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Poly(borosilazane) Precursors to Ceramic Nanocomposites

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Single-component polymeric precursors to SiC/Si_3N_4/C/BN and Si_3N_4/BN ceramic nanocomposites were synthesized via hydroboration and dehydrocoupling of vinyl-containing cyclotrisilazanes. The polymer-to-ceramic conversion process was investigated by ^{13}C, ^{29}Si, and ^{11}B solid-state magic-angle spinning (MAS) NMR spectroscopy, FTIR spectroscopy, thermal analysis, elemental analysis, X-ray diffraction (XRD), and transmission electron microscopy. The yields, processibility, and resulting microstructure of the ceramics were dependent on the starting Si/B ratio in the polymers and the atmosphere used for pyrolysis. Thermal conversion of the polymers from 200 to 600 °C involved loss of vinyl functionality, an increase in the amount of B−N environments, and possibly some degradation of the silazane ring structure. Conversion of the polymeric environment to that of mixed-phase ceramic was complete between 600 and 1000 °C; XRD, however, showed the products to be amorphous even after heating to 1600 °C. Heating the N_2 pyrolyzed products to 1800 °C resulted in β-Si_3N_4, β-SiC, and t-BN peaks in the XRD powder patterns, while α-Si_3N_4 and β-Si_3N_4 peaks were observed for the NH_3 pyrolyzed products.

Introduction

In recent years, there has been considerable interest in preparing mixed ceramic phases containing Si, N, C, and B since the addition of elemental B or BN was reported to improve the thermal and mechanical properties of such composites over those of Si_3N_4 or SiC phases alone.[1−6] SiNCB-based ceramics were reported to have reduced crystallinity up to 1800 °C and high thermal stabilities (up to 2000 °C),[7−11] thus providing the possibility of extending the practical upper temperature limit of 1500 °C for Si_3N_4-based ceramics. Schmidt and co-workers have prepared previously a high surface area Si_3N_4 powder by the controlled decomposition of a vinylic polysilane in NH_3[12] and demonstrated that the addition of BN or elemental B significantly reduced the surface area of the powder and suppressed crystallinity.[13] Mixing polymeric precursors to the individual Si_3N_4 and BN ceramic phases prior to pyrolysis gave similar results.[14]

In contrast to studies of polymeric precursors to single-phase BN,[15] specific efforts to prepare SiNCB ceramic from polyborosilazanes have been limited. Polyborosiloxanes were used to prepare mixed SiC and B_4C ceramic phases directly,[16] or as a binder for the sintering of SiC or Si_3N_4 powders.[17,18] SiCB ceramics have been synthesized by reaction of organosilane monomers[19] or polymers[20,21] with boranes, and researchers at NASA Ames Research Center synthesized B-containing organosilicon polymers and pulled fibers which are reportedly superior to NICALON fibers.[22] Funayama and coworkers at Tonen Corporation reported the synthesis of poly(borosilazanes) from reactions between perhydropolysilazane and boron compounds such as $(CH_3O)_3B$

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and $(CH_3NH)_3B$;[23] these precursors were used to prepare amorphous SiBON ceramics.

SiNCB ceramic precursors were prepared recently either by polymerizing Si- and B-containing monomers[7,10,11,24−26] or by reacting organosilicon polymers with boron compounds.[27,28] Both routes have yielded precursors with potential fiber and/or ceramic matrix applications. Seyferth and Plenio reported the synthesis of "borasilazane" precursors to borosilicon nitride.[24] These materials were prepared by the reaction of the adduct $(CH_3)_2S{\cdot}BH_3$ with cyclic silazane oligomers of the type $[CH_3SiHNH]_n$ with an average n of 4 to 5. They report ceramic yields, ranging from 64 to 90%, which depended on the Si/B ratio and the pyrolysis atmosphere. Riedel et al.[10] synthesized a polyorganoborosilazane by hydroboration of a vinylsilane followed by ammonolysis. Pyrolysis to 1000 °C in Ar resulted in a 62% ceramic yield. Baldus et al.[11] reported the synthesis of a polyborosilazane by reaction of $Cl_3SiNHBCl_2$ or $(Cl_3SiNH)_2BCl$ with ammonia or methylamine. Pyrolysis resulted in a SiNB(C) ceramic in which the composition and yield depended on the pyrolysis atmosphere (N_2, Ar, or NH_3). Sneddon et al.[25] reacted borazine with two silazanes $(Me_3SiNH)_3SiH$ (TTS) and $(Me_2SiNH)_3$ (HCT) to produce two different borazine/silazane copolymers. Pyrolysis of the TTS-based polymer at 1400 °C resulted in a boron nitride-rich BNSi ceramic while the HCT-based polymer yielded SiNCB ceramics after pyrolysis to 1800 °C. Sneddon et al.[27] also reported the reaction of hydridopolysilazane (HPZ)[29] with borazine and various monofunctional boranes to produce polymeric precursors to SiNCB ceramics. Fibers were melt spun from a pinacolborane-modified HPZ and pyrolysis to 1200 °C in Ar resulted in SiNCB fiber.

