate; argon atmosphere).

yields (Table 3) with average densities of ~2.2–2.4 g/cm³. Elemental analyses indicate that boron is retained in all ceramics to 1400 °C, and the amount of boron varies directly with the degree of modification. Representative compositions of the PIN-HPZ-2, BCP-HPZ-2, and DEB-HPZ-2 derived ceramics are Si_{1.00}B_{0.10}N_{0.95}C_{0.51}(O_{0.12})³⁷ Si_{1.00}B_{0.04}N_{1.10}C_{0.50}, and Si_{1.00}B_{0.12}N_{1.07}C_{0.54}, respectively. Typical boron contents were 0.5 to 3.4%, with the highest boron contents found in the PIN-HPZ-6 derived sample. Increases in the

(37) Oxygen content calculated by difference.

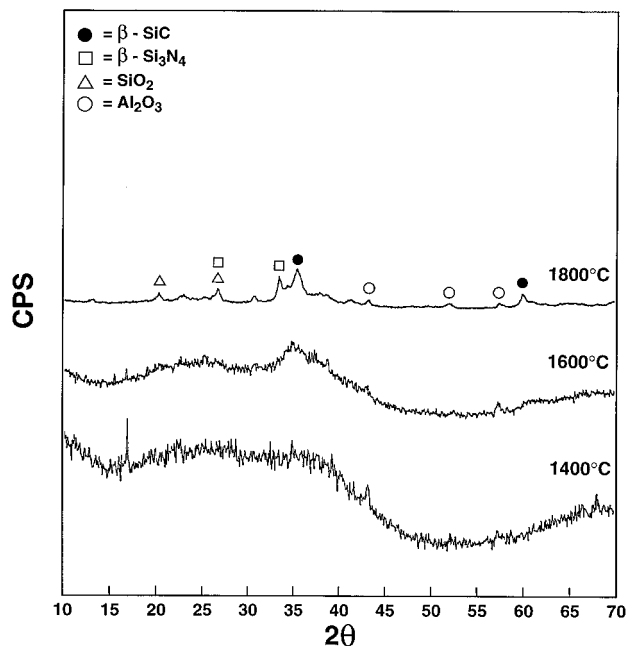


Figure 12. Powder XRD spectra of PIN-HPZ-3 pyrolyzed to (a) 1400, (b) 1600, and (c) 1800 °C. See the Experimental Section for details of the pyrolyses conditions.

carbon and heteroatom (O or N) contents of the 1400 °C ceramics were observed with increasing polymer modification.

XRD spectra of the ceramics fired to 1400 °C showed the materials were amorphous. DRIFT spectra show no evidence of N-H, C-H, B-H, or Si-H stretches in the ceramic indicating that polymer decomposition is complete by 1400 °C. Also absent in the DRIFT spectra of the 1400 °C ceramics was the characteristic B-N stretch (1410 cm^{-1}) of boron nitride.

Bulk Ceramic Conversion >1400 °C. Pyrolysis to higher temperatures produced black, glassy ceramics at 1600 °C and dark gray-green ceramics at 1800 °C. In contrast, the ceramics derived from HPZ appeared green at 1600 and yellowish green at 1800 °C. The densities of all ceramics were 2.2–2.4 g/cm^3 .

Elemental analyses indicate boron is still retained in the higher temperature ceramics derived from the modified polymers with boron contents of 1.4–3.1% at 1600 °C and 2.0–3.6% at 1800 °C, with the highest boron content being achieved in the PIN-HPZ based ceramics (Table 4). Small differences in boron content, however, produced significant changes in ceramic compositions and crystallinity. For example, the HPZ, BCP-HPZ, and DEB-HPZ derived ceramics, as well as PIN-HPZ based ceramics with low boron contents, showed almost complete nitrogen loss. Typical compositions of the HPZ, BCP-HPZ, and DEB-HPZ polymers at 1800 °C are $\text{Si}_{1.00}\text{C}_{0.94}\text{N}_{0.03}$, $\text{Si}_{1.00}\text{B}_{0.12}\text{N}_{0.19}\text{C}_{1.30}$, and $\text{Si}_{1.00}\text{B}_{0.04}\text{N}_{0.05}\text{C}_{0.86}$, respectively. Similar to the B-HPZ polymers,^{12a-d} however, the PIN-HPZ-3 based ceramics had high nitrogen retention, with 23% nitrogen in the 1800 °C ceramic corresponding to a composition of $\text{Si}_{1.00}\text{B}_{0.18}\text{N}_{0.91}\text{C}_{0.68}(\text{O}_{0.28})$.³⁷

