Synthesis, Characterization, and Ceramic Conversion Reactions of Borazine-Modified Hydridopolysilazanes: New Polymeric Precursors to SiNCB Ceramic Composites

Kai Su,[1] Edward E. Remsen,*,[2] Gregg A. Zank,*,[3] and Larry G. Sneddon*,[1]

Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323; Physical Sciences Center, Monsanto Corporate Research, Monsanto Company, 700 Chesterfield Village Parkway, St. Louis, Missouri 63198; and The Advanced Ceramics Program, Dow Corning Corporation, Midland, Michigan 48686-0995

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The high-yield synthesis of borazine-substituted hydridopolysilazanes has been achieved by the reaction of liquid borazine with hydridopolysilazane (HPZ) at temperatures between 60 and 90 °C. The spectroscopic data for the polymers and a model study of the reaction of hexamethyldisilazane with borazine indicate that the new polymers have retained their hydridopolysilazane backbones but are substituted with pendant borazines by means of a borazine–boron to polymer–nitrogen linkage. Such linkages may have been formed by either hydrogen or trimethylsilane elimination reactions. Molecular weight and distribution studies suggest an inhomogeneous distribution of borazine throughout the molecular weight distribution. A decrease in molecular weight with increasing borazine content was observed that apparently results from chain scission reactions of Si–N bonds in the polymer backbone. Studies of the thermolytic reactions of the polymers demonstrated that they are converted in high ceramic and chemical yields to SiNCB ceramic composites. The ceramic yield is increased over that observed for the unmodified hydridopolysilazane due to both the retention of borazine–boron and –nitrogen in the ceramic and a borazine cross-linking reaction which retards the loss of polymer backbone components. Significant differences in the onset, phases and extent of crystallization in the ceramic products obtained from HPZ and the modified polymers were observed. In contrast to the ceramic materials obtained from HPZ, the borazine-modified polymers yield ceramics that are amorphous to 1400 °C. Furthermore, only partial crystallization, giving a mixture of β-SiC, α-Si_3N_4, and β-Si_3N_4, is observed upon heating at 1700 °C. According to the XRD analysis, at 1800 °C, β-Si_3N_4 and β-SiC are the major crystalline phases in the boron-modified ceramics, while the ceramic derived from HPZ contains only β-SiC at 1700 and 1800 °C. Better retention of nitrogen at high temperatures (>1400 °C) is also observed for the boron-containing ceramics.

Introduction

Polysilazanes have been shown to be excellent polymeric precursors to silicon nitride or SiNC ceramic materials.[4] Chemical modification of the polysilazane to include other elements has also been proposed as a means of modifying and enhancing the properties of the polymer and/or the final ceramic materials.[5–8] For example, the incorporation of boron in the silazane has been claimed to decrease the crystallinity of the Si_3N_4 ceramics derived from these polymers.[6–8] This is an important result because, in specific applications, the effective use-temperature of these ceramics could be extended if they remain amorphous to higher temperatures. Therefore, given the potential technological importance of SiNCB composites, we have now initiated joint studies aimed at the generation of new classes of hybrid polymers that might serve as processible precursors to such composite ceramics.

One synthetic approach to such hybrid polymers that we are currently exploring involves the reactions of preformed silicon-based preceramic polymers, such as the hydridopolysilazanes, with borazine. The derivatization of small molecule silazane oligomers by boron reagents dates back to the formation of functionalized borazines from the reaction of diborane with hexamethyldisilazane reported by Nöth.[9] More recently, the reactions of borane reagents with silazane oligomers has been explored by Seyferth[7,10] and Funayama.[6] The reactions of functionalized borazines with small molecule silazanes have also

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(1) University of Pennsylvania.
(2) Monsanto Co.
(3) Dow Corning Corp.
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been investigated by Paine.[11] The reaction of silazane oligomers with borazine is claimed in a U.S. Patent issued to Tonen Corp., but the patent provides a detailed example of only the reaction of a substituted borazine $(MeNBH)_3$ with $(H_2SiNH)_x$.[6b] Aside from this patent, there have been no reports of the reactions of the parent borazine, $B_3N_3H_6$, with polysilazane polymers. We demonstrate in this paper that the reaction of hydridopolysilazane (HPZ)[12] with borazine under mild conditions results in the formation of new types of processable borazine-substituted polysilazanes that upon pyrolysis yield SiNCB composite materials. Furthermore, depending on the boron contents, these ceramics exhibit significant differences in stability and crystallinity when compared to the ceramic derived from unmodified HPZ.

Experimental Section

All synthetic manipulations were carried out using standard high-vaccum or inert-atmosphere techniques as described by Shriver.[13]

Materials. Hydridopolysilazane (HPZ)[12] samples of the general formula $(HSi)_{0.33}(Me_3Si)_{0.17}(NH)_{0.33}N_{0.17}$ were produced at Dow Corning Corp. The HPZ polymer is typically prepared in 25-pound lots within the Advanced Ceramics Program at Dow Corning. The lot used in this study exhibited a softening point (80 °C, as measured by TMA) and molecular weights (as described in the Results and Discussion section) typical of other HPZ polymer lots. HPZ polymer is a white solid which is soluble in hydrocarbons, benzene, borazine, and esters. Exposure of the polymer to moisture results in an increase in molecular weight concomitant with liberation of ammonia, but HPZ shows no appreciable reactivity to dry air at ambient temperature. Borazine was purchased from Callery Chemical Co. and purified by refractionation through a −45, −78, and −196 °C trap series, with only the material collected at −78 °C used. Borazine is a moisture-sensitive liquid at room temperature which is soluble and stable in most common aprotic organic solvents.[14] Hexamethyldisilazane was distilled before use. Triethylsilane was obtained from Alrich and used as received. Benzene was freshly distilled from sodium benzophenone.

Physical Measurements and Instrumentation. Diffuse-reflectance IR spectra were obtained on a Perkin-Elmer 7770 Fourier transform spectrophotometer equipped with the appropriate diffuse-reflectance attachment. ^{11}B NMR spectra at 64.2 MHz and ^1H NMR at 200 MHz were obtained on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. All ^{11}B chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton chemical shifts were measured relative to the lock solvents and then referenced to Me_4Si (0.0 ppm). High-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. GC-MS analysis was performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 5970 Series mass-selective detector. The composition of each compound was established both by its observed m/e cutoff and by comparison of the calculated and observed isotope patterns in the parent and/or fragment envelopes. Product compounds were separated using a Varian Aerograph Series 1400 gas chromatograph equipped with a 7-ft, 7.8% SE 30 on Chromosorp W column. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were obtained on a Seiko TG-DTA 320 and a du Pont 910 thermal analyzer with a 910 DSC cell base, respectively. Densities were measured by flotation in a mixture of halocarbon liquids.

All furnace firings were done in an Astro graphite furnace equipped with Eurotherm temperature controllers. Temperatures were monitored by a type K thermocouple below 900 °C and an Ircon Modeline Plus optical pyrometer for temperatures above 900 °C. The resulting ceramic chars were ground employing a mortar and pestle molded of finely powdered synthetic sapphire.

Elemental analyses were performed at Dow Corning Co. For both the polymers and the ceramics, carbon, hydrogen and nitrogen analyses (C, H, and N) were done on a Control Equipment Corporation 240-XA elemental analyzer. Silicon and boron were determined by a fusion (molten KOH) technique which consisted of converting the material to soluble forms of silicon or boron and analyzing the solutes for total elements by atomic absorption spectrometry.

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 (Millipore Co.) operated at a temperaure of 35 °C.