The use of organometallic precursors to prepare ceramic composites can provide control of the resulting microstructure as well as the desired uniform distribution of phases. As part of a broad study of nanocomposites that are generated by pyrolysis of polymeric precursors, a single precursor containing Si, C, N, and B was prepared that would decompose directly into a homogeneous nanocomposite of two or more ceramic phases including BN. This paper reports the preparation of poly(borosilazane) precursors, synthesized by the hydroboration of vinyl-substituted cyclotrisilazane of the formula, $[CH_2{=}CH(CH_3)SiNH]_3$, by the borane adduct $(CH_3)_3N{\cdot}BH_3$, to mixed ceramic phases. The vinyl groups provide a means to incorporate B into the polymer via hydroboration to yield C−B−C linkages, while dehydrocoupling reactions result in N−B−C and N−B−N linkages.

Experimental Methods

1. General. All precursor handling and preparation was done in a N_2-filled glovebox or with Schlenk techniques to minimize oxidation and/or contamination by atmospheric moisture. Nitrogen was purified in-line by deoxygenation over activated copper catalyst and dried over 3 Å molecular sieves. Ammonia was dried in-line over a mixture of flaked KOH and 3 Å molecular sieves and then passed through a commercial purifier (Nanochem 1600 Purification System). Thermal gravimetric analysis (TGA) was performed to 1200 °C in flowing N_2 or NH_3 (0.05−0.1 standard cubic feet per hour (scfh)) using a Perkin-Elmer 7 Series thermal analysis system at a heating rate of 10 °C/min. Transmission infrared spectra were obtained with a Perkin-Elmer 1850 Fourier transform spectrophotometer which was equipped with a Deltech dry air purge assembly. Samples for FTIR analysis were transferred in N_2-filled bags to minimize oxidation/contamination and referenced against KBr blanks. Liquids were examined as smears between KBr plates; solids were diluted with KBr powder and hand-pressed as transparent windows. Elemental analysis of the polymers was performed at Galbraith Laboratories, Inc., Knoxville, TN. Powder X-ray diffraction (XRD) was performed on finely ground samples using a Philips PW1710 automated diffractometer, equipped with a monochromator in the exit beam, using Cu Kα radiation.

Transmission electron microscopy, coupled with selected area diffraction (TEM/SAD), was performed using a JEOL 100CXII electron microscope at 100 keV. Ceramic samples for TEM analysis were prepared by the following steps: (1) a glass slide was coated with a thin film of a dispersion containing a sample of finely ground, pyrolyzed ceramic char in a solution of 1% nitrocellulose in amyl acetate; (2) the dried film was removed by scoring and gently floated on distilled/deionized water; (3) copper TEM grids were distributed on top of the floating film; (4) the film and grids were transferred by wicking onto filter paper and air-dried; and (5) the dried grids were lightly coated with carbon and/or gold to prevent charging by the electron beam during microscopic examination.

2. Polymer Preparation. Poly(borosilazane) (PBS) precursors were prepared by refluxing mixtures of 1,3,5-trimethyl-1′,3′,5′-trivinylcyclotrisilazane (TMTVS) (Petrarch Systems,

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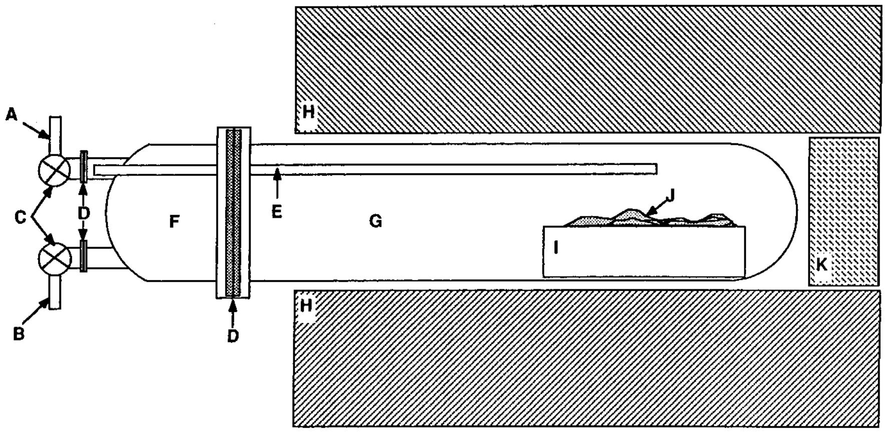

Figure 1. Schematic diagram of the furnace tube used for pyrolysis of PBS precursors to 1000 °C in either NH_3 or N_2 showing (a) Pyrex gas inlet line, (b) Pyrex gas outlet line, (c) Rotaflo valves, (d) elastomer O-ring joints, (e) fused-silica inlet tube, (f) Pyrex end cap, (g) fused-silica furnace tube, (h) furnace cross-section, (i) molybdenum pyrolysis boat, (j) pyrolyzed product, and (k) furnace end plug.

Bristol, PA) with borane−trimethylamine adduct $(CH_3)_3N{\cdot}BH_3$ (Aldrich Chemical Co., Milwaukee, WI) in dry toluene (110 °C) for up to 24 h in a N_2 atmosphere. Reactions were performed using starting Si/B molar ratios of 9 (PBSa), 3 (PBSb), and 1 (PBSc). The borane adduct dissolved completely at temperatures near 80 °C, and gas bubbles evolved with foaming near 100 °C, suggesting that reaction occurred between the TMTVS and the adduct. Provided sufficient toluene was present in the reaction mixture (silazane concentration of about 0.2−0.3 M), the polymer remained in solution throughout the reaction. In all cases, residual solvent was removed by vacuum, with optional gentle heating of the reaction flask to 60 °C. Resulting PBS precursors ranged from a clear, colorless liquid (PBSa) to a colorless, hard, glassy solid (PBSb) to a white powder (PBSc). PBSb and PBSc could not be redissolved once the solvent was removed. All PBS precursors solidified and turned more yellow on prolonged exposure to air. Samples of TMTVS that were refluxed under similar conditions without the addition of borane adduct remained unchanged.

