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Synthesis, Characterization, and Ceramic Conversion Reactions of Borazine/Silazane Copolymers: New Polymeric Precursors to SiNCB Ceramics

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The first borazine/silazane backbone copolymers derived from the parent borazine, $B_3N_3H_6$, have been obtained by the thermal condensation of borazine with two silazanes, tris(trimethylsilylamino)silane (**TTS**), and 1,1,3,3,5,5-hexamethylcyclotrisilazane (**HCT**). Both series of copolymers are proposed to contain borazine−boron to silazane−nitrogen linkages. Elemental analyses of the **TTS** copolymers are consistent with an approximate $[[(-B_3N_3H_4)\text{-}NH]_3SiH]_x$ structural unit, while the **HCT** copolymers have compositions ranging from $(B_3N_3H_4)_{1.00}(N)_{1.81}(SiMe_2)_{1.57}(H)_{1.6}$ to $(B_3N_3H_4)_{1.00}(N)_{1.07}(SiMe_2)_{1.28}(H)_{0.9}$. Molecular weight studies indicate large polydispersities, and when molecular weight data are combined with intrinsic viscosity results, highly branched structures are suggested. Despite their similar compositions, the two series of copolymers yield different types of ceramic materials upon pyrolysis. The **TTS** copolymers yield BNSi ceramics that are amorphous to 1400 °C. Pyrolyses to 1800 °C result in further loss of silicon to produce ceramics of variable silicon contents with compositions ranging from $B_{1.00}N_{0.90}Si_{<0.01}C_{<0.01}$ to $B_{1.00}N_{0.91}Si_{0.14}C_{0.07}$. While their DRIFT spectra are consistent with the presence of boron nitride, the XRD spectra of these materials showed no crystalline boron-containing species, but instead, peaks due to small amounts of crystalline β-Si_3N_4, β-SiC and elemental Si. The ceramics derived from the **HCT** copolymers at 1400 °C were also amorphous, but showed greater retention of silicon and carbon with typical compositions of $B_{1.0}N_{1.5}Si_{0.4}C_{0.2}$. Pyrolyses of the **HCT** copolymers to 1800 °C yielded materials with compositions ranging from $B_{1.00}N_{2.58}Si_{0.94}C_{0.30}$ to $B_{1.00}N_{0.86}Si_{0.16}C_{0.19}$. The DRIFT spectra of the ceramics obtained at both temperatures again indicate the presence of boron nitride. XRD spectra, however, show crystalline phases of β-Si_3N_4, β-SiC, and Si, but no diffraction from any boron-containing species.

Introduction

Non-oxide ceramics, such as silicon carbide, silicon nitride, boron carbide, and boron nitride have been used in a variety of hostile environments because of their refractory, high performance, and oxidation resistant properties.[4,5] Compared to these single-component ceramics, ceramic composites often offer many additional advantages. For example, incorporation of boron into silicon-based ceramics has been shown to increase their thermal stability and retard crystallization, properties that may increase the effective use-temperature of these materials in many applications where amorphous ceramics are required.[6−10]

The conventional powder approach[11] to forming ceramic composites employs high pressures and/or temperatures to promote the solid-state diffusion of individual ceramic grains, conditions that limit the size and shapes of the resulting articles. An alternative synthetic approach to composites, which has already been used to form many single-phase ceramic shapes, films, and fibers, could employ a polymeric ceramic precursor that is processed at the polymer stage and then converted to the desired composite with retention of form.[12]

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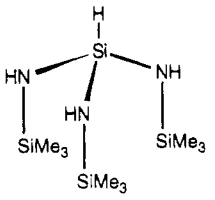
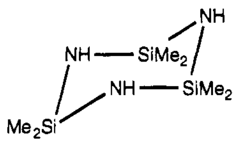
Thus, if a "single-source" polymer could be designed to contain those elements desired in the final composite, then a compositionally homogeneous ceramic, in a processed form, should be attainable.

Previously, we reported that hydridopolysilazane (**HPZ**) polymers can be successfully modified by the addition of borazine, $B_3N_3H_6$.[10] The resulting borazine-modified **HPZ** polymers are meltable and soluble in organic solvents and are converted to ceramic materials in excellent chemical and ceramic yields. Furthermore, the resulting SiNCB ceramics have decreased crystallinity and improved thermal stability compared to the ceramics from unmodified hydridopolysilazanes. Others have also recently synthesized related types of polyborosilazane precursors to SiNCB composites[6,7,9,13,14] and reported similar enhanced ceramic properties from the incorporation of boron. In this paper, we report the synthesis, characterization and ceramic conversion reactions of the first examples of two new types of borazine/silazane backbone copolymers, obtained by the thermal condensation of $B_3N_3H_6$ with two silazanes, tris(trimethylsilylamino)silane (**TTS**), and 1,1,3,3,5,5-hexamethylcyclotrisilazane (**HCT**).



TTS



HCT

Experimental Section

All synthetic manipulations were carried out using standard high-vacuum or inert atmosphere techniques as described by Shriver.[15]

Materials. Borazine was either purchased from Callery Chemical Co. or synthesized in the laboratory[16] and purified by fractionation through a series of −45, −78, and −196 °C traps, with only the material from the −78 °C trap used for experiments. Tris(trimethylsilylamino)silane, $[(SiMe_3)NH]_3SiH$, was obtained from Dow Corning Corp. and used as received. The 1,1,3,3,5,5-hexamethylcyclotrisilazane, $(Me_2SiNH)_3$, was purchased from Hüls Petrarch Systems and used without further purification.

Physical Measurements and Instrumentation. Diffuse-reflectance IR spectra of the copolymers were recorded on a Perkin-Elmer 1600 series Fourier transform spectrophotometer with a diffuse-reflectance attachment. The ^{11}B NMR spectra were obtained at 64.2 MHz and ^1H NMR spectra were obtained at 200.1 MHz on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. All ^{11}B chemical shifts are referenced to $BF_3{\cdot}O(C_2H_5)_2$ (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 referenced to Me_4Si (0.0 ppm). The ^{29}Si NMR spectra were obtained at 39.7 MHz on a Bruker AM-200 using a DEPT pulse sequence and referenced to Me_4Si (0.0 ppm). 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 compound was established both by its observed mass spectral parent ion cutoff and by the agreement of the calculated and observed isotope patterns in the parent and/or fragment envelopes. Elemental analyses of the copolymers were performed at Robertson Microlit Laboratories, Inc., Madison, NJ. Elemental analyses of the ceramics were performed at the Nesmeyanov Institute of Organoelement Compounds (INEOS), Moscow, Russia.

Thermogravimetric analyses were obtained on a Perkin Elmer TGA 7 thermogravimetric analyzer using an argon gas purge. TGA/MS analyses were performed on a Seiko Instruments Model 320 TG/DTA with a Fison Thermalab mass spectral analyzer. X-ray powder diffraction spectra of the ceramic chars were obtained on a Siemens D5000 using Cu Kα radiation with a graphite monochromator. Bulk polymer pyrolyses to 1400 °C were carried out in mullite pyrolysis tubes using a Lindberg 54000 series tube furnace with an Eurotherm 818 temperature control unit. Argon gas (99.999% pure), passed through a LabClear (No. DGP-250-R1) oxygen scavenger, was used as the purge gas. All furnace firings to 1800 °C 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. Control of the system was accomplished with a CAMILE control system. Densities of the ceramic materials were determined by flotation 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 (Millipore Co.) operated at 35 °C.

A bank of four Ultrastyragel SEC columns (Millipore Co.) with mean permeabilities 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. 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. In the case of the **TTS** copolymers, rapid solubility was obtained in THF and the solutions were immediately analyzed for molecular weight. **HCT** copolymers dissolved very slowly in THF and visually appeared to be fully soluble 6 weeks after preparation. Molecular weight distribution averages for the **HCT** copolymers were measured eight weeks after preparation to ensure complete copolymer solubility.