Composition data across size-exclusion chromatograms were obtained by connecting a Spectroflow 757 variable-wavelength ultraviolet absorbance (UV) detector (ABI Analytical Inc.) to the SEC/VISC system. The UV detector was placed in-line between the SEC/VISC system's internal viscometric (VISC) and differential refractive index (DRI) detectors. The resulting SEC/VISC/UV system provided simultaneous molecular weight and composition analysis.

A bank of four Ultrastyragel SEC columns (Millipore Co.) with mean permeabilities of 10^5, 10^4, 10^3, and 10^2 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. Concentrations of injected polymer solutions were typically 10 mg/mL. An injection volume of 400 μL was used.

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 to 1.1×10^6 g/mol. The Mark–Houwink relationship needed for the universal calibration was obtained by using the SEC/VISC/UV system to determine an intrinsic viscosity, $[\eta]$, for each calibrant. The resulting Mark-Houwink relationship for polystyrene in THF at 35 °C was

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

where M is the peak molecular weight of the calibrant.

A fourth-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 described[15] methodology. Prior to these calculations, DRI and UV chromatograms were offset to account for the time delay between the three detectors. Offset times were obtained from the peak elution times of chromatograms for the polystyrene calibrants. Times of 20.8 and 7.8 s were found and used as the offsets between the DRI-to-VISC and UV-to-VISC detectors, respectively. Concentrations at each chromatographic data point, c_i, were obtained from the DRI peak height,

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Table I. Synthesis and Polymer Characterization Data

Reaction Conditions

polym	HPZ/ Borazine (g)	T (°C)/ time (h)	product (g)	polym compositions
HPZ				$Si_{1.00}N_{1.04}C_{1.16}H_{4.69}$
1	5.16/8.00	65/2.2	5.31	$Si_{1.00}B_{0.08}N_{0.84}C_{1.08}H_{4.58}$
2	26.00/21.68	73/2.2	26.8	$Si_{1.00}B_{0.13}N_{1.13}C_{1.17}H_{4.84}$
3	1.52/3.24	73/7.0	1.56	$Si_{1.00}B_{0.43}N_{1.22}C_{1.02}H_{4.67}$
4	1.51/3.15	73/17.5	2.28	$Si_{1.00}B_{1.68}N_{2.59}C_{1.04}H_{6.25}$

Polymer Molecular Weights

polym	M_n	M_w	M_w/M_n
HPZ	25 800	149 200	5.78
HPZ (Δ)	34 500	214 800	6.22
1	24 000	130 100	5.43
2	23 300	117 900	5.06
3	13 300	63 000	4.78
4	5 492	55 903	10.18

h_i, and the mass of polymer injected, m:

$$c_i = m(h_i)/v_i \sum h_i \tag{2}$$

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

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

$$M_i = \phi_i/[\eta_i] \tag{3}$$

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 the mean values of three determinations which were reproducible to within ±10% of the indicated values.

Data acquisition and reduction was provided by a micro pdp 11/23+ computer (Digital Equipment). Data acquisition was performed with a modified version of program MOLWT3 (LDC/Analytical). Universal calibration and molecular weight calculations were performed with computer programs written to analyze MOLWT3-acquired SEC/VISC/UV data.

Reactions of Hydridopolysilazane with Borazine. In a typical reaction, a hydridopolysilazane sample was charged under a nitrogen atmosphere into an 88-mL Fisher pressure reaction vessel (part no. 100-205-0003) which was then evacuated at −196 °C. Borazine was vacuum distilled into the reactor which was then sealed and brought to room temperature. The hydridopolysilazane gradually dissolved to form a clear solution. The mixture was then heated in an oil bath at temperatures from 60 to 80 °C as summarized in Table I. The borazine-modified polymers were isolated as white solids after vacuum evaporation of hydrogen and volatiles, including excess borazine, from the reaction vessel. Anal. Found for HPZ: C, 21.94%; B, <0.20%; N, 23.10%; Si, 44.30%; H, 7.42%; 1, C, 21.40%; B, 1.33%; N, 19.36%; Si, 45.99%; H, 7.53%. 2: C, 21.39%; B, 2.24%; N, 24.13%; Si, 42.80%; H, 7.43%. 3: C, 18.69%; B, 7.10%; N, 25.97%; Si, 42.70%; H, 7.12%. 4: C, 11.96%; B, 17.42%; N, 35.15%; Si, 26.90%; H, 6.00%. NMR data for polymer 3: ^{11}B NMR (64.2 MHz, C_6D_6, ppm, Hz): 31.0 (d, B4,6, J_{BH} = 112), 25.8 (s, B2); ^{1}H NMR (200 MHz, C_6D_6, ^{11}B spin decoupled, ppm, Hz): 5.19 (br, NH), 4.38 (br, BH), 0.30 (br, $SiCH_3$). The NMR spectra of 1, 2, and 4 showed resonances at the same chemical shifts, but with the relative intensities depending upon the borazine content of the polymer.

Vacuum line fractionation of the volatiles obtained from the above reaction through −90 and −196 °C traps led to the isolation of small amounts of trimethylsilane (in −196 °C trap) the identity of which was established by its ^{1}H NMR spectrum.

A control experiment to determine any thermally-induced molecular weight changes in the starting hydridopolysilazane was carried out by heating 0.53 g of hydridopolysilazane dissolved in 6.0 g of benzene at 70 °C for 30 h. Molecular weight analysis of the white solid, HPZ(Δ), that was obtained upon solvent evaporation is also presented in Table I.

Table II. Polymer Ceramic Conversions at 1400 °C

sample	char yield (%)	composition	density
HPZ	57.0	$C_{1.00}N_{2.35}Si_{2.43}$	2.58
2	70.0	$C_{1.00}N_{2.42}B_{0.20}Si_{2.25}$	2.31
3	68.3	$C_{1.00}N_{2.88}B_{0.50}Si_{2.30}$	2.32
4	76.5	$C_{1.00}N_{4.77}B_{2.57}Si_{1.94}$	1.84

Table III. High-Temperature Pyrolysis Results

	temp (°C)	char yield (%)	composition
HPZ	1400	62.3	$C_{1.00}N_{2.35}Si_{2.43}$
	1500	61.3	$C_{1.00}N_{2.42}Si_{2.48}$
	1600	55.5	$C_{1.00}N_{1.66}Si_{2.23}$
	1700	44.1	$C_{1.00}N_{0.13}Si_{1.15}$
	1800	42.4	$C_{1.00}N_{0.03}Si_{1.06}$
polymer 2	1400	68.8	$C_{1.00}N_{2.42}B_{0.20}Si_{2.25}$
	1500	69.9	$C_{1.00}N_{2.36}B_{0.21}Si_{2.25}$
	1600	62.9	$C_{1.00}N_{2.24}B_{0.21}Si_{2.21}$
	1700	59.1	$C_{1.00}N_{1.66}B_{0.21}Si_{1.94}$
	1800	51.1	$C_{1.00}N_{0.80}B_{0.18}Si_{1.72}$

Ceramic Conversions Reactions. An aliquot of the resin was weighed into a graphite crucible in a Vacuum Atmospheres drybox and quickly transferred into an Astro furnace. The furnace was then evacuated to <20 Torr and backfilled with argon. Under a purge of argon, the sample was heated to 1400 °C at 10 °C/min and held at temperature for 1 h before cooling to room temperature. After pyrolysis to temperatures >1400 °C, all manipulations of the ceramics were carried out in air. The corresponding char yields, compositions, and densities for the ceramics derived from the polymers are presented in Table II. Anal. Found for HPZ: C, 10.72%; N, 29.34%; Si, 60.54%. 2: C, 10.53%; B, 1.91% N, 29.89%; Si, 55.48%. 3: C, 9.69%; B, 4.40%; N, 32.66%; Si, 52.31%. 4: C, 7.39%; B, 17.11%; N, 41.19%; Si, 33.55%.