3. Polymer Pyrolysis. Bulk samples of PBS were pyrolyzed in either N_2 or NH_3 to 1000 °C in molybdenum foil boats placed within a gas-tight fused silica tube (Figure 1). The tube's end cap was equipped with inlet and outlet valves which allowed for the flow of gas (1 atm, 0.3−0.5 scfh). Samples were typically heated at rates of 100 °C/h; if desired, samples were held at the soak temperature for up to 10 h. Solid pyrolysis products were collected in the glovebox, ground with a B_4C mortar and pestle, and annealed at temperatures up to 1800 °C for 2−4 h in flowing (0.5−1.0 scfh) dry N_2. To further investigate the polymer-to-ceramic conversion process, portions of PBSb were heated in N_2 to several intermediate temperatures below 1000 °C (based on TGA weight loss regions), retrieved in the glovebox following furnace cooling, and analyzed by ^{13}C, ^{29}Si, and ^{11}B solid-state MAS NMR spectroscopy.

4. NMR Spectroscopy Methods. NMR spectra were obtained at room temperature. ^1H, ^{13}C, ^{11}B, and ^{29}Si solution NMR spectra were acquired in benzene-d_6 on a Varian XL-200 NMR spectrometer; chemical shifts were referenced at 0.00 ppm to tetramethylsilane (TMS) (H, C, and Si) or $BF_3{\cdot}OEt_2$ (B).

High-speed ^{11}B MAS NMR spectroscopy was carried out at 14.0 T on a Bruker AM-600 spectrometer using a high-speed MAS probe built in-house and tuned to 192.55 MHz.[30−32] Samples were spun in 4.5 mm o.d. cylindrical Vespel rotors at a speed of 12−14 kHz. Single pulse excitation using a 90° (3.5 μs) solids pulse was employed.[33,34] A 1.0-s recycle delay was used in all cases. Daba blocks of 1K (3000−5000 scans) were acquired using a 100 kHz spectral width and then zero-filled to 8K before Fourier transformation using 25 Hz line broadening. ^{11}B chemical shifts were referenced to the high-shielding resonance of Borax ($Na_2B_4O_7{\cdot}10\ H_2O$) for which the chemical shift is 2.0 ppm relative to $BF_3{\cdot}OEt_2$.[35] Peak shifts were reported relative to $BF_3{\cdot}OEt_2$ at 0.0 ppm.

^{13}C MAS NMR spectra were acquired on a modified NT-150 spectrometer using cylindrical Kel-F rotors[32] and an MAS probe built in-house and tuned to 37.74 MHz. ^{29}Si MAS spectra were similarly acquired at an observe frequency of 29.81 MHz. Single pulse excitation using a 30° (3.5 μs) pulse was employed for both ^{13}C and ^{29}Si along with high-power proton decoupling during data acquisition. Data blocks of 1K (20000−40000 transients) were acquired, using a 10 kHz spectral width and 10-s recycle delay (^{13}C), or a 15 kHz spectral width and 15-s delay (^{29}Si). The resulting data was zero-filled to 4K and Fourier transformed using 50 Hz line broadening. Carbon and silicon chemical shifts were referenced relative to liquid TMS whose chemical shift was taken to be 0.0 ppm.

Results

1. Solid-State MAS NMR Spectroscopy. The ^{13}C solid-state MAS NMR spectra of PBSb samples pyrolyzed in N_2 are shown in Figure 2. Four major peaks are observed in the as-synthesized polymer (Figure 2a), corresponding to vinyl groups (141.9 and 131.9 ppm),[36,37] methyl and methylene groups attached to the silicon atom (1.9 ppm)[36,38,39] and methylene groups bonded to boron functionality (as $-CH_2-BH-$ bridges) at 12.1 ppm.[37] The chemical shifts of the vinyl peaks and the methyl peak in the polymer precursor are consistent with shifts observed in the solution NMR spectrum of TMTVS; the methylene resonance at 12.1 ppm is not

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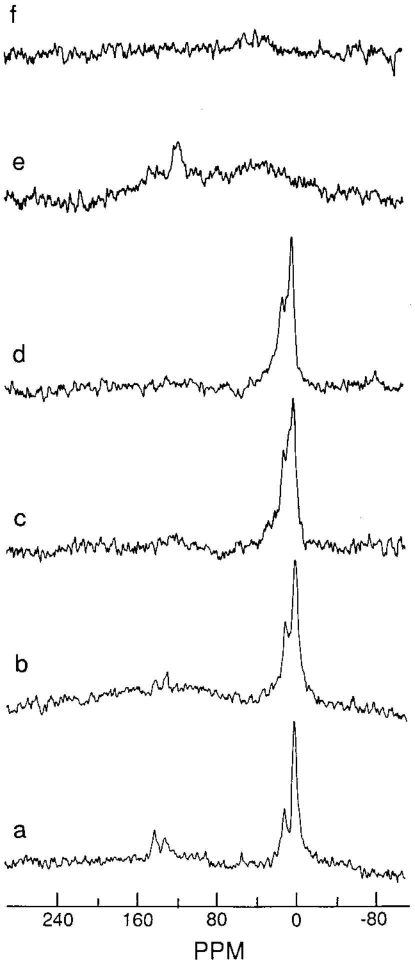