A universal calibration curve was generated from the DRI chromatograms of sixteen nearly monodisperse ($M_w/M \le 1.1$) 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 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 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

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Table 1. Synthesis and Copolymer Composition

copolymer	borazine/silazane (g (mmol)/g (mmol))	time (h) at 90 °C	copolymer yield (g/wt %)	composition
	Borazine and Tris(trimethylsilylamino)silane (TTS)			
TTS-1	3.08 (38.3)/6.07 (20.7)	285	7.06/77.2	$(B_3N_3H_4)_{1.00}(N)_{1.12}(SiMe_3)_{1.24}(SiH)_{0.35}$
TTS-2	3.30 (41.0)/5.90 (20.1)	210	6.62/72.0	$(B_3N_3H_4)_{1.00}(N)_{1.17}(SiMe_3)_{1.16}(SiH)_{0.34}$
TTS-3	2.37 (29.4)/4.02 (13.7)	112	4.17/65.3	$(B_3N_3H_4)_{1.00}(N)_{0.99}(SiMe_3)_{0.98}(SiH)_{0.23}$
	Borazine and 1,1,3,3,5,5-Hexamethylcyclotrisilazane (HCT)			
HCT-1	3.50 (43.5)/5.34 (24.3)	110	5.91/66.9	$(B_3N_3H_4)_{1.00}(N)_{1.81}(SiMe_2)_{1.57}(H)_{1.6}$
HCT-2	3.43 (42.6)/4.61 (21.0)	120	6.45/80.2	$(B_3N_3H_4)_{1.00}(N)_{1.67}(SiMe_2)_{1.49}(H)_{1.5}$
HCT-3	3.96 (49.2)/4.92 (22.4)	113	5.13/57.8	$(B_3N_3H_4)_{1.00}(N)_{1.07}(SiMe_2)_{1.28}(H)_{0.9}$

following previously described[17] 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:

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

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 $[\eta_i]$:

$$M_i = \phi_i/[\eta_i] \qquad (3)$$

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. The average intrinsic viscosity, $[\eta]$, was computed as a weight-average by summation of measured $[\eta_i]$ and c_i across a chromatogram. Reported molecular weight and intrinsic viscosity averages are mean values of two determinations.

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 data.

Polymer Synthesis. General Procedures. In a typical reaction, a sample of either tris(trimethylsilylamino)silane (**TTS**) or 1,1,3,3,5,5-hexamethylcyclotrisilazane (**HCT**) was charged under a nitrogen atmosphere into a 88 mL Fischer Porter 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 to form a clear, colorless solution. The mixture was heated in a 90 °C 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 evolved hydrogen was measured by expansion into a known volume. The reaction was allowed to continue until the mixture became highly viscous and the stirbar could no longer move. The reaction vessel was then opened to the vacuum line and any volatile materials were vacuum evaporated. The volatile products were then separated by vacuum fractionation through −90 and −196 °C traps. Materials in the −90 °C trap were analyzed by both GC/MS and NMR techniques, while the products in the −196 °C trap were determined by mass spectral analysis, NMR, and IR. The polymeric product that remained in the reaction vessel was removed under an inert atmosphere.

Borazine/Tris(trimethylsilylamino)silane (TTS) Copolymers: The borazine/**TTS** copolymers were isolated as white solids after removal of the volatile materials. Anal. Found: **TTS-1**, C, 22.19%; H, 8.40%; B, 16.15%; N, 28.73%; Si, 22.22%; **TTS-2**, C, 21.94%; H, 8.33%; B, 17.00%; N, 30.56%; Si, 22.17%;[18] **TTS-3**, C, 20.53%; H, 8.28%; B, 18.90%; N, 32.59%; Si, 19.70%.[18]

NMR data for copolymer **TTS-2**: ^{11}B NMR (δ, 64.2 MHz, THF-d_8) 31.6 (br, B−H), 28.5 (s, B−N); ^1H NMR (δ, 200 MHz, THF-d_8), 5.3−2.2 (numerous peaks), 0.4 to −0.1 ($SiMe_3$ resonances); ^{29}Si NMR (δ, 39.7 MHz, THF-d_8) 8.80, 7.39, 6.57, 5.10, 4.15; 1.84, 1.75, 1.37, 1.13, 0.71, 0.55 ($SiMe_3$), −41.0, −44.0 (SiH). IR data for **TTS-2**: 3430 (s) (N−H), 3420 (sh, m) (N−H), 2950 (s) (C−H), 2895 (m) (C−H), 2495 (s) (B−H), 2440 (sh, m), 2145 (s) (Si−H), 1950 (w), 1460 (vs, br) (B−N), 1255 (m), 915 (m), 855 (m), 755 (m) cm^{-1}. Both the IR and NMR spectra for **TTS-1** and **TTS-3** were similar to **TTS-2**.

Separation of the volatile components from a typical synthesis of **TTS-2**, which employed 3.30 g (41.0 mmol) of borazine and 5.90 g (20.1 mmol) of tris(trimethylsilylamino)silane, by vacuum fractionation through a −90 °C trap into a -196 °C trap yielded 0.76 g (10.3 mmol) of trimethylsilane in the −196 °C trap. GC/MS analysis of the material stopping in the −90 °C trap (1.04 g) indicated the major products were hexamethyldisilazane (25%) and $(SiMe_3NH)-B_3N_3H_5$ (40%), but also showed evidence of numerous smaller products (<10%) corresponding to unreacted borazine, other silazanes, and silazane-substituted borazines.

Borazine/1,1,3,3,5,5-Hexamethylcyclotrisilazane (HCT) Copolymers: The borazine/**HCT** copolymers were also isolated as white solids after vacuum evaporation of all the volatile materials. Anal. Found: **HCT-1**, C, 19.38%; H, 7.77%; B, 16.70%; N, 34.71%; Si, 19.58%; **HCT-2**, C, 18.67%; H, 7.59%; B, 16.88%; N, 34.08%; Si, 22.78%;[18] **HCT-3**, C, 17.79%; H, 7.31%; B, 18.70%; N, 32.86%; Si, 22.95%.

NMR data for copolymer **HCT-2**: ^{11}B NMR (δ, 64.2 MHz, THF-d_8) 31.4 (br, B−H); 28.1 (s, B−N); ^1H NMR (δ, 200 MHz, THF-d_8) 4.6−1.6 (numerous resonances), 0.4−0.0 ($SiMe_2$ resonances); ^{29}Si NMR (δ, 39.7 MHz, THF-d_8), −5.1 (m, $SiMe_2$), −9.4, −14.1 (br, m, $Me_2SiH-NH-$). IR data for **HCT-2**: 3445 (s, N−H), 2955 (s, C−H), 2900 (m, C−H), 2805 (w), 2500 (s, B−H), 2445 (sh, s), 2385 (sh, m), 2345 (sh, w), 2305 (sh, w), 2120 (s, Si−H), 1920 (w), 1805 (w), 1460 (vs, br, B−N), 1305 (s, B−N), 1190 (s), 1084 (m), 950 (s), 885 (s), 820 (s), 724 (s), 611 cm^{-1} (sh, w). The NMR and IR spectra of copolymers **HCT-1** and **HCT-3** are similar to those of copolymer **HCT-2**, but the relative intensities vary according to the borazine content of the copolymers.

Separation of the volatile components from a typical synthesis of **HCT-2** employing 3.43 g (42.6 mmol) of borazine and 4.61 g (21.0 mmol) of 1,1,3,3,5,5-hexamethylcyclotrisilazane, by vacuum fractionation through a −90 °C trap into a −196 °C trap yielded 0.23 g (3.8 mmol) of dimethylsilane in the −196 °C trap. GC/MS analysis of the material stopping in the −90 °C trap (0.39 g) indicated the major borazine containing product was $((Me_2SiH)NH)-B_3N_3H_5)$ but also included numerous smaller products (<10%) corresponding to unreacted borazine, other silazanes and silazane-substituted borazines.