Samples for the IR studies of the ceramic conversion reactions were prepared by heating small samples (~20 mg each) of HPZ, 3 and 4 in porcelain boats in separate experiments to 260, 420, 550, and 800 °C at 15 °C/min under argon. Upon reaching each temperature, the samples were immediately cooled to room temperature and stored under nitrogen prior to infrared analysis. The 1400 °C samples were prepared as described above.

In other experiments, aliquots of HPZ and 2 were weighed into a graphite crucible and transferred into an Astro graphite furance. The furnace was then evacuated to <20 Torr and backfilled with argon. Under a purge of argon, the samples were heated to temperatures of 1400, 1500, 1600, 1700, and 1800 °C at a rate of 10 °C/min and then held at the respective temperature for 1 h, before cooling to room temperature. The corresponding char yields and compositions for the ceramics derived from HPZ and 2 are presented in Table III. Anal. Found for HPZ: *1400 °C*, C, 10.72%; N, 29.34%; Si, 60.54%; *1500 °C*, C, 10.15%; N, 28.93%; Si, 59.27%; *1600 °C*, C, 12.29%; N, 23.76%; Si, 63.68%; *1700 °C*, C, 26.22%; N, 4.11%; Si, 70.39%; *1800 °C*, C, 28.81%; N, 1.00%; Si, 71.66%. Anal. Found for 2: *1400 °C*, C, 10.53%; B, 1.91%; N, 29.89%; Si, 55.48%; *1500 °C*, C, 10.45%; B, 1.92%; N, 28.79%; Si, 54.88%; *1600 °C*, C, 10.79%; B, 2.06%; N, 28.57%; Si, 56.53%; *1700 °C*, C, 12.97%; B, 2.40%; N, 25.14%; Si, 58.85%; *1800 °C*, C, 16.47%; B, 2.75%; N, 15.26%; Si, 66.00%.

Reaction of Hexamethyldisilazane with Borazine. A 0.78-g sample of hexamethyldisilazane was placed into a Fisher pressure reaction vessel which was then evacuated at −196 °C. A 0.90-g sample of borazine was vacuum distilled into the flask, the flask was sealed, and then the mixture heated at 70 °C for 22 h. The flask was then cooled to room temperature, connected to a preparative vacuum line and the volatile materials vacuum distilled into a −196 °C trap. A GC-MS analysis of the volatile products showed the compounds: $B_3N_3H_5N(SiMe_3)_2$ (cutoff m/e 240 (5%), 225 (100%, $-CH_3$), $(B_3N_3H_5)NH(SiMe_3)$ (cutoff m/e 168 (5%), 153 (100%, $-CH_3$) and $(B_3N_3H_5)_2NH$ (cutoff m/e 176, 100%). The identity of these compounds was then confirmed by their isolation, as discussed below, or by comparison of their GC retention times and mass spectral data with those of authentic samples.

A larger scale reaction was then carried out under more severe conditions in order to allow the separation and characterization of the major products. In this reaction, 1.52 g of hexamethyldisilazane and 1.27 g of borazine were heated at 83 °C for 48 h.

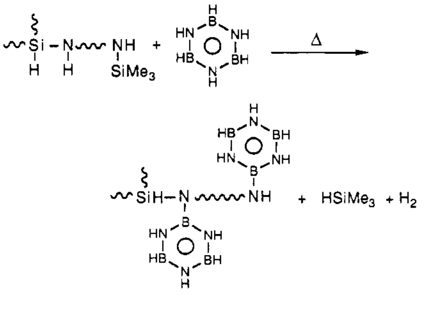
The flask was then cooled to room temperature, opened to the vacuum line and the volatiles (~2.5 g) vacuum distilled into a −196 °C trap. Two of the major products were then separated by preparative GLC: B-(N(SiMe$_3$)$_2$)-B$_3$N$_3$H$_5$, low volatile liquid, R_v = 12.3 (THF, R_v = 1.0). ^{11}B NMR (64.2 MHz, CD$_2$Cl$_2$, ppm, Hz): 30.9 (d, B4,6 J_{BH} = 142), 28.3 (s, B2). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$, ^{11}B spin decoupled, ppm, Hz): 4.78 (br, 3 H, NH), 4.38 (s, 2 H, BH), 0.15 (s, 18 H, SiCH$_3$). Exact mass calcd for ^{12}C$_6$^{11}B$_3$^{14}N$_4$^{28}Si$_2$^{1}H$_{23}$: 240.1740, found 240.1767. N-Me$_3$Si-(B$_3$N$_3$H$_5$), R_v = 6.2; ^{11}B NMR (64.2 MHz, C$_6$D$_6$, ppm, Hz): 31.9 (d, B2,6, J_{BH} = 122), 30.2 (d, B4, J_{BH} = 120). ^{1}H NMR (200 MHz, CD$_2$Cl$_2$ ^{11}B spin decoupled, ppm, Hz): 0.22 (s, 9 H, Si-CH$_3$), 4.46 (s, BH, 1 H), 4.70 (s, BH, 2 H), 5.19 (t, NH, 2 H, J_{NH} = 53.6); exact mass calcd for ^{12}C$_3$^{11}B$_3$^{14}N$_3$^{28}Si^{1}H$_{14}$: 153.1236, found 153.1242.

Reaction of Triethylsilane with Borazine. A Fisher pressure reaction vessel was charged with a 1.43 g sample of triethylsilane and evacuated at −196 °C. A 1.02-g sample of borazine was vacuum distilled into the flask, the flask sealed, and the mixture heated at 83 °C for 47 h. The reactor was then cooled, opened to the vacuum line and the volatile materials vacuum distilled into a −196 °C trap. A GC-MS analysis of the volatile mixture showed no evidence for the formation of triethylsilyl-substituted borazine products.

Results and Discussion

As summarized in Table I, hydridopolysilazane (HPZ) reacts smoothly with liquid borazine at moderate temperatures to give borazine-substituted polymers in high yields. These new polymers were isolated as moisture sensitive white solids following vacuum evaporation of excess borazine. The polymers are soluble in most common organic solvents, including benzene and ethers, but it was found that their solubility decreased with increased borazine contents. Likewise, the lower borazine-containing polymers (**1**, **2**, and **3**) could be melted, whereas high-borazine polymers (**4**) could not. Depending upon the reaction times and temperatures, the amounts of borazine incorporated into the hydridopolysilazane could be readily controlled. For example, polymers **2** and **3**, which were prepared by heating HPZ in excess borazine at 73 °C for 2.2 and 7.0 h, have elemental compositions consistent with the formulas (B$_3$N$_3$H$_5$)$_{0.02}$(HSi)$_{0.30}$(Me$_3$Si)$_{0.19}$ (NH)$_{0.26}$N$_{0.23}$ and (B$_3$N$_3$H$_5$)$_{0.07}$(HSi)$_{0.34}$(Me$_3$Si)$_{0.18}$(NH)$_{0.13}$N$_{0.28}$, respectively.