Figure 2. Solid-state ^{13}C MAS NMR spectra (37.74 MHz) of PBSb (Si/B = 3) samples pyrolyzed to various temperatures in N_2: (a) as-synthesized polymer, (b) 220 °C, (c) 350 °C, (d) 600 °C, (e) 1000 °C, and (f) 1600 °C.

observed in the spectrum of unreacted silazane. Upon heating to 220 °C, the intensity of the vinyl peaks at 141.9 and 131.0 ppm decreases and that of the methylene functionality at 12.1 ppm increases (Figure 2b) relative to peaks in the as-synthesized precursor. The methyl peak has shifted slightly to lower shielding at 2.2 ppm. By 350 °C, the peak intensity for the vinyl groups is essentially gone, additional methylene functionality has appeared (new peaks at 20.0 (minor) and 6.5 ppm), and the methyl peak has shifted further to 2.6 ppm. At 600 °C, major peaks are observed at 12.1 ppm (methylene groups) and 7.0 ppm (peak originally at 6.5 ppm); the methyl peak has shifted to 3.2 ppm. Between 600 and 1000 °C, total loss of the methyl/methylene functionality has occurred, and only graphitic carbon is clearly identifiable in the 1000 °C sample at 117.2 ppm.[40] The presence of carbidic carbon is not confirmed in either the 1000 or 1600 °C sample spectra, but this does not preclude the existence of SiC in these samples; others have noted similar difficulty due to the extremely long relaxation time of ^{13}C in SiC.[41–43]

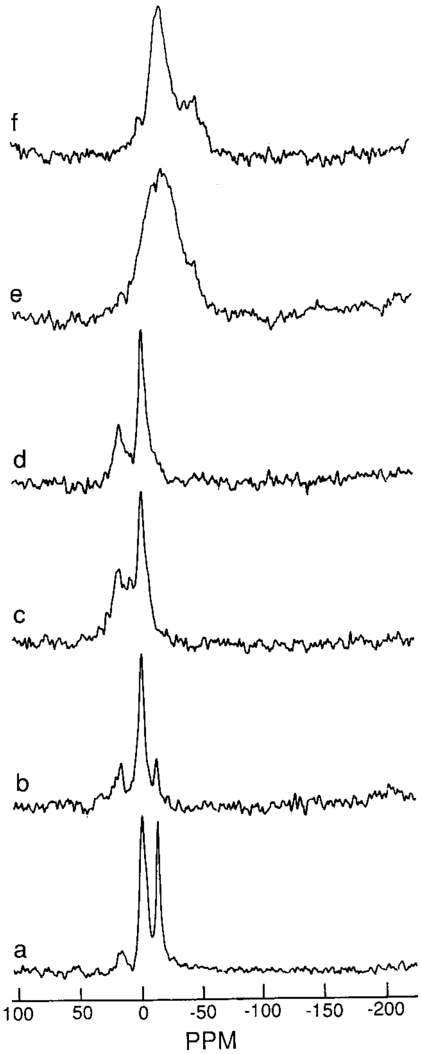

Figure 3. Solid-state ^{29}Si MAS NMR spectra (29.81 MHz) of PBSb (Si/B = 3) samples pyrolyzed to various temperatures in N_2; (a) as-synthesized polymer, (b) 220 °C, (c) 350 °C, (d) 600 °C, (e) 1000 °C, and (f) 1600 °C.

The solid-state ^{29}Si MAS NMR spectra for PBSb samples are shown in Figure 3. The spectrum of as-synthesized PBSb (Figure 3a) shows two major, relatively sharp peaks at −3.2 ppm and −15.9 ppm, and a minor broad peak at 14.8 ppm. The peak at −15.9 ppm corresponds to silicon atoms in intact silazane rings within the polymer, since the identical chemical shift is seen in the solution ^{29}Si NMR spectrum of the starting silazane. The peak at −3.2 ppm indicates saturation of the vinyl groups on the Si atoms in the ring and the peak at 14.8 ppm suggests the formation of B−N bonding with the silazane ring, resulting in a deshielded silicon environment. With heating to 220 °C, the peak at −15.9 ppm decreases in intensity relative to the peak at −3.2, while the peak at 14.8 ppm increases in relative intensity. By 350 °C, the peak at −15.9 ppm is essentially gone, and the peak at 14.8 ppm is broader. A new peak at 5.3 ppm is apparent. The peak at −3.2 ppm has broadened slightly. After heating at 600 °C, only two peaks are observed at 14.8 and −3.7 ppm. At 1000