Control Experiments. Control experiments to determine the extent of silazane homopolymerization were carried out by heating neat ~1 g samples of each liquid silazane in vacuo at 90 °C for several months. The lack of generation of hydrogen or other volatile products in these reactions suggests no appreciable homopolymerization occurs under these condi-

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(18) Silicon content determined by difference.

Table 2. Copolymer Molecular Weights and Intrinsic Viscosities

copolymer	M_w	M_n	M_w/M_n	[η] (dL/g)
Borazine and Tris(trimethylsilylamino)silane (TTS)				
TTS-1	10244	1679	6.10	0.034
TTS-2	6846	1356	5.05	0.036
TTS-3	8167	1510	5.41	0.031
Borazine and 1,1,3,3,5,5-Hexamethylcyclotrisilazane (HCT)				
HCT-1	49032	3538	13.9	0.050
HCT-2	48488	3201	15.1	0.049
HCT-3	85304	3915	21.8	0.060

Table 3. Ceramic Conversion of Borazine/TTS Copolymers

copolymer	bulk ceramic conversion (wt %)	composition	d (g/cm^3)
		1400 °C	
TTS-1	37.8	$B_{1.00}N_{1.05}Si_{0.19}C_{0.04}$	1.7
TTS-2	37.3	$B_{1.00}N_{1.06}Si_{0.17}C_{<0.01}$	1.6
TTS-3	42.1	$B_{1.00}N_{1.17}Si_{0.19}C_{0.05}$	1.8
		1800 °C	
TTS-1	26.1	$B_{1.00}N_{0.86}Si_{0.01}C_{<0.01}$	2.3
TTS-2	27.2	$B_{1.00}N_{0.91}Si_{0.14}C_{0.07}$	2.3
TTS-3	24.2	$B_{1.00}N_{0.90}Si_{<0.01}C_{<0.01}$	2.3

tions. GC/MS of the heated silazanes showed no evidence of the formation of oligomers.

Ceramic Conversion Reactions. For the 1400 °C bulk conversions, mullite pyrolysis tubes were flame dried under $<10^{-6}$ Torr vacuum and back-filled with argon. Copolymer samples of 1–2 g were weighed under nitrogen, quickly transferred into boron nitride boats, and placed in the pyrolysis tube. After purging the system with argon for 20 min, the samples were heated to 1400 °C at 10 °C/min and held for 1 h before cooling to room temperature. After pyrolysis, all manipulations of ceramics were carried out in the air. Anal. Found: **TTS-1.1**, C, 0.99%; H, 1.88%; B, 22.62%; N, 30.83%; Si, 11.36%; **TTS-2.1**, C, <0.5%; H, 1.20%; B, 23.67%; N, 32.41%; Si, 10.44%; **TTS-3.1**, C, 1.19%; H, 2.23%; B, 22.52%; N, 34.00%; Si, 11.38%. **HCT-1.1**, C, 5.78%; H, 2.92%; B, 22.68%; N, 42.54%; Si, 21.84%; **HCT-2.1**, C, 5.68%; H, 3.59%; B, 22.60%; N, 41.00%; Si, 20.91%; **HCT-3.1**, C, 5.65%; H, 3.18%; B, 24.46%; N, 46.97%; Si, 22.04%. While the ceramics derived from the **HCT** copolymers appeared black and glassy, the **TTS**-based ceramics were gray. Additional properties of these ceramics are presented in Table 3.

For bulk conversions to 1800 °C, polymer samples were weighed into graphite crucibles and placed into an Astro graphite furnace. The furnace was then evacuated to less than 5 Torr and refilled with argon. The samples were then heated at a rate of 10 °C/min to 1800 °C and held 1 h before cooling. Anal. Found: **TTS-1.2**, C, <0.5%; H, <0.5%; B, 46.93%; N, 52.01%; Si, 0.97%; **TTS-2.2**, C, 2.93%; H, 1.47%; B, 37.79%; N, 44.73%; Si, 13.65%; **TTS-3.2**, C, <0.5%; H, <0.5%; B, 46.35%; N, 53.79%; Si, <0.5%. **HCT-1.2**, C, 4.67%; H, 2.84%; B, 14.00%; N, 46.86%; Si, 34.04%; **HCT-2.2**, C, 7.82%; H, 4.41%; B, 26.40%; N, 35.65%; Si, 25.56%; **HCT-3.2**, C, 7.53%; H, 3.77%; B, 35.08%; N, 39.28%; Si, 14.25%. The **HCT** based ceramics appeared dark gray, but the **TTS** ceramics were off-white. Additional properties of these ceramics are presented in Table 4.

Results and Discussion

Borazine, $B_3N_3H_6$, and its alkyl derivatives, 2,4,6-$R_3B_3N_3H_3$, have recently been shown to readily undergo dehydrocoupling reactions with hydridopolysilazanes to yield new preceramic polyborosilazanes containing pendant $B_3N_3H_5$– or $R_3B_3N_3H_2$– substituents.[6b,10,19]

Table 4. Ceramic Conversion of Borazine/HCT Copolymers

copolymer	bulk ceramic conversion (wt %)	composition	d (g/cm^3)
		1400 °C	
HCT-1	43.0	$B_{1.00}N_{1.45}Si_{0.37}C_{0.23}$	1.6
HCT-2	54.3	$B_{1.00}N_{1.40}Si_{0.36}C_{0.23}$	1.7
HCT-3	57.8	$B_{1.00}N_{1.48}Si_{0.35}C_{0.21}$	1.6
		1800 °C	
HCT-1	38.0	$B_{1.00}N_{2.58}Si_{0.94}C_{0.30}$	2.1
HCT-2	36.2	$B_{1.00}N_{1.04}Si_{0.37}C_{0.27}$	2.0
HCT-3	38.3	$B_{1.00}N_{0.86}Si_{0.16}C_{0.19}$	2.1

Paine[5,20] and Paciorek[21] have also shown that chloroborazines react with hexamethyldisilazane with elimination of trimethylsilyl chloride to give polyaminoborazines. However, until the work presented herein, there appears to have been no reported examples of the synthesis of hybrid borazine/silazane backbone copolymers via copolymerization reactions of silazanes with the parent borazine.

As summarized in Table 1, the thermal condensation of borazine with either of the two silazanes, tris(trimethylsilylamino)silane (**TTS**) or 1,1,3,3,5,5-hexamethylcyclotrisilazane (**HCT**) was found to produce new borazine/silazane copolymers in high yields. The polymers were isolated as white solids after vacuum evaporation of all the volatile materials. The freshly prepared polymers are meltable and readily soluble in ethers but only slightly soluble in hydrocarbons. The solubility of the polymers was found to decrease with elongated reaction times.

Spectroscopic analyses and molecular weight distribution studies suggest that both series of copolymers have highly complex, branched structures, consistent with the multiple reactive sites on the silazane and borazine units. Previous studies have demonstrated that the reaction of borazine with both hexamethyldisilazane and hydridopolysilazanes occurs primarily through borazine–boron to silazane–nitrogen linkages.[10] These results suggest that during the copolymerization of borazine with either **TTS** or **HCT**, the B–H group of borazine reacts preferentially with secondary N–H bonds of the silazanes. Consistent with this conclusion, it was found in control experiments that neither silazane would polymerize in the absence of

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[19] Seyferth has generated silylborazine units in the backbone of silazane polymers by the reaction of silylamines with boranes and by the thermolysis of silylamine-borane adducts. See ref 7.