Polymer Characterizations. The elemental analyses and the spectroscopic data discussed below clearly show the incorporation of borazine in the modified hydridopolysilazanes. The HPZ polymer[12] has a complex structure containing highly branched polymer chains with N–H and N–SiMe$_3$ and Si–H functional groups; however, the spectroscopic data indicate a borazine–boron to hydridopolysilazane–nitrogen linkage, which could result from both trimethylsilane and hydrogen elimination reactions, is formed between the pendant borazines and the polymer backbone, as shown in following scheme:



(4)

The products observed for the reaction of borazine with hexamethyldisilazane (discussed below) suggest that both trimethylsilane and hydrogen elimination reactions can occur, but since only small amounts of trimethylsilane product could be isolated following the reaction of borazine with HPZ, the hydrogen elimination pathway would appear to be strongly favored for the polymer.

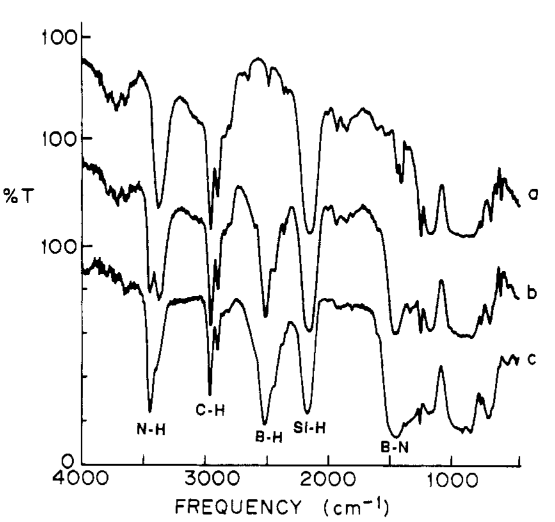


Figure 1. Infrared spectrum of HPZ and borazine-modified HPZ: (a) HPZ; (b) **3**, (c) **4**.

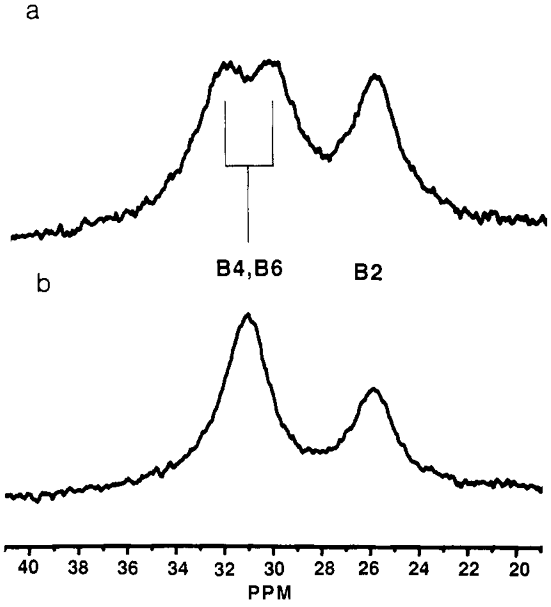
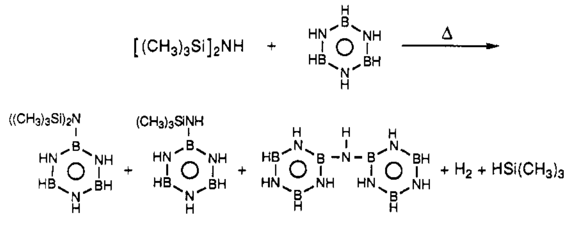


Figure 2. ^{11}B NMR spectrum of **3**: (a) proton coupled; (b) proton decoupled.

The IR spectra of **3** and **4**, Figure 1, show absorptions characteristic of the borazinyl BH (2510 cm^{-1}) and NH (3450 cm^{-1}), polymer NH (3380 cm^{-1}), SiH at (2160 cm^{-1}) and saturated CH (2900–3000 cm^{-1}) with the relative intensities of these absorptions changing according to the polymer composition. With increasing borazine content, the backbone NH, SiH, and CH absorptions decrease, while the borazine BH and NH absorptions increase. The ^{11}B-decoupled proton NMR spectra of all samples showed broad resonances centered at 5.19 ppm (NH), 4.60 ppm (BH), and a very strong resonance at 0.2 ppm (saturated C–H attached to Si) with the relative intensities characteristic of their borazine and silazane compositions. As can be seen in Figure 2, the ^{11}B NMR spectrum of **3** is composed of a singlet at 25.8 ppm and a doublet at 31.0 ppm (J_{BH} = 112 Hz) in a 1:2 integrated ratio, indicating the borazine unit is connected to the hydridopolysilazane through one of the three boron atoms in the borazine ring. The chemical shifts are characteristic of those observed for substituted borazines suggesting no ring-opening reaction has occurred. Furthermore, the chemical shift of the singlet boron resonance is typical of that observed for a borazine–boron connected to a nitrogen atom in a substituent group.[16] The ^{11}B NMR spectra for all modified polymers contained similar features; however, the resonances in the higher borazine content polymers were broadened.

A boron–nitrogen linked borazine–hydridopolysilazane structure is further supported by studies of the reactions of borazine with hexamethyldisilazane and triethylsilane. Thus, heating a mixture of hexamethyldisilazane and borazine in vacuo at 70 °C for 22 h produced several B–N linked products which resulted from both hydrogen and trimethylsilane elimination reactions (eq 5).



(5)

Under these reaction conditions neither borazanaphthalene nor diborazine, products which are found during the dehydropolymerization of borazine,[17] were detected. This suggests that the N–H bond in borazine is much less reactive than either the secondary N–H or N–SiMe$_3$ bonds toward B–H. The possibility that only a mixture of polyborazylene and hydridopolysilazane, instead of a borazine-modified polysilazane was formed, can also be ruled out by the molecular weight studies discussed below. The formation of either Si–N or Si–B bonds through the dehydrocoupling of Si–H with N–H or B–H also does not seem likely in view of the fact that borazine does not react with triethylsilane under even more severe conditions.

Molecular Weight Analysis. Molecular weight distribution averages were determined for HPZ from the SEC/VISC chromatograms shown in Figure 3. Both DRI and VISC chromatograms for HPZ were multimodal suggesting possible microstuctural and/or compositional heterogeneity. The polymer's broad molecular weight distribution, as indicated by its molecular weight distribution averages, M_n = 25 800 g/mol and M_w = 149 200 g/mol, (M_w/M_n = 5.78) mirrored its apparent heterogeneity.

A comparison of normalized DRI chromatograms for HPZ and the borazine-modified polymers, 3 and 4, did not reveal chromatographic changes indicative of molecular weight increases, which might arise from either borazine addition or cross-linking reactions. The most significant differences, as shown in Figure 4, occurred between 30–35 and 40–45 min. Detector response decreased in the 30–34-min region and increased in the 40–44-min region when borazine levels were increased in modified hydridopolysilazane samples.

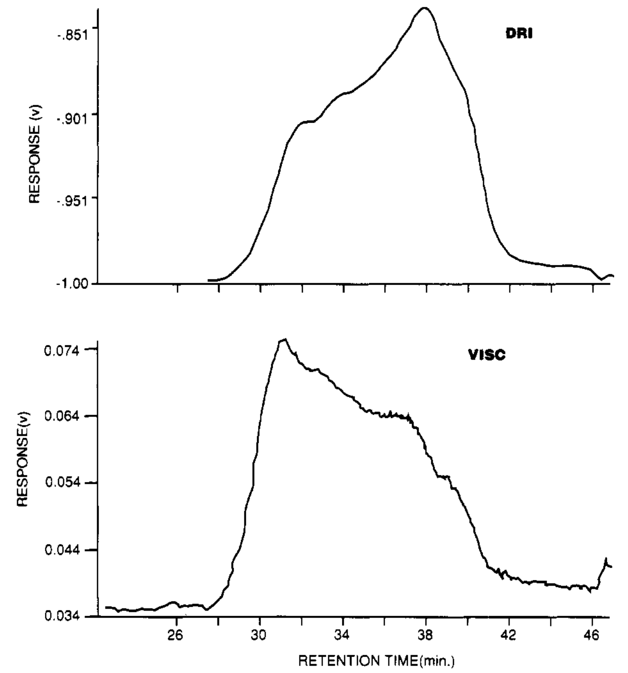


Figure 3. SEC/VISC chromatograms for HPZ. Top: differential refractive index (DRI) chromatogram. Bottom: viscometer (VISC) chromatogram.