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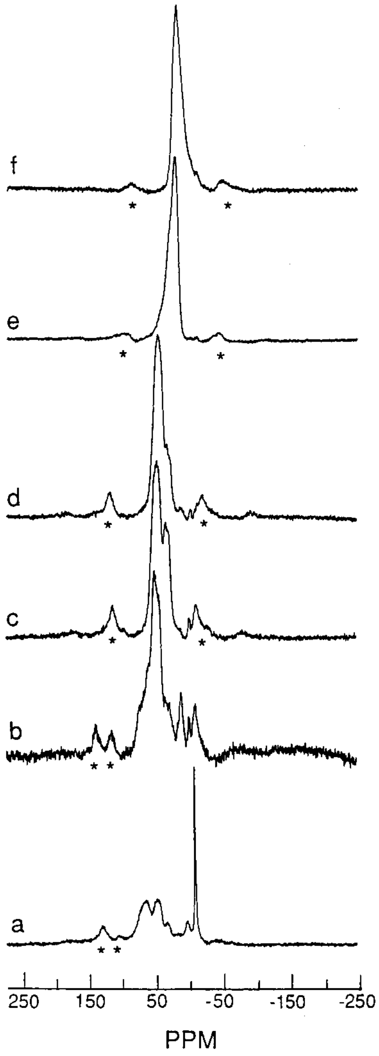

Figure 4. Solid-state ^{11}B MAS NMR spectra (192.5 MHz) of PBSb (Si/B = 3) samples pyrolyzed to various temperatures in N_2: (a) as-synthesized polymer, (b) 220 °C, (c) 350 °C, (d) 600 °C, (e) 1000 °C, and (f) 1600 °C. Note that the spinning sidebands (*) on the left side of the major peak in spectra a and b are apparent, whereas those sidebands on the right side in these spectra are hidden under real peaks and may contribute slightly to the peak intensity.

°C, a single broad peak centered at −20 ppm is observed, indicating the formation of SiC.[44−46] After the sample is annealed at 1600 °C, this peak is resolved into a major peak at −20.1 ppm (SiC[44−46]), a smaller peak near −50 ppm (−46.4 ppm for amorphous Si_3N_4[47]), and a minor peak at −4.2 ppm.

The solid-state ^{11}B MAS NMR spectra are displayed as a function of temperature for the same PBSb samples in Figure 4. The spectrum of the as-synthesized polymer shows several spinning sidebands (*), two broad peaks centered at 64.8 and 47.5 ppm, along with minor peaks at 32.6, 19.0, and −44.0 ppm. A very sharp peak is centered at −8.1 ppm. These peaks do not correspond with the peaks in the solid-state ^{1}H-decoupled ^{11}B NMR spectrum of the starting borane adduct (singlet centered at −15.9 ppm). The peaks found at chemical shifts ranging from 90 to 15 ppm are attributed to trigonally coordinated B atoms while those from 10 to −40 ppm are assigned to tetrahedrally coordinated B atoms.[48] With heating to 220 °C, the spectrum is quite complex; the sharp peak previously at −8.1 ppm shifts to −8.5 ppm, broadens, and significantly decreases in intensity. The major broad peaks increase in intensity, with significant shoulders at 72.4, 60.2, 50.9, 46.0, and 30.0 ppm. New sharp peaks are seen at 12.5 and 1.5 ppm. Further heating to 350 °C simplifies the spectrum, with major peaks centered at 48.3 and 33.5 ppm. A small peak at 1.0 ppm is observed. After the polymer is heated to 600 °C, the major peak is at 48.0 ppm with a shoulder at 36.5 ppm. Additional heating to 1000 °C causes this shoulder to disappear, and the major peak shifts to higher shielding at 25.4 ppm. A very minor peak also occurs at −8.7 ppm. Following annealing at 1600 °C, the major peak sharpens slightly and shifts further to 22.3 ppm, consistent with the formation of turbostratic BN.[49] A minor shoulder is noted at −7.6 ppm.

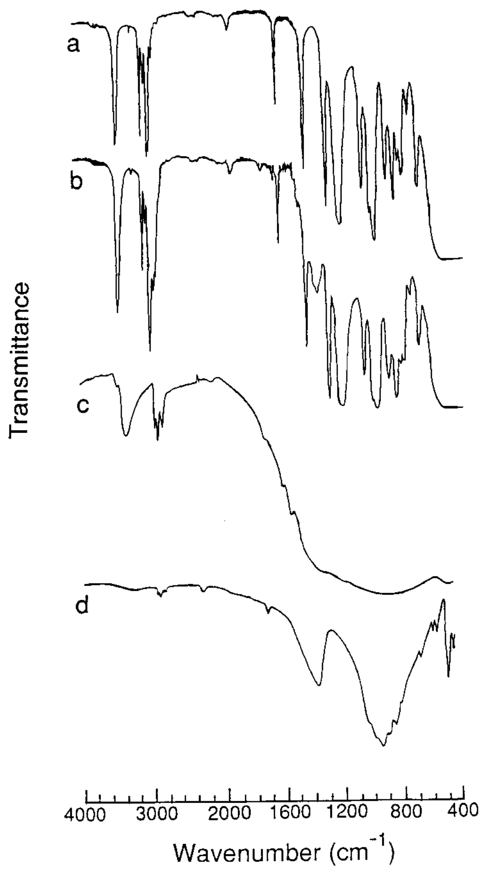

Figure 5. Fourier transformed transmittance infrared spectra of (a) the untreated silazane TMTVS, (b) PBSa, (c) PBSa pyrolyzed to 1000 °C in NH_3, and (d) PBSa further annealed at 1600 °C in N_2.