[20] (a) Narula, C. K.; Paine, R. T.; Schaeffer, R. In *Inorganic and Organometallic Polymers: Macromolecules Containing Silicon, Phosphorus, and Other Inorganic Elements*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; American Chemical Society: Washington, DC, 1988; pp 378–384. (b) Narula, C. K.; Schaeffer, R.; Datye, A. K.; Borek, T. T.; Rapko, B. M.; Paine, R. T. *Chem Mater.* **1990**, *2*, 384–389. (c) Rye, R. R.; Borek, T. T.; Lindquist, D. A.; Paine, R. T. *J. Am. Ceram. Soc.* **1990**, *73*, 1409–1412. (d) Narula, C. K.; Schaeffer, R.; Paine, R. T.; Datye, A.; Hammetter, W. F. *J. Am. Chem. Soc.* **1987**, *109*, 5556–5557. (e) Paine, R. T. *J. Inorg. Organomet. Polym.* **1992**, *2*, 183–195. (f) Paine, R. T. Jr.; Narula, C. K.; Schaeffer, R. O.; Lindquist; D. A.; Borek, T. T. U.S. Patent No. 5,204,295, Apr 20, 1993.

[21] (a) Paciorek, K. J. L.; Kratzer, R. H.; Harris, D. H.; Krone-Schmidt, W. U.S. Patent No. 4,707,556, Nov 17, 1987. (b) Paciorek, K. J. L.; Kratzer, R. H. *Ceram. Eng. Sci. Proc.* **1988**, *9*, 993–1000. (c) Paciorek, K. J. L.; Masuda, S. R.; Kratzer, R. H.; Schmidt, W. R. *Chem. Mater.* **1991**, *3*, 88–91.

[22] Homopolymerization of **TTS** has not been reported, although it has been used as a crosslinking agent for polysilazanes; see ref 13b. **HCT** will not thermally polymerize at moderate temperatures; however, polymerization of **HCT**, or other cyclosilazanes, using a variety of other conditions has been reported, see: Laine, R. M.; Blum, Y. D.; Tse, D.; Glaser, R. In *Inorganic and Organometallic Polymers: Macromolecules Containing Silicon, Phosphorus, and Other Inorganic Elements*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; American Chemical Society: Washington, DC, 1988; pp 124–142 and references therein.

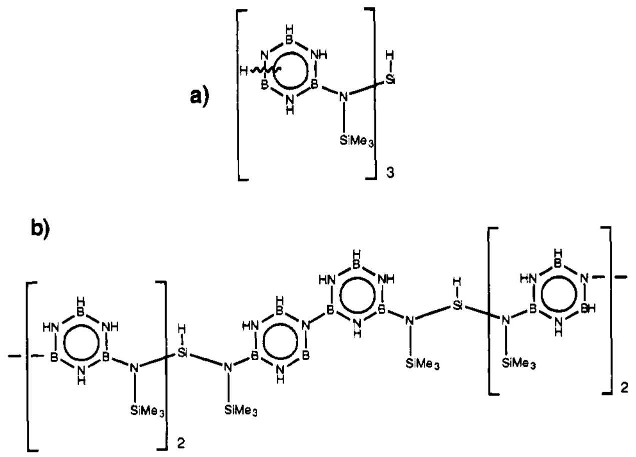


Figure 1. (a) **TTS** copolymer fragment, (b) possible copolymer structure.

borazine under comparable reaction conditions.[22] Likewise, attempts to form polymers using borazine/silazane molar ratios ≤1.5 yielded only oligomers after ~1 month at 90 °C, further evidence that borazine units are incorporated into the polymer backbone. The homopolymerization of neat borazine to produce polyborazylene, $(B_3N_3H_{\sim4})_x$, however, has been described previously.[23] Therefore, it is likely that the copolymers could contain some repeating borazine units or pendant borazines on the copolymer backbone.

Borazine/Tris(trimethylsilylamino)silane Copolymers. The spectroscopic properties and compositions of the borazine/**TTS** copolymers clearly show that they contain both borazine and silazane units. For example, the empirical formula determined by total elemental analyses of **TTS-1**, $(B_3N_3H_4)_{1.00}(N)_{1.12}(SiMe_3)_{1.24}(SiH)_{0.35}$,[24] is consistent with the fragment shown in Figure 1a that could be produced by the dehydrocoupling of borazine rings at the three **TTS** N–H sites. Polymer chains based on this unit could arise via borazine-borazine B–N linkages as shown in Figure 1b. Such a polymer structure would explain the inability to form polymers using low borazine/silazane ratios in the feed. Increasing the borazine content in the feed was found to increase the ratio of borazine/silazane units in the copolymers (Table 1), suggesting repeating borazine units or pendant borazines may be present in the copolymers. Indeed, as mentioned above, the thermal dehydropolymerization of neat borazine to form polyborazylene, $(B_3N_3H_{\sim4})_x$, has been previously shown[23] to occur under conditions similar to those employed for the borazine/**TTS** copolymerizations.

During polymerization, hydrogen gas was produced in almost equimolar amounts compared to the consumed borazine, again indicating that the polymerization occurs primarily through dehydrocoupling reactions. Analysis of the condensable volatile products from the copolymerization of borazine and **TTS**, however, provides evidence for additional reaction pathways or side reactions. For example, vacuum fractionation of the volatile products (see Experimental Section) yielded approximately 0.25 mol of trimethylsilane for each mole of borazine in the feed, suggesting a Si–N cleavage reaction such as seen in eq 4.

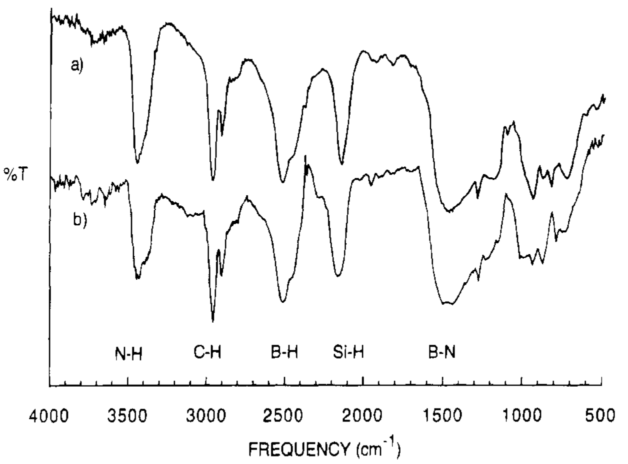
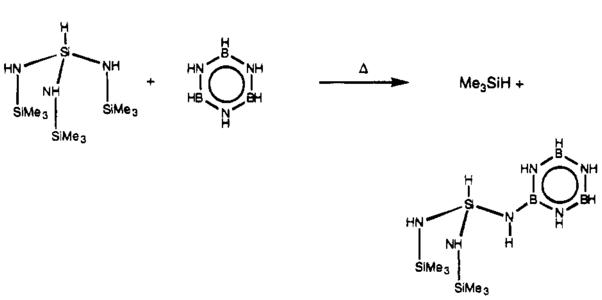


Figure 2. Infrared spectra of borazine/silazane copolymers: (a) **TTS-2**, (b) **HCT-2**.



(4)

Indeed, previous studies of the reaction of borazine with both hexamethyldisilazane and hydridopolysilazanes[10] have shown that Si–N bond cleavage is a significant process for borazine–silazane coupling.