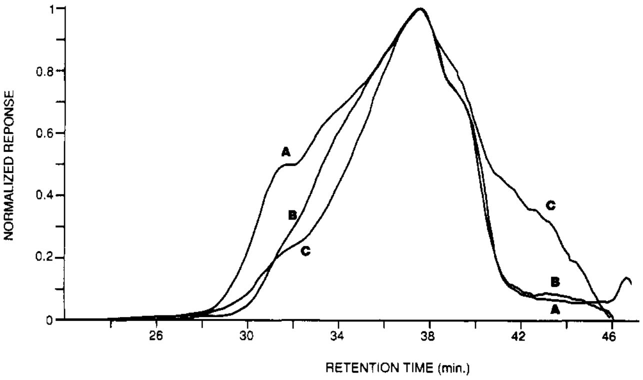


Figure 4. Overlay of peak height-normalized DRI chromatograms: (A) HPZ; (B) 3; (C) 4.

Before attributing the observed chromatographic changes to reaction of HPZ with borazine, the thermal stability of HPZ was tested by refluxing the polymer in benzene solution. The molecular weight results summarized in Table I reveal that the molecular weight of the HPZ(▵) did not decrease, but instead increased after reaction. These results indicate that HPZ is stable to chain scission under the conditions that borazine additions were achieved. They further suggest that the polymer may have cross-linked to a small extent in the absence of borazine.

The observed stability of the unmodified hydridopolysilazane to thermally induced chain scission establishes the dependence of the chromatographic changes on the reaction of HPZ with borazine. These changes are consistent with chain scission, particularly for the highest molecular weight chains of HPZ (30–34-min region). The accompanying increase in low molecular weight material (40–44-min region) with increasing borazine content in the reaction mixture lends further evidence of chain scission during reaction with borazine. Calculated molecular weight averages, listed in Table I, clearly demon-

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(16) Nöth, H.; Wrackmeyer, B. In *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: New York, 1978; pp 188–196.

(17) (a) Fazen, P. J.; Beck, J. S.; Lynch, A. T.; Remsen, E. E.; Sneddon, L. G. *Chem. Mater.* **1990**, 96–97. (b) Fazen, P. J.; Remsen, E. E.; Sneddon, L. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 544–545. (c) Sneddon, L. G.; Su, K.; Fazen, P. J.; Lynch, A. T.; Remsen, E. E.; Beck, J. S. In *Inorganic and Organometallic Oligomers and Polymers*; Harrod, J. F., Laine, R. M., Eds.; Kluwer: Boston, 1991; pp 199–208.

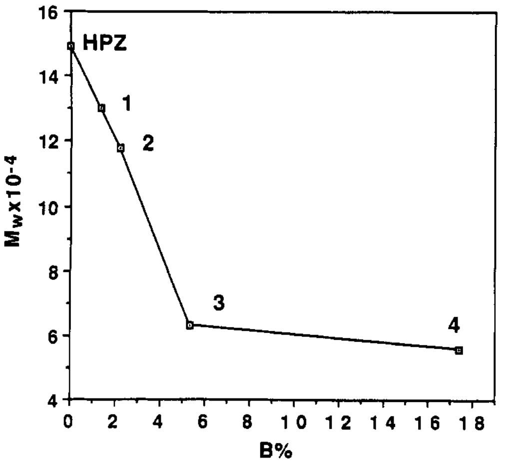
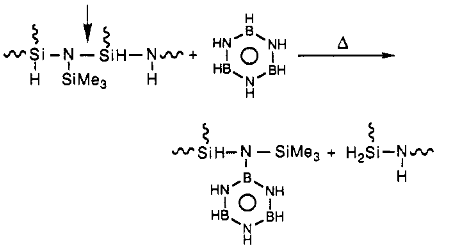


Figure 5. Dependance of M_w on B% in HPZ and polymers 1–4.

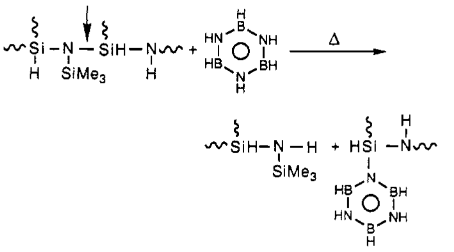
strate the extent of polymer chain scission during reaction with borazine.

All borazine-modified polymers exhibited chain scission, with the extent increasing with increasing borazine content. Consistent with the model study, the chain scission reactions probably occur at Si–N bonds in the polymer backbone.

The cleavage of a Si–N bond could be induced either by formation of B–N or Si–N bonds as shown in eqs 6 and 7. But it would appear that the transamination reaction



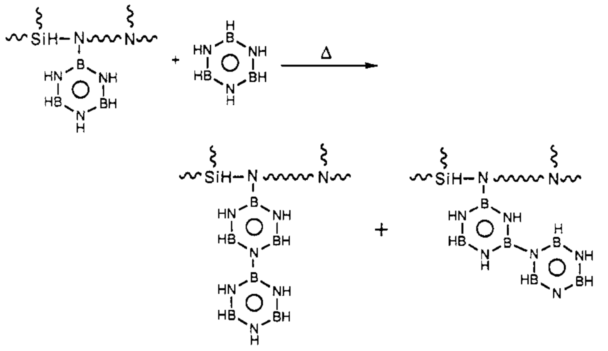
(6)



(7)

(eq 7) requires more vigorous conditions, since when hexamethyldisilazane and borazine were heated at 70 °C for 22 h, no borazine N–Si coupled product was detected. But, when the mixture was heated at 83 °C for 48 h, N–Me_3-Si–($B_3N_3H_5$) was formed along with other products. Therefore, under the conditions described above for the modification of HPZ, the B–H-induced cleavage of backbone Si–N bonds (eq 6) should be responsible for the polymer chain scissions. Consistent with the fact that the chance for chain scission is proportional to the total number of Si–N bonds in the polymer backbone, the high molecular weight components of the borazine-modified polymers were smaller fractions of their molecular weight distributions than those of HPZ.

The dependence of molecular weight on boron content in the polymer is shown in Figure 5. A nearly linear relationship between the borazine content and decreased molecular weight is observed at the early stages (shorter times) of reaction suggesting that the borazine units are added to the polymer backbone independently. A deviation from this trend is observed for the highest borazine containing polymer 4, suggesting that there may be an additional reaction pathway for borazine incorporation in this polymer. As borazine is incorporated into the polymer, the total number of reactive nitrogen backbone sites will be decreased, and thus, in high borazine content polymers such as 4, borazine addition might preferentially occur through a dehydrocoupling reaction of borazine with the pendant-borazine units as shown in eq 8. The broad peak



(8)

observed in the ^{11}B NMR spectrum of 4 is consistent with this interpretation, since pendant polyborazylene chains would have many inequivalent borons that should give rise to overlapping resonances.