2. Infrared Spectroscopy. The infrared spectrum of as-synthesized PBSa (Figure 5b) shows loss of intensity for the vinyl stretches (3048 and 1595 cm^{-1})[50]

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Table 1. Elemental Analysis Data of PBS Samples[a]

	% Si	% N	% B	% C	% H	empirical formula
PBSa	29.27 (32.39)	16.4 (16.15)	1.32 (1.39)	40.54 (41.55)	8.67 (8.52)	$Si_{3.0}N_{3.37}B_{0.35}C_{9.72}H_{24.76}$ ($Si_{3.0}N_{3.0}B_{0.33}C_{9.0}H_{22.0}$)
PBSb	28.57 (31.28)	15.02 (15.60)	3.39 (4.01)	41.35 (40.13)	8.97 (8.98)	$Si_{3.0}N_{3.16}B_{0.92}C_{10.15}H_{26.25}$ ($Si_{3.0}N_{3.0}B_{1.0}C_{9.0}H_{24.0}$)
PBSc	23.39 (28.36)	11.28 (14.15)	5.98 (10.92)	33.51 (36.69)	8.38 (10.18)	$Si_{3.0}N_{2.90}B_{1.99}C_{10.05}H_{29.95}$ ($Si_{3.0}N_{3.0}B_{3.0}C_{9.0}H_{30.0}$)

[a] Theoretical % by weight shown in parentheses (see text). Empirical formula normalized to three Si atoms.

Table 2. Elemental Analysis Data of PBS Samples Pyrolyzed to 1000 °C in a Nitrogen Atmosphere

	% Si	% N	% B	% C	empirical formula[a]
PBSa	48.48	17.15	1.80	28.84	$Si_{3.0}N_{2.13}B_{0.29}C_{4.18}$
PBSb	41.90	17.97	4.42	30.03	$Si_{3.0}N_{2.58}B_{0.82}C_{5.03}$
PBSc	34.29	13.68	8.51	28.47	$Si_{3.0}N_{2.40}B_{1.93}C_{5.83}$

[a] Empirical formula normalized to three Si atoms

Table 3. Elemental Analysis Data of PBS Samples Pyrolyzed to 1000 °C in an Ammonia Atmosphere

	% Si	% N	% B	% C	empirical formula[a]
PBSa	44.85	25.60	0.16	0.90	$Si_{3.0}N_{3.43}B_{0.03}C_{0.14}$
PBSb	34.98	24.21	0.85	13.74	$Si_{3.0}N_{4.16}B_{0.19}C_{2.76}$
PBSc	32.21	27.74	5.11	3.95	$Si_{3.0}N_{5.18}B_{1.24}C_{0.86}$

[a] Empirical formula normalized to three Si atoms.

Table 4. Summary of PBS Thermogravimetric Experiments[a]

sample	Si/B starting ratio	atmosphere	char yield (1200 °C)
PBSa	9	nitrogen	55
		ammonia	38
PBSb	3	nitrogen	40
		ammonia	20
PBSc	1	nitrogen	45
		ammonia	25

[a] Heating rate: 10 °C/min. Atmosphere flow rate: 0.05–0.1 scfh.

relative to that of the alkyl C–H stretch (2850–3000 cm^{-1})[50] in the starting silazane (Figure 5a), as well as a new band near 1330 cm^{-1} which suggests the formation of B–N bonding.[23,50] Additionally, however, another new peak at 2104 cm^{-1} is observed in the spectrum of PBSb, which is consistent with an Si–H stretch. No indication of a band characteristic of the Si–O stretch is seen near 1100 cm^{-1}.[51] Following pyrolysis of as-synthesized PBSa to 1000 °C in NH_3, the infrared spectrum shows a broad envelope from 1600 to 500 cm^{-1}. Subsequent heating of this sample to 1600 °C in N_2 sharpens the bands, which are consistent with Si–N[52,53] and B–N stretching vibrations,[53] thus supporting the formation of a Si_3N_4/BN composite.

3. Elemental Analysis. Elemental analysis for PBSa, PBSb, and PBSc are shown in Table 1 along with the theoretical weight percents shown in parentheses. The theoretical weight percents assume that all of the borane added to the silazane reacts by hydroboration and that the trimethylamine of the adduct does not take part in the reaction. The elemental analysis data for PBS samples agree reasonably well with the theoretical weight percents, although all elemental analysis data are low in silicon.

Elemental analysis of the ceramic products produced by pyrolysis of PBSa, PBSb, and PBSc to 1000 °C in N_2 and NH_3 atmospheres are shown in Tables 2 and 3, respectively. Following pyrolysis to 1000 °C in N_2, the relative concentration of nitrogen and boron decreases slightly compared to the silicon content. The reduction of the boron concentration is so small, however, that it is not possible to positively conclude that the difference is significant and it appears that the Si:B ratio in the polymers is maintained even after pyrolysis to 1000 °C in N_2. The carbon content, however, is reduced to nearly half of its original composition (relative to the silicon content), suggesting that the byproducts of the polymer's decomposition to ceramic products are mostly hydrocarbon-based.