Spectroscopic studies further support a borazine/silazane backbone structure for the **TTS** copolymers. Their IR spectra, Figure 2a, show absorptions characteristic of silazane and borazine N–H (3430 cm^{-1}), silazane C–H (2950, 2895 cm^{-1}), borazine B–H (2450 cm^{-1}), and silazane Si–H (2145 cm^{-1}), as well as borazine and borazine-silazane B–N (1460 cm^{-1}). Their ^{11}B NMR spectra (Figure 3a) exhibit a broad peak at 31.6 ppm and a broad singlet at 28.5 ppm. Both chemical shifts are similar to those reported for the borazine-modified **HPZ** polymers[10] and fall in the region expected for borazine ring compounds, with the upfield shift of the singlet being characteristic of a boron bound to an electronegative ring substituent such as nitrogen.[25] It is important to note that the shifts are also similar to those found in the B–N coupled diborazine compound, 1:2′-$[B_3N_3H_5]_2$,[23a] since this compound provides a structural model for the proposed linked-borazine backbone fragment of the polymer. The ^{1}H NMR spectra of these copolymers show numerous broad resonances in the 5.3–2.2 ppm region due to unreacted borazine/silazane N–H and borazine B–H groups, as well as peaks near 0.2 ppm arising from silazane $-SiCH_3$ groups. The ^{29}Si NMR spectrum of the starting **TTS** monomer shows two peaks (2.4 and −39.4 ppm) that have been assigned to the $-SiMe_3$ and $-SiH$

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[23] (a) Fazen, P. J.; Remsen, E. E.; Beck. J. S.; Carroll, P. J.; McGhie, A. R.; Sneddon, L. G., *Chem. Mater.* **1995**, *7*, 1942–1956. (b) Fazen, P. J.; Beck, J. S.; Lynch, A. T.; Remsen, E. E.; Sneddon, L. G. *Chem. Mater.* **1990**, *2*, 96–97.

[24] Due to chain branching and cross-linking, it is likely that the number of hydrogens on the borazine units is, on average, less than 4.

[25] Gaines, D. F.; Borlin, J. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975, pp 245–246.

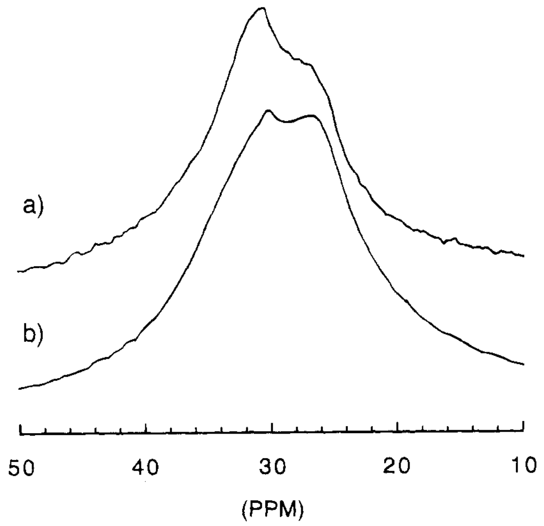

Figure 3. $^{11}B\{^1H\}$ NMR spectra of borazine/silazane copolymers: (a) **TTS-2**, (b) **HCT-2.**

silicons, respectively. The presence of numerous resonances in the ^{29}Si NMR spectra of the polymer in the 2.0 to 0.5 ppm and −40 to −45 ppm regions strongly support the presence of similar $-SiMe_3$ and SiH units in the polymer. However, additional smaller peaks observed between 4 and 9 ppm also suggest that the polymer structure contains more complicated fragments, some of which could be $-(B_3N_3H_4)-NH-SiMe_3$ units.[26]

Borazine/1,1,3,3,5,5-Hexamethylcyclotrisilazane Copolymers. Similar to the copolymers formed from **TTS**, the **HCT** copolymers are proposed to contain borazine-silazane linkages formed as a result of either dehydrocoupling or Si−N cleavage reactions, and the ratio of the borazine and silazane units in the **HCT** copolymers could be varied by changing the ratio of the monomers in the feed. For example, as is summarized in Table 1, the copolymer composition changed from $(B_3N_3H_4)_{1.00}(N)_{1.81}(SiMe_2)_{1.57}(H)_{1.6}$ to $(B_3N_3H_4)_{1.00}(N)_{1.07}(SiMe_2)_{1.28}(H)_{0.9}$ as the borazine-to-silazane molar feed ratio increased from 1.79 (**HCT-1**) to 2.20 (**HCT-3**).[24,27] Again, it is likely that there are pendant borazines and/or repeating borazine units in the polymer backbone. Furthermore, as the polymerization proceeds and the silazane is consumed, the relative concentration of borazine/silazane would be expected to increase, thereby increasing the degree of the borazine−borazine coupling.

Volatile products of the copolymerization reactions consisted of mostly hydrogen gas, supporting dehydrocoupling as the primary means of copolymer formation. However, the isolation of smaller amounts of dimethylsilane and the observation by GC/MS of $((Me_2SiH)NH)-B_3N_3H_5$, suggest that N−Si cleavage reactions may also occur, as shown in Figure 4. Following ring opening by Si−N cleavage, the $((Me_2SiH)NH)-B_3N_3H_5$ fragment could further condense with other borazine or silazane units to become incorporated into the copolymer.

Spectroscopic studies of the copolymers provide further evidence for the proposed polymerization steps. The IR spectra of the **HCT** copolymers (Figure 2b) show features similar to those of the **TTS** copolymers, including C−H, B−H, N−H, and B−N stretches arising from both the borazine and silazane functional groups. In addition, an absorption at 2120 cm^{-1} arising from Si−H stretch was observed, which strongly suggests a ring opening reaction, such as shown in Figure 4. Borazinyl N−H and B−H stretches were observed to increase relative to C−H stretches when the borazine/silazane ratio was increased in the copolymer.

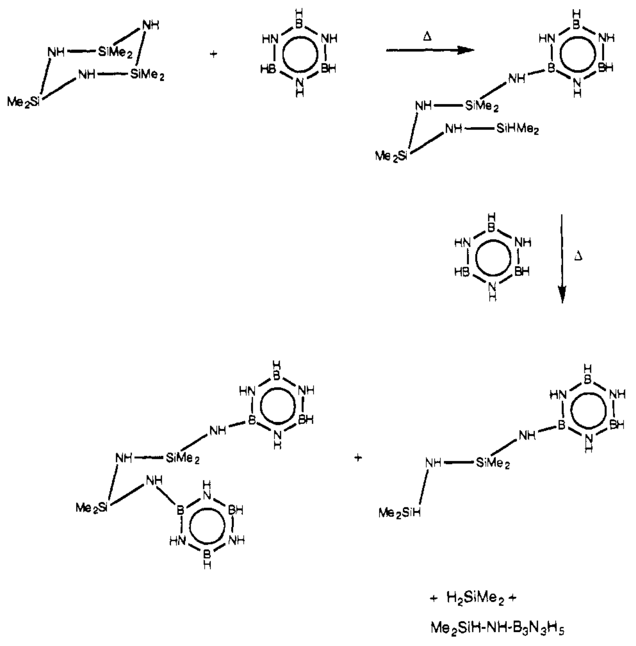

Figure 4. Possible ring-opening reactions of **HCT** with borazine.

The ^{11}B NMR spectra of the **HCT** copolymers (Figure 3b) are similar to those of the **TTS** copolymers, consisting of a broad peak centered at 31.4 ppm and a broad singlet at 28.1 ppm, and suggest the presence of similar borazine ring fragments in the two copolymers. The ^{29}Si NMR spectra of the **HCT** copolymers show resonances centered at −5.1 ppm consistent with the $-SiMe_2$ group of **HCT** (−4.7 ppm). The numerous resonances that were also observed from −8 to −10 and −12 to −14 ppm are consistent with $Me_2SiH-NH-$ groups that could arise from the ring opening of the silazane.[26] The ^1H NMR spectra of the **HCT** copolymers show broad resonances due to unreacted borazine/silazane N−H and borazine B−H (4.6−1.6 ppm) and silazane $-SiMe_2$ groups (0.4−0.0 ppm). Broad resonances at 2.6 ppm, possibly resulting from Si−H groups, were also observed in the ^1H NMR spectra of some of the **HCT** copolymers, providing further evidence for a ring-opening polymerization mechanism.