The cross-linking reaction of a pendant borazine with another polymer chain could produce an increase in molecular weight. However, all the reactions described above were carried out in the presence of a large excess of borazine and under such conditions cross-linking should not be significant.

Polymer compositional information was obtained by a SEC/UV and SEC/DRI study. A comparison of ultraviolet absorbance (UV) chromatograms for HPZ and the borazine-modified polymers was made to test for the presence of added borazine in the borazine-modified materials. Previous studies[17c,18] of poly(*B*-vinylborazine) and poly(styrene-*co*-*B*-vinylborazine) demonstrated that borazine can be readily detected by UV absorbance at 230 nm in a SEC experiment. Overlayed UV chromatograms for HPZ and the borazine-modified polymers revealed the addition of borazine. A representative example, shown in Figure 6, compares the UV chromatograms of 4 and HPZ. To account for differences in the injected polymer mass, the UV chromatogram of HPZ was scaled to give the response corresponding to the injected mass of the borazine-modified polymers. The data in Figure 6 clearly show greater UV absorption throughout the molecular weight distribution for the borazine-modified polymer versus HPZ on a per gram basis, strongly supporting borazine addition.

SEC/DRI/UV was also used to study the uniformity of borazine addition across the HPZ polymer chain length distribution. This was determined from the degree of chromatographic overlap for normalized, time-delayed-corrected UV and DRI chromatograms of borazine-modified polymers. Previous studies[17c,18] of composition heterogeneity in poly(styrene-*co*-*B*-vinylborazine) copolymers have demonstrated the utility of this approach for

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(18) (a) Su, K.; Remsen, E. E.; Thompson, H. M.; Sneddon, L. G. *Macromolecules* **1991**, *24*, 3760–3766. (b) Su, K.; Remsen, E. E.; Thompson, H. M.; Sneddon, L. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 481–482.

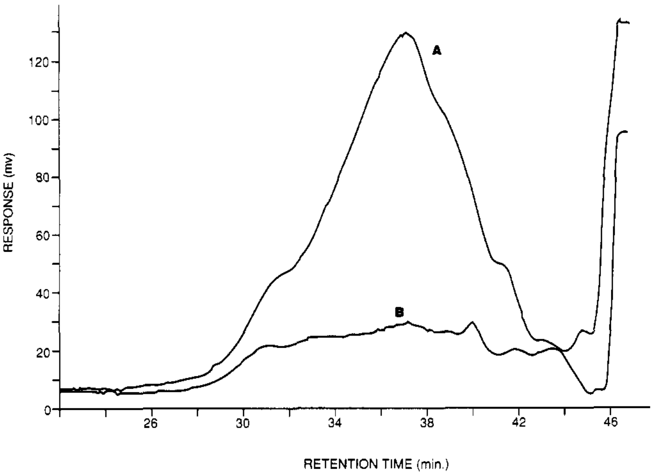

Figure 6. Overlay of mass-normalized UV chromatograms: (A) 4; (B) HPZ.

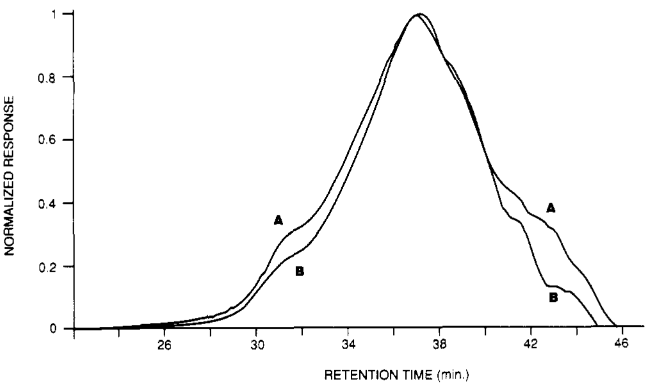

Figure 7. Overlay of peak height-normalized DRI and UV chromatograms for 4: (A) UV; (B) DRI.

borazine-containing polymers. Representative results are presented in Figure 7 for 4. Deviations between the chromatograms are apparent in the high molecular weight region between 30 and 35 min and in the low molecular weight tail between 40 and 45 min. In both chromatographic regions, more UV absorbance relative to DRI response was found. Consequently, borazine was not uniformly added across the hydridopolysilazane molecular weight distribution. The highest and lowest molecular weight polymer chains of hydridopolysilazane were either more reactive toward borzine or contained, on average, more reactive sites per monomer unit. The latter interpretation implies that the HPZ parent may be compositionally heterogeneous; however, further spectroscopic characterization of the polymer as a function of chain length will be needed to verify this hypothesis. Alternatively, as mentioned above, an additional pathway for borazine addition may be preferred in the high borazine content polymers involving the dehydrocoupling of borazine with the pendant borazine (eq 8). Likewise, the poor overlay at the low molecular weight end for 4 may also be due to the presence of small amounts of polyborazylene oligomers that could be formed by the dehydrocoupling of borazine molecules.[17]

Ceramic Conversion Reactions. The ceramic conversion reactions of the borazine-modified HPZ polymers were studied to determine whether they could be used to produce composite SiNCB composites and, if so, whether these new materials would have properties different than those of the ceramics derived from HPZ.

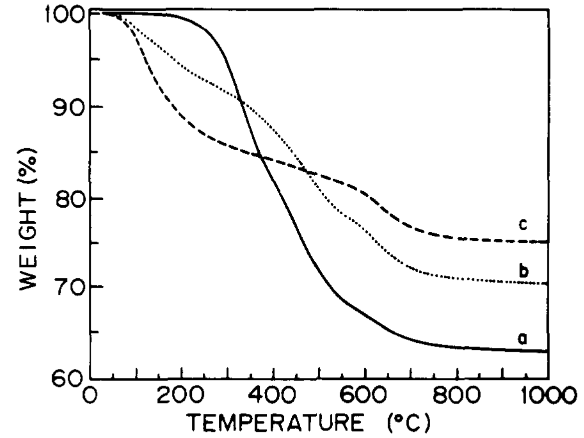

Figure 8. TGA analyses of HPZ and borazine-modified HPZ: (a) HPZ; (b) 3; (c) 4.

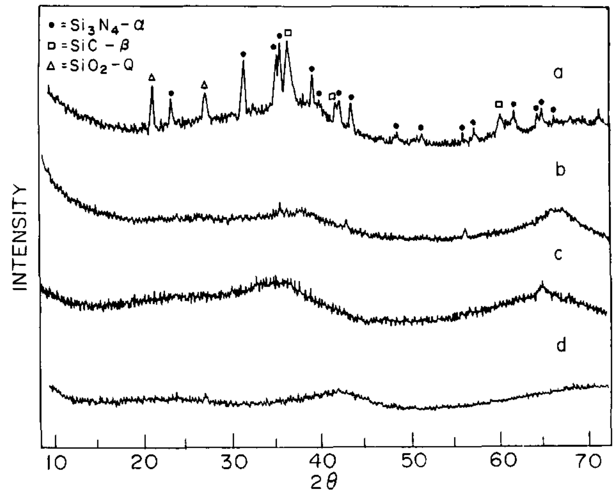

Figure 9. XRD spectra of 1400 °C ceramic materials derived from HPZ and borazine-modified HPZ: (a) HPZ (the SiO_2 may have resulted from oxidation during sample preparation); (b) 2; (c) 3; (d) 4.