Analysis of the ceramic products obtained after pyrolysis in NH_3 to 1000 °C showed an increase in the nitrogen content, a decrease in the boron content, and a substantial decrease in the carbon content, relative to the starting polymers. The reduction in the boron content suggests that NH_3 reacts with the boron to produce volatile amine borane compounds. The reduction of carbon content during pyrolysis of polyvinylsilanes in NH_3 was observed previously.[12]

Because the elemental analyses for the NH_3 pyrolyzed products were low, it is possible that oxygen incorporation occurred. Although the percent oxygen can be estimated by difference, this would most likely be an overestimate of the amount of oxygen actually present. Furthermore, the IR spectra of the ammonia-pyrolyzed products do not support the likelihood of significant oxygen incorporation. Others have reported low elemental analyses for organosilicon ceramic precursors.

4. Thermal Analysis. TGA experiments showed that the as-received silazane, the borane adduct, and the silazane refluxed *without* adduct for several hours in toluene volatilized completely (0% remaining char yield) by ~150 °C in either N_2 or NH_3. Conversely, char yields for the PBS precursors varied with the Si/B ratio and the pyrolysis atmosphere, and ranged from a low of 20% for PBSb in NH_3, to a high of 55% for PBSa in N_2 (Table 4). Samples pyrolyzed in N_2 had char yields from 40 to 55%; those pyrolyzed in NH_3 had lower yields (20–38%). As the Si/B ratio in the starting polymer decreased from 9 to 1 (PBSa, b, and c), the temperature of the initial weight loss in the TGA curve increased.

All bulk samples pyrolyzed to 1000 °C in N_2 were black. The relatively fast heating rate of 10 °C/min in flowing NH_3 did not allow complete removal of excess carbon as noted by the black color of nearly all of the TGA samples. The bulk samples pyrolyzed in NH_3 at ~1.5 °C/min however, were significantly lighter, ranging in color from gray/tan at 1000 °C to gray/white at 1600 °C. A representative TGA for PBSb (Figure 6) shows the following three weight loss regions: 25–200 °C (very minor), 225–350 °C (major), and 350–600 °C (minor).

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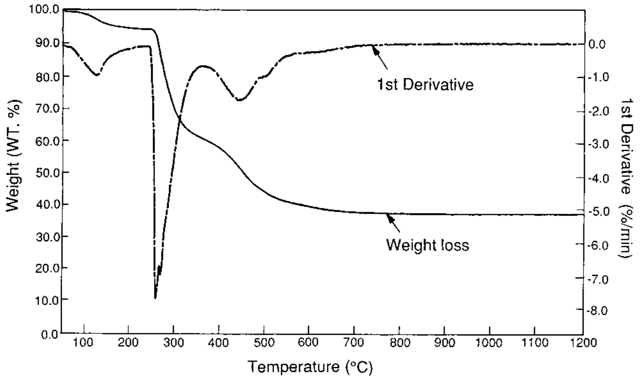

Figure 6. Temperature/weight loss profile (TGA) of PBSb (Si/B = 3) in flowing N_2 (0.05−1.0 scfh); heating rate: 10 °C/min, char yield 40%, sample size 28.702 mg.

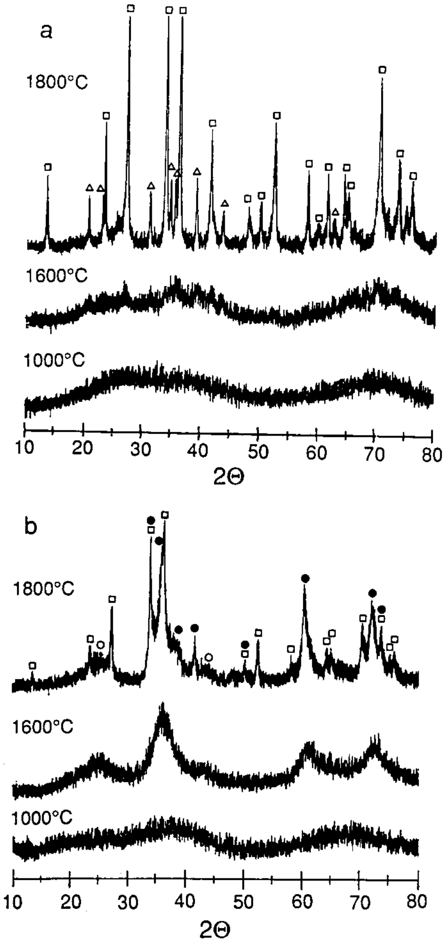

Figure 7. Powder X-ray diffraction patterns of PBSc (Si/B = 1) pyrolyzed in (a) NH_3 and (b) N_2 to 1000, 1600, and 1800 °C: ○, t-BN, ●, β-SiC, △, α-Si_3N_4, and □, β-Si_3N_4.

Bulk samples of PBSb that were heated in N_2 to various intermediate temperatures were solids and ranged in color from white (220 °C and 600 °C), to yellow (350 °C) to black (1000 °C and 1600 °C).