Molecular Weight Analysis. Representative SEC/VISC chromatograms of borazine/**TTS** copolymers are shown in Figure 5, and representative chromatographs of the borazine/**HCT** copolymers are shown in Figure 6. Both DRI and VISC chromatograms for the two copolymers were multimodal suggesting structural and/or compositional heterogeneity. Reported molecular weight distribution averages and polydispersity (M_w/M_n) in Table 2 also reflect the multimodal character of the chromatograms. The observation of multimodal features is not surprising since the polymers were formed by a series of condensation/redistribution reactions.

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(26) Marsmann, H. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springler-Verlag: New York, 1981; Vol. 17, pp 65−235, and references therein.

(27) The value of (H) may be due to unreacted NH units and/or $-HSiMe_2$ groups produced by ring opening reactions of the silazane.

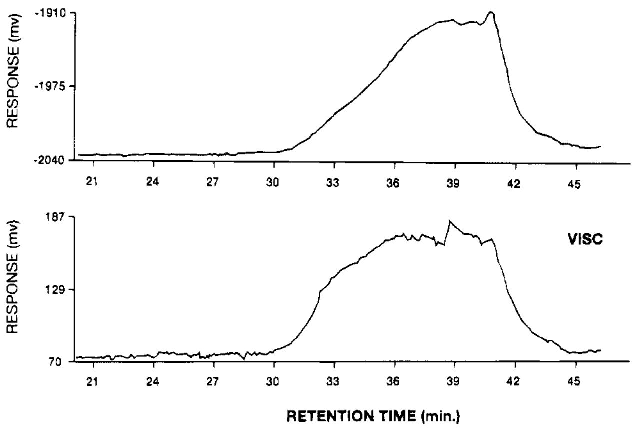

Figure 5. DRI and VISC chromatograms of **TTS-2**.

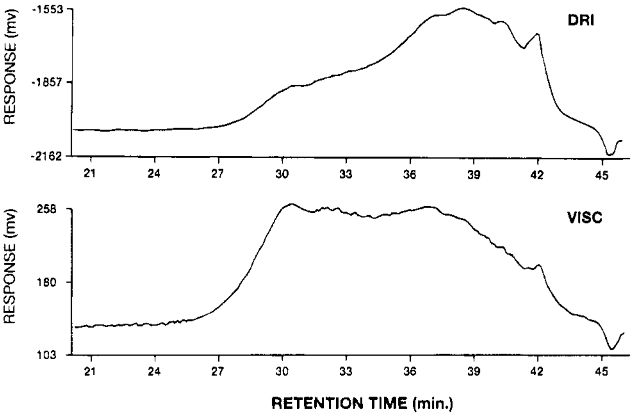

Figure 6. DRI and VISC chromatograms of **HCT-2**.

For both silazane systems, the major chain building reactions that occur at the initial stage of reaction could be the simple condensation of the borazine–BH with the silazane–NH. As the concentration of the silazane–NH group decreases, the polymer scission via Si–N cleavage induced by the B–H on borazine can become more significant. The fragments that contain borazine units, resulting from such chain cleavage reactions, could further condense with other fragments or polymers through the B–H functionality, to produce highly polydispersed polymers. Because of the cyclic nature of the **HCT**, the first borazine Si–N cleavage reaction does not produce small fragments. Therefore, as seen in Table 2, the molecular weight distribution averages for copolymers containing **HCT** were consistently higher than the corresponding copolymers of **TTS**.

If the polymerization occurs only through the N–H unit on the silazanes and the B–H on borazine, both copolymer systems would be considered as A_3-B_3 systems and should produce three-dimensional polymers after the gelation points. Therefore, soluble polymers can only be obtained when the polymerization is stopped before extensive cross-linking occurs. The Si–N chain cleavage reaction should help to postpone the gelation point, however, the formation of polymer gel was indeed observed when the polymerization was carried out for longer times.

Large polydispersities ($M_w/M_n > 5.0$), high M_z values (greater than 500 000 g/mol in a few cases), and the slow dissolution of **HCT**-containing copolymers (see Experimental Section) suggest possible cross-linking and/or chain branching. Molecular weight data and intrinsic viscosity ($[\eta]$) data strongly support this conclusion for the **TTS** copolymers. As shown in Table 2, increasing M_w (6846 g/mol to 10 244 g/mol) for the **TTS** copolymers was accompanied by near equivalence of average $[\eta]$ (0.036 to 0.034 dL/g). If observed molecular weight increases were due to increases in linear chain length, intrinsic viscosity would increase. The near equivalence of $[\eta]$ for the **TTS** copolymers of differing molecular weight indicates the presence of branched chains. The trend in intrinsic viscosity/molecular weight data for **HCT** copolymers does not match that observed for the **TTS** copolymers. Some linear chain length growth for the highest molecular weight copolymer (**HCT-3**) relative to the lowest molecular weight copolymer (**HCT-2**) is suggested by the increase in $[\eta]$ (0.049 to 0.060 dL/g). However, solubility and polydispersity results for **HCT** copolymers are consistent with the presence of high molecular weight branched and cross-linked chains. It is reasonable to conclude that both linear and branched chain growth occurs during polymerization of **HCT** copolymer, but further study will be needed to evaluate the relative amounts of linear and branched chain content.

Ceramic Conversion Reactions. Ceramic conversion reactions of both copolymer systems were investigated as possible new single-source routes to SiNCB ceramic composites. Despite similarities in the elemental compositions of the two series of copolymers, upon pyrolysis, significant differences in the compositions of the resulting ceramics were observed, as described below.

Borazine/TTS Derived Ceramics. The bulk pyrolyses under argon of 1–2 g samples of **TTS** copolymers to 1400 °C were found to afford gray ceramic materials in 37–42% ceramic yields (Table 3). Elemental analyses showed primarily boron, nitrogen, and smaller amounts of silicon, but relatively little carbon.[28] Similar ceramic yields and compositions were found for each of the samples in the **TTS** series (Table 3). In agreement with the analytical results, the diffuse reflectance infrared spectra of the ceramics clearly show an absorption centered at 1460 cm^{-1} (B–N stretch) characteristic of boron nitride. Furthermore, the 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. Consistent with the pyrolyses of other polyborosilazanes at similar temperatures,[6,7,8b,9,10] the XRD spectra of the 1400 °C ceramic chars showed these materials to be amorphous (Figure 7a) with only broad, featureless humps centered at 22°, 42°, and 75° 2θ being observed in most samples. Weak diffraction from α-Si_3N_4 was found in some of the samples. The measured densities of these ceramics were $\sim$1.7 g/cm^3 and are similar to those observed for amorphous boron nitride samples formed from polymeric precursors.[5,7,23,29]

TGA studies of the ceramic conversion of the borazine/**TTS** copolymers over the range 25–1000 °C, Figure 8a, showed the major weight loss of $\sim$50% occurred over the range of 100–350 °C, followed by a more gradual 10% loss continuing up to $\sim$800 °C. TGA/MS analysis of the volatiles during the first weight loss showed an

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(28) It should be noted that the sum of the elemental analyses for each of the 1400 °C **TTS**-based ceramics added to only $\sim$70%. Repeated attempts in several analytical laboratories gave similar results.

(29) See: Beck, J. S.; Albani, C. R.; McGhie, A. R.; Rothman, J. B.; Sneddon, L. G. *Chem. Mater.* **1989**, *1*, 433–438 and references therein.