For comparison with the results from the modified polymers, the ceramic conversion reactions and the resulting ceramic product of the starting HPZ polymer were initially examined. TGA analysis (Figure 8a) of HPZ shows that the polymer to ceramic conversion occurs over the range 200–800 °C resulting in a 64% ceramic yield. Bulk pyrolysis of HPZ to 1400 °C gave a 57% ceramic yield of a material which exhibited an elemental composition consistent with the formation of a $(Si_3N_4)_{0.37}(SiC)_{0.41}C_{0.22}$ mixture. XRD analyses (Figure 9a) of this ceramic supports this formulation, since the presence of both crystalline α-Si_3N_4 and β-SiC are clearly evident.

TGA studies of the ceramic conversion reactions of 3 and 4 showed multiple-step weight losses. The first loss began at a lower temperature, 60–300 °C, than that observed in the unmodified polymer with the magnitude of the loss depending upon the borazine content of the polymer (Figure 8b,c). Previous studies[17] of the ceramic conversion of polyborazylene to BN have established that the initial weight loss observed in the 100–300 °C region corresponds to polymer cross-linking by a dehydrogenation reaction which results in the formation of additional boron-nitrogen bonds. Thus, the initial weight loss in 3 and 4 could arise through a similar cross-linking reaction involving reaction of the borazine BH groups with polymer backbone NH groups, Si–N linkages or with the NH units in other pendant borazines. Consistent with the presence

Figure 10. Differential scanning calorimetry (DSC) analyses of HPZ and borazine-modified HPZ: (a) HPZ; (b) **3**; (c) **4**.

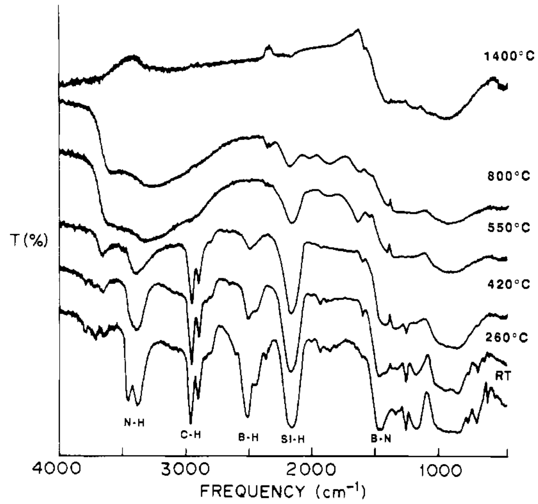

Figure 11. DRIFT spectra of **3** pyrolyzed at different temperatures.

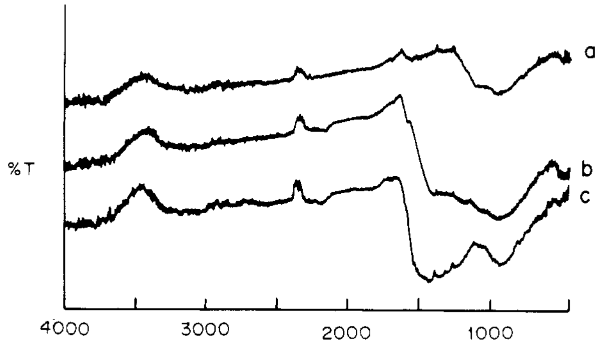

Figure 12. DRIFT spectra of 1400 °C ceramics: (a) HPZ; (b) **3**; (c) **4**.

of a lower temperature crosslinking reaction, differential scanning calorimetry (DSC) studies of **3** and **4** (Figure 10) showed exothermal events below ~250 °C, while the first exotherm observed in the HPZ started at ~300 °C. The remaining weight losses for **3** and **4** began near 300 °C and were completed, as in the HPZ, at 800 °C. Previous studies[12,19] of the ceramic conversion reactions of HPZ and related polysilazanes have established that at these temperatures homolytic cleavage of Si–C bonds and the evolution of gaseous products, such as methane and ammonia, occur. The TGA ceramic yields observed for **3** (72%) and **4** (76%) are both significantly higher than those found for HPZ itself.

An infrared study of the ceramic conversion process of **3** (Figure 11) revealed a stepwise loss of functional groups and supports the reaction sequence proposed above involving an initial borazine crosslinking reaction. At 260 °C, the bands due to BH and NH are decreased relative to the SiH and CH absorptions. At 420 °C, the BH and NH stretching bands are further decreased, and the loss of SiH and CH begins. At 550 °C, the SiH band is still present, but both the CH and BH absorptions are absent. The Si–H remains as the predominant feature in the spectrum at 800 °C, but is completely gone upon heating at 1400 °C. Similar results were observed in an infrared study of the ceramic conversion reaction of polymer **4**. The presence of Si–H in ceramic materials derived from the pyrolysis of polysilazanes at temperatures up to 800 °C has previously been observed.[19]

Bulk pyrolyses of **2**, **3**, and **4** at 1400 °C for 1 h also gave significantly higher ceramic yields (**2**, 70%, **3**, 68% and **4**, 77%) than that observed for HPZ (57%). It is important to note that the increased ceramic yields observed for the borazine-modified polymers results both from the inclusion of borazine boron and nitrogen, presumably as boron nitride, in the product and from better retention of silicon and nitrogen. Thus, the introduction of the pendant borazine units into the polymer induces the low temperature (100–300 °C) dehydrogenation reaction that effectively cross-links the polymer and apparently retards the loss of backbone fragments up to 1400 °C. Elemental analyses of the ceramic products confirm that both boron and additional nitrogen had been retained and are consistent with the compositions $(BN)_{0.11}(Si_3N_4)_{0.32}(SiC)_{0.33}C_{0.24}$ (**2**), $(BN)_{0.24}(Si_3N_4)_{0.28}(SiC)_{0.25}C_{0.22}$ and $(BN)_{0.62}(Si_3N_4)_{0.13}(SiC)_{0.07}C_{0.17}$ (**4**). These boron-containing composite ceramics are not simple mixtures of the above components, as can be seen in the XRD spectra in Figure 9. As mentioned above, the ceramic derived from HPZ at 1400 °C most closely resembles a rule of mixtures composition with α-Si_3N_4 and β-SiC clearly visible by XRD along with a broad featureless peak centered at 36° 2θ, as shown in Figure 9a. The ceramics that are derived from the modified hydridopolysilazanes show no truly crystalline species, only broad peaks centered at 23°, 42°, and 70° 2θ, suggesting that either the crystallization of the α-Si_3N_4 and β-SiC phases have been retarded or that other, perhaps ternary, species are present. Likewise, h-BN was not observed by XRD; however, the DRIFT spectra of these ceramics (Figure 12) show absorptions at 1400 and 890 cm^{-1}, characteristic of boron nitride.[20]

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[19] (a) Han, H. N.; Lindquist, D. A.; Haggerty, J. S.; Seyferth, D. *Chem. Mater.* **1992**, *4*, 705–711. (b) Burns, G. T.; Angelotti, T. P.; Hanneman, L. F.; Chandra, G.; Moore, J. A. *J. Mater. Sci.* **1987**, *22*, 2609–2614. (c) Peuckert, M.; Vaahs, T.; Bruck, M. *Adv. Mater.* **1990**, *2*, 398. (d) Blum, Y. D.; McDermott, G. A.; Hirschon, A. S. In *Inorganic and Organometallic Oligomers and Polymers*; Harrod, J. F., Laine, R. M. Eds.; Kluwer: Boston, 1991; pp 161–175. (e) Blum, Y. D.; Schwartz, K. B.; Laine, R. M. *J. Mater. Sci.* **1989**, *24*, 1707–1718. (f) Burns, G. T.; Chandra, G. *J. Am. Ceram. Soc.* **1989**, *72*, 333–337.