The BCP-HPZ and DEB-HPZ derived ceramics showed no reduction in crystallinity compared to unmodified HPZ. On the other hand, PIN-HPZ-3 derived ceramics were completely amorphous to 1600 °C (Figure 12b) and show only weak diffraction from β -SiC at 1800

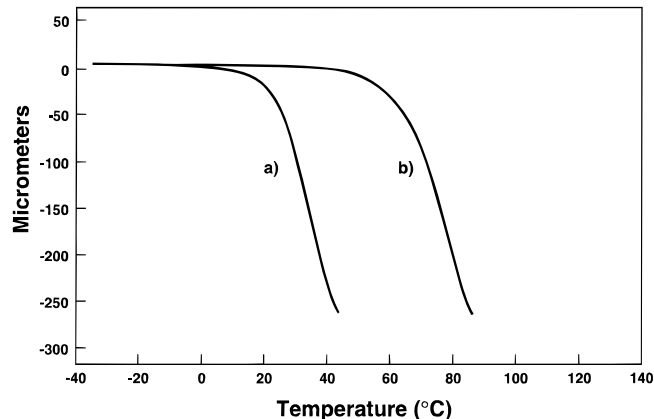


Figure 13. TMA spectra of (a) DEB-HPZ-3 and (b) DEB-HPZ-3.2.

°C (Figure 12c).³⁸ The DRIFT spectra of the 1800 °C PIN-HPZ-3 ceramic clearly showed absorptions (1460 and 910 cm^{-1}) characteristic of boron nitride. While pure boron nitride would be expected to have crystallized by these temperature, the absence of BN diffraction in the XRD of the PIN-HPZ-3 ceramic is consistent with the results from other SiNCB systems.⁶⁻²⁰

Conclusions

Because of its established chemical and rheological properties, the HPZ polymer provides an exceptional platform for the construction of polyborosilazane polymers with controlled properties. The work described above has demonstrated a viable design strategy for the formation of *processable* SiNCB precursor polymers, based on the controlled functionalization of HPZ with pendent groups of suitable compositions and cross-linking properties. Of the three monofunctional borane-based systems reported herein, the PIN-HPZ based ceramics showed enhanced properties similar to those of the previous B-HPZ ceramics, with both reduced crystallinities and increased thermal stabilities (up to 1800 °C) compared to the ceramics derived from the parent HPZ. But most significantly, the PIN-HPZ polymers, unlike the B-HPZ polymers, are processible and can be easily melt spun into polymer fibers which can then be pyrolyzed to SiNCB fibers with retention of shape.

It has been suggested that in order to achieve the very remarkable high temperature thermal (>1800 °C) and oxidative (1200–1600 °C) stabilities that have recently been reported^{15d,e,16c,17,18} for some SiNCB materials, boron contents of 5–17% are necessary. While the highest boron contents of the PIN-HPZ, BCP-HPZ, and DEB-HPZ polymers were only ~3%, our preliminary studies have now shown that the boron content, as well as the T_g and rheological properties, of these polymers can be further adjusted by additional reactions with difunctional boranes, such as monoethylborazine (MEB-H). For example, when DEB-HPZ-3 was reacted with MEB-H, the boron content of the resulting DEB-HPZ-3.2 polymer rose from 5.1% to 10.1%, and its T_g increased from 23 to 67 °C. The DEB-HPZ-3.2

(38) It should be noted that the reduction in crystallinity of the PIN-HPZ ceramics could be at least in part due to the formation of oxide glasses made possible by the oxygen present in the pinacol pendants.

polymer also showed a smooth and discrete softening profile (Figure 13), suggesting that the MEB-H served to cross-link the polymer through its two reactive B-H groups.³⁹ Polymers such as DEB-HPZ-3.2 should be excellent candidates for high boron content SiNCB ceramic fibers. We are presently exploring the synthesis and properties of these "third-generation" SiNCB polyborosilazne precursors.

(39) Indeed, when HPZ was modified with neat MEB-H as described in the Experimental Section, a sparingly soluble gel was obtained.

Acknowledgment. We thank the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, and the National Science Foundation for their support of this research.

Supporting Information Available: Structure determination, positional parameters, thermal parameters, and bond distances and angles of **1** (6 pages). Ordering information is given on any current masthead page.

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