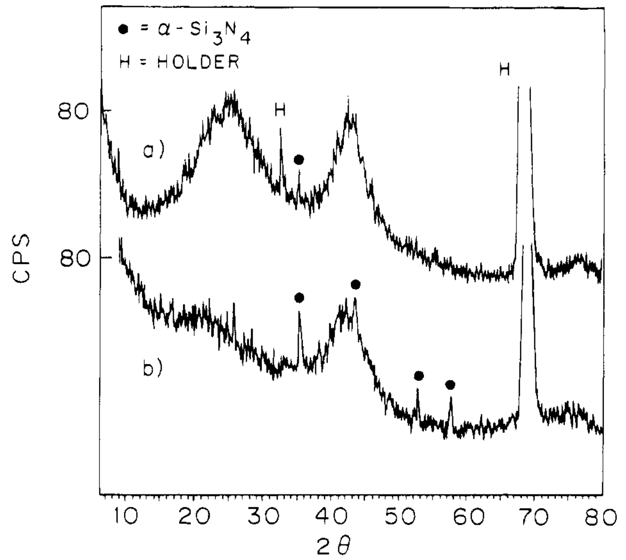

Figure 7. XRD spectra of 1400 °C ceramics derived from (a) **TTS-2** and (b) **HCT-2**.

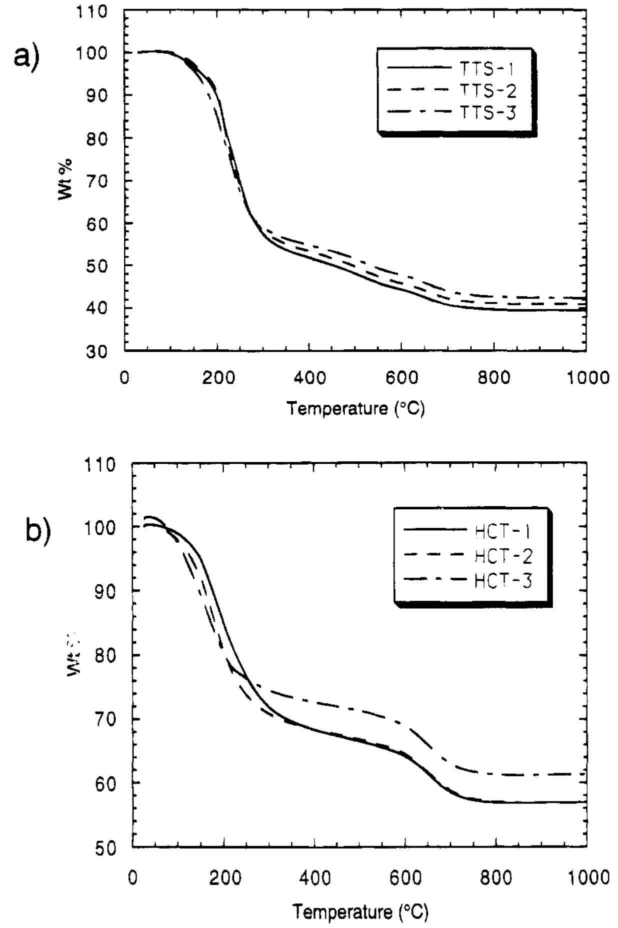

Figure 8. TGA to 1000 °C of the (a) **TTS** copolymers and (b) **HCT** copolymers.

almost continuous series of peaks up to 112 amu, as well as several higher mass envelopes at 126, 131, 138, 147, and 155 amu. The mass spectral analyses of the volatile materials in the 500–800 °C temperature range showed an increase in the fragments with mass 12–17 amu. These masses are most likely methane or ammonia which arise from the homolytic cleavages of the Si–C and Si–N bonds. Funayama,[6d] Legrow,[12c] Seyferth,[30] and Peuckert[31] have previously described similar evolution of methane and ammonia from silazane polymers at comparable temperatures.

If all polymer backbone elements were retained in the ceramic, with loss of only the pendant $-SiMe_3$ groups and hydrogen during ceramic conversion, then a ceramic composite with a $B_{1.00}N_{1.33}Si_{0.33}$ composition would be obtained in a theoretical ceramic yield of 51.6%. Such a material is reasonably close in composition to the **TTS**-based ceramics obtained at 1400 °C. The high retention of backbone elements in the **TTS** ceramic conversion is reasonable, given that their loss would require the cleavage of two or more bonds in the backbone. The facile loss of trimethylsilane has been observed in the ceramic conversions of a variety of silicon preceramic polymers that contain trimethylsilyl groups[32] and the efficiency of this process can account for the low carbon contents of the **TTS** copolymer derived ceramics.

Pyrolysis of the **TTS** copolymers to 1800 °C resulted in a further reduction of the silicon content relative to the 1400 °C chars to produce ceramics of variable silicon contents with compositions ranging from $B_{1.0}N_{0.90}Si_{<0.01}C_{<0.01}$ (**TTS-1** and **TTS-3**) to $B_{1.00}N_{0.91}Si_{0.14}C_{0.07}$ (**TTS-2**, Table 3). The silicon loss may have occurred by evaporation of elemental silicon,[33] and since the rate of silicon evaporation would be dependent on the surface area of the ceramic, this could account for the variable silicon contents (0–14%) of different samples. The presence of carbon in the **TTS-2** sample most likely results from reactions of the ceramic with the carbonaceous atmosphere of the graphite-furnace used in obtaining the high-temperature chars.

Despite their high boron-nitrogen contents, the XRD spectra (Figure 9a) of these materials show no crystalline boron-containing species but rather weak peaks due to small amounts of crystalline β-Si_3N_4, β-SiC, and elemental Si. While conversion of α-Si_3N_4 to β-SiC in the presence of carbon at these temperatures occurs readily,[34,35] the conversion of α-Si_3N_4 to β-Si_3N_4 in the absence of any oxide sintering aids is less facile.[36] The low carbon contents of the ceramics and the inclusion of boron into the ceramic lead to the conversion of α-Si_3N_4 to β-Si_3N_4. Similar results have been found for other boron-containing ceramics derived from the pyrolysis of borazine-modified **HPZ**[10] and polyborosilazanes[6,8b,9,37] under inert atmospheres. Although pure boron nitride would normally be expected to have crystallized by these temperatures, the absence of

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(30) Han, H. N.; Lindquist, D. A.; Haggerty, J. S.; Seyferth, D. *Chem. Mater.* **1992**, *4*, 705–711 and references therein.

(31) Peuckert, M.; Vaahs, T.; Brück, M. *Adv. Mater.* **1990**, *2*, 398–404.

(32) See, for example: Corriu, R. P. J.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Chem Mater.* **1992**, *4*, 711–716.

(33) Vp of Si = 1 mm at 1724 °C. Sax, N. I.; Lewis, R. J. Sr. *Dangerous Properties of Industrial Materials*, 7th ed.; Van Nostrand Reinhold: New York, 1989; p 3024.

(34) (a) Schwark, J. M.; Sullivan, M. J. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 807–812. (b) Schwark, J. M. *Polym. Prepr.* **1991**, *32*, 567–568.

(35) Nickel, K. G.; Hoffman, M. J.; Greil, P.; Petzow, G. *Adv. Ceram. Mater.* **1988**, *3*, 557–562.

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

(37) These results, however, are in contrast to work by Schaible et. al who reported formation of exclusively β-SiC at temperatures up to 1800 °C. Schaible, S.; Riedel, R.; Boese, R.; Werner, E.; Klingebiel, U.; Nieger, M. *Appl. Organomet. Chem.* **1994**, *8*, 491–498.