[20] Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73–91.

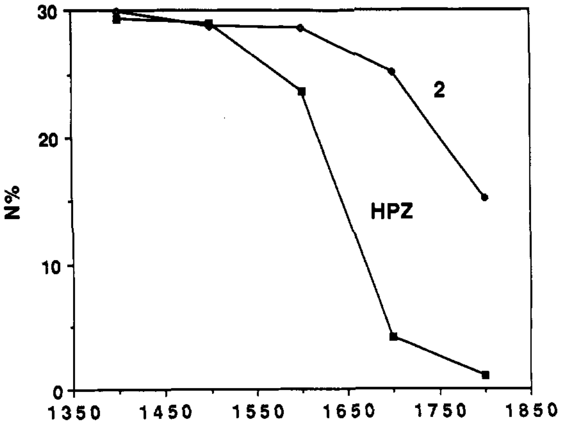

Figure 13. Nitrogen content of ceramic materials derived from HPZ and 2 as a function of pyrolysis temperature.

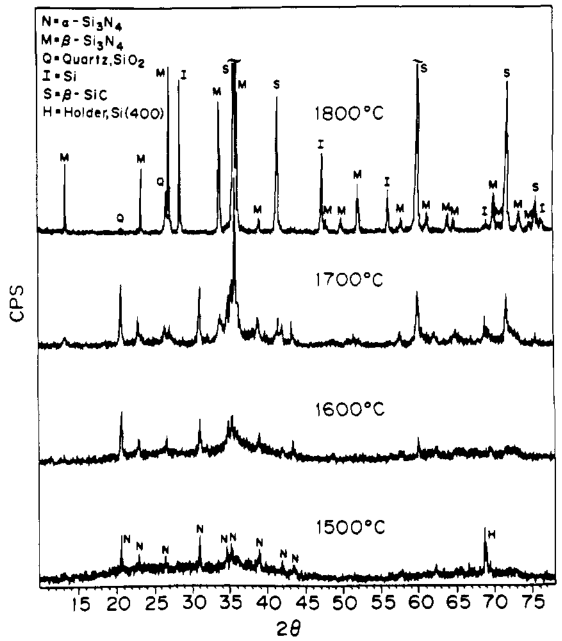

Figure 14. XRD spectra of ceramic materials obtained from 2 at >1400 °C pyrolysis temperatures.

Pyrolyses carried out to higher temperatures also demonstrated higher ceramic yields at every temperature for 2 compared to HPZ. Significantly, as shown in Figure 13, the elemental analyses showed much higher retention of nitrogen at high temperatures for the boron-containing ceramics compared to the ceramic derived from the HPZ polymer. For example, while the HPZ-derived ceramics contained only 4.11% nitrogen at 1700 °C and 1.00% at 1800 °C, the ceramics derived from 2 contained 25.14% and 15.26% nitrogen, respectively, at these temperatures. Thus, the ceramics derived from the modified polymers are compositionally more stable at temperatures at which HPZ derived ceramics normally evolve nitrogen.

Significant differences in the onset, phases and extent of crystallization in the ceramic products obtained from HPZ and the modified polymers were observed. As shown in Figure 14 for the product from polymer 2, the ceramics resulting from the borazine-modified polymers do not show any major crystallinity until 1700 °C, at which temperature a mixture of α-Si_3N_4, β-Si_3N_4, and β-SiC is observed. In contrast, the XRD spectrum of the ceramic derived from HPZ (Figure 15) shows substantial amounts of crystalline α-Si_3N_4 at 1500 °C, both α-Si_3N_4 and β-SiC at 1600 °C, and only β-SiC above 1700 °C. These results are consistent with the previous reports of the suppression of crystallization of silicon nitride ceramics by boron nitride.[6,7,8]

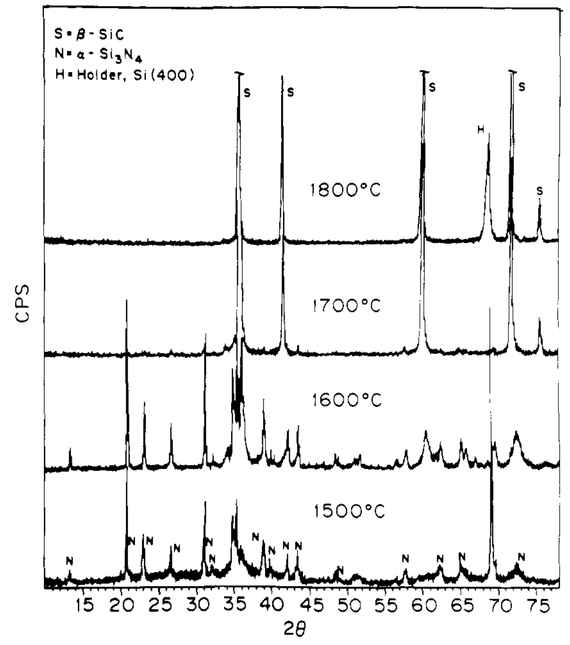

Figure 15. XRD spectra of ceramic materials obtained from HPZ at >1400 °C pyrolysis temperatures.

The ceramic materials obtained above 1700 °C for the HPZ and the borazine-modified HPZ polymers also show significant differences in the compositions of their crystalline phases. The XRD spectrum of the HPZ ceramic shows only β-SiC above 1700 °C, whereas those of the borazine-modified ceramics show a mixture of β-Si_3N_4 and β-SiC. A similar conversion of α-Si_3N_4 to β-Si_3N_4 was also reported[8b] by Interrante upon the pyrolysis to 1750 °C of other boron-modified silazane precursors. The formation of β-Si_3N_4 is surprising, since it would be expected that crystalline α-Si_3N_4 should, in the absence of any oxide sintering aids, only slowly convert to the β-phase, even when derived from amorphous precursors.[21] However, as discussed above, the inclusion of boron into the ceramic has retarded the loss of nitrogen at high temperatures and has thus apparently stabilized the Si_3N_4 toward decomposition (loss of N_2) to temperatures (1800 °C) where the α to β transformation can take place.

In conclusion, the results presented above have demonstrated (1) borazine can be incorporated in a controlled fashion as pendant substituents at the backbone nitrogen sites of the HPZ polymer, (2) the molecular weights of the resulting borazine-modified polymers are decreased relative to HPZ owing to borazine-induced chain scission reactions, (3) the modified polymers can be used to incorporate substantial amounts of boron, presumably as BN, into the final ceramics, (4) the significantly increased ceramic yields that are observed to 1400 °C for the borazine-modified polymers result from a low-temperature cross-linking reaction that is induced by the pendant borazine units, (5) in contrast to HPZ, these new composite ceramics retain significant amounts of nitrogen up to 1800 °C, (6) the crystallization of SiC and Si_3N_4 ceramic phases in the composite ceramics is retarded to above 1700 °C and, (7) at 1800 °C, the ceramic materials derived from

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(21) Burns, G. T.; Ewald, J. A.; Mukherjee, K. *J. Mater. Sci.* **1992**, *27*, 3599–3604.

borazine-modified polymers are mixtures of β-Si_3N_4 and β-SiC, while only β-SiC is present in HPZ ceramic.

Because of their ease of synthesis and processability, as well as the increased thermal stabilities and reduced crystallinity of their derived ceramics, these new hybrid borazine-modified hydridopolysilazanes polymers may prove to be reasonable precursors for enhanced SiNCB fibers, matrices for ceramic–ceramic or carbon–carbon composites and/or binders for nitrogen-based ceramic powders. These applications are presently under investigation.

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