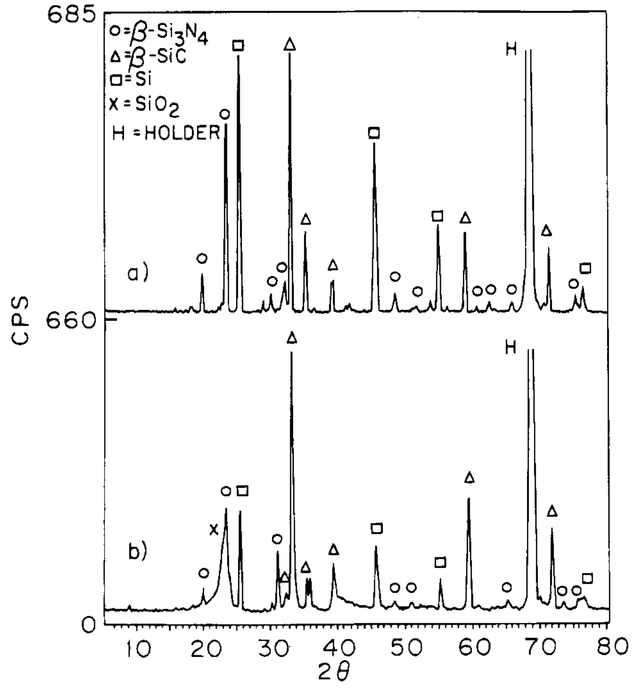

Figure 9. XRD spectra of 1800 °C ceramics derived from (a) **TTS-2** and (b) **HCT-2**.

crystalline BN in these ceramics is likewise consistent with the results from the other boron-containing silazane preceramic systems.[6,7,8b,9,10]

The DRIFT spectra (Figure 10a) of the copolymers heated to 1800 °C show distinct absorptions at both 1460 and 910 cm^{-1} characteristic of boron nitride. Likewise, the off-white appearance of the chars is similar to that of boron nitride, but the observed densities (2.3 g/cm^3) are higher than expected for an amorphous BN ceramic, supporting the presence of silicon in the ceramics.

Borazine/HCT-Derived Ceramics. Pyrolyses under argon of 1–2 g **HCT** copolymer samples gave black SiNCB ceramics in 43–58% ceramic yields (Table 4). Elemental analyses of the **HCT** based ceramics at 1400 °C indicated greater Si and C contents than the ceramics from the **TTS** copolymers. For example, the pyrolysis of **HCT-2** to 1400 °C can be represented by eq 5.

$$\underset{\textbf{HCT-2}}{(B_3N_3H_4)_{1.00}(N)_{1.67}(SiMe_2)_{1.49}(H)_{1.5}} \xrightarrow{1400\ ^\circ\text{C, Ar}} \underset{\textbf{HCT-21}}{B_{1.00}N_{1.40}Si_{0.36}C_{0.23}} \quad (5)$$

The composition of the **HCT** ceramics was also found to vary directly with the borazine contents in the corresponding copolymers. For example, when the borazine/silazane ratio was increased from 1.79 (**HCT-1**) to 2.20 (**HCT-3**), the B/Si ratio in the chars increased from 2.7 to 2.9 and the B/C ratio from 4.4 to 4.8. Increasing ceramic yields with increasing borazine content was observed, most likely due to the ability of unreacted B–H and N–H groups on the borazine units to further crosslink at moderate temperatures and reduce the loss of volatiles. The higher Si and C contents, as well as the increased ceramic yields relative to the **TTS** ceramics, are expected for "cyclomatrix polymers",[38] as loss of $=Si(CH_3)_2$ groups from the polymer requires cleavage of two Si–N bonds. The ceramic yields are also significantly improved over those found by Seyferth[7b] (2%) for copolymers obtained by the reaction of **HCT** with $BH_3{\cdot}SMe_2$.

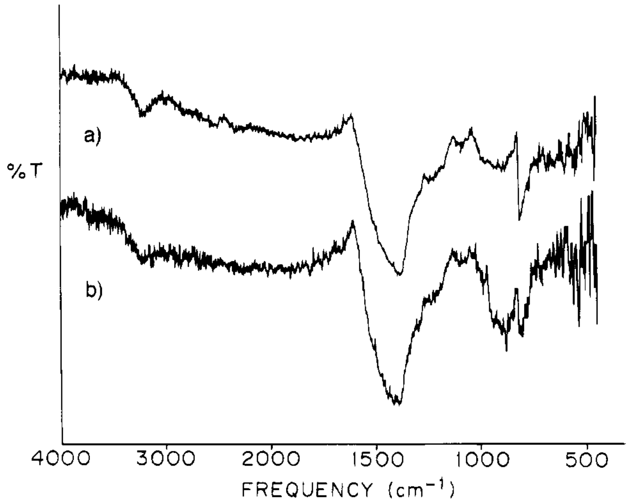

Figure 10. DRIFT spectra of 1800 °C ceramics derived from (a) **TTS-2** and (b) **HCT-2**.

Similar to the **TTS** based ceramics at 1400 °C, DRIFT spectra of the **HCT** ceramics showed absorptions characteristic of boron nitride, but no N–H, C–H, B–H, and Si–H functionalities. XRD studies (Figure 7b) indicate the **HCT** based ceramics also remain amorphous to 1400 °C. Densities of the ceramics pyrolyzed to 1400 °C were ~1.6 g/cm^3.

TGA (Figure 8b) and MS analyses of the ceramic conversion of the **HCT** copolymers over the range 25–1000 °C showed a two step weight loss with the first weight loss of ~20–30%, occurring between 100 and 300 °C. The evolution of hydrogen, as well as numerous fragments below 121 amu, were observed over this range, while the materials evolved during the second weight loss, 500–800 °C (~15%), appeared to be methane and ammonia (12–17 amu). Consistent with the difficulty of cleaving $=Si(CH_3)_2$ groups from the copolymer, no ions corresponding to $(CH_3)_2SiH_2$ were detected in the TGA mass spectra. Furthermore, in contrast to the TGA/MS studies of the **TTS** copolymers, no masses greater than 121 amu were observed in the TGA/mass spectra of the **HCT** copolymers.

The bulk pyrolyses of the **HCT** copolymers to 1800 °C were found to afford dark gray ceramic materials with average densities of ~2.1 g/cm^3. Ceramic yields were again found to increase with increasing borazine contents. The **HCT** based ceramics still contained Si and C to 1800 °C, with both the B/Si and the B/C contents increasing with increasing borazine content in the corresponding copolymer. The DRIFT spectra (Figure 10b) of the copolymers heated to 1800 °C again showed distinct absorptions at both 1460 and 910 cm^{-1} characteristic of boron nitride. The XRD spectra (Figure 9b) of these ceramics showed peaks corresponding to crystalline β-Si_3N_4 and β-SiC and Si. Again, no crystalline boron nitride was observed.

Conclusions

New hybrid polyborazinylsilazane backbone copolymers can be formed in high yields by the copolymeri-

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(38) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*, Prentice Hall: Englewood Cliffs, NJ, 1981; pp 8–9.

zation of silazanes with the parent borazine. Both series of copolymers are proposed to be formed through borazine−B to silazane−N linkages by dehydrocoupling as well as Si−N cleavage reactions. Despite similarities in elemental composition of the two copolymer series, structural differences in the copolymers result in different ceramic compositions upon pyrolysis. While the **HCT** copolymers are converted to SiNCB ceramic materials with retention of Si and C to 1800 °C, the facile loss of $-SiMe_3$ groups from the **TTS** based ceramics yields low carbon content SiNB ceramics at 1400 °C. Further loss of Si produces dense BN-rich ceramics at 1800 °C. Both series of ceramics are amorphous to 1400 °C, but show crystalline phases of β-Si_3N_4 and β-SiC, as well as elemental Si at 1800 °C. All boron-containing species in both ceramic systems are amorphous to 1800 °C.

The differences in the composition of the ceramics derived from these two copolymer systems allow for significantly different potential applications. While the **HCT** based ceramics could serve as effective precursors to high BN content SiNCB ceramic matrix materials, the efficient elimination of both Si and C from the **TTS**-based copolymers suggest they may be better suited as precursors for amorphous BN coatings on carbon and/or ceramic fibers.

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