5. X-ray Diffraction. Typical XRD powder patterns are shown in Figure 7 for various PBSc samples. All PBS ceramics heated to 1000 °C in either NH_3 (Figure 7a) or N_2 (Figure 7b) were amorphous by XRD as suggested by broad, featureless powder patterns. Samples pyrolyzed in NH_3 also appeared amorphous by XRD after heating to 1600 °C in N_2 for 4 h. Significant crystallization did not occur in these samples until after heating to 1800 °C for 2 h in N_2, at which point a mixture of α- and β-Si_3N_4 phases was apparent. This result is consistent with Funayama's[23] and Baldus' [11] observations that poly(borosilazanes) remained primarily amorphous even after heating to 1700 °C. Sharp, easily identifiable XRD peaks were not observed for BN in the heated PBS samples, and others have reported the lack of crystallinity for similar precursor-derived turbostratic BN samples.[14,54−56] PBS samples that were pyrolyzed in N_2 were somewhat more crystalline after heating at 1600 °C, and showed peaks indicative of poorly crystalline β-SiC and t-BN. Increased heating to 1800 °C sharpened the XRD peaks, so that β-SiC, β-Si_3N_4, and t-BN phases could be distinguished.

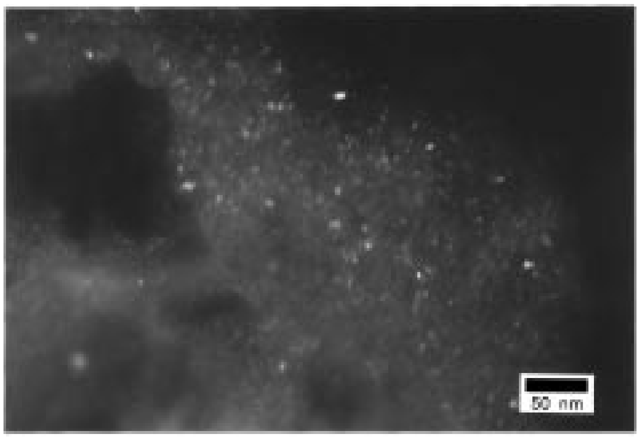

Figure 8. Dark field transmission electron micrograph of PBSa (Si/B = 9) ceramic obtained after pyrolysis in N_2 to 1000 °C, followed by 4 h anneal at 1600 °C in N_2.

6. Transmission Electron Microscopy. TEM analysis of the ceramics heated to 1000 °C showed poorly crystalline, relatively unstructured material. Isolated crystallites were less than 10 Å in size and too unstable in the electron beam for suitable study. NH_3-pyrolyzed PBS samples showed similar features following the 1600 °C anneal, although crystals were more stable and slightly larger. Samples derived from the N_2 pyrolysis and 1600 °C anneal of PBS polymers contained homogeneous distributions of much larger (10−25 Å), stable crystallites. Figure 8 shows a typical TEM micrograph of the PBSa sample, which was pyrolyzed in N_2 prior to a 4-h anneal in N_2 at 1600 °C. The micrograph shows a uniform distribution of SiC and Si_3N_4 nanocrystallites in a noncrystalline matrix. Additional heating to 1800 °C significantly increased the number and size (50−100 Å) of the crystallites, which was consistent with the XRD results.

Discussion

The thermal decomposition of poly(borosilazane) precursors, prepared by the polymerization reaction of vinyl-containing cyclotrisilazanes and a borane adduct,

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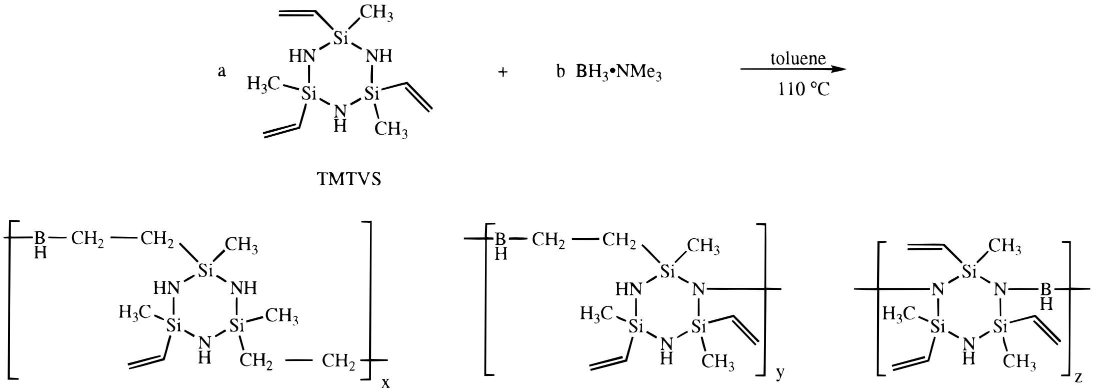
Scheme 1. Proposed Reaction Pathway for the Polymerization of PBS Precursors by Hydroboration and Dehydrocoupling



is an effective route to prepare intimately mixed nanocrystalline ceramic phases containing Si and B. The composition and quantity of these phases depends on the pyrolysis atmosphere, the heating conditions, and the Si/B ratio in the starting precursor. The borane adduct provides a source of B and also induces polymerization, as noted by the gelling of the reflux mixtures (for toluene solutions of silazane greater than 0.3 M), as well as the significant improvement in the char yields of the resulting polymers relative to the starting reagents.

The polymers used in this study were prepared by reacting 1,3,5-trimethyl-1′,3′,5′-trivinylcyclotrisilazane with borane−trimethylamine in a toluene solution (Scheme 1), in initial Si/B ratios of 9:1 (PBSa), 3:1 (PBSb), or 1:1 (PBSc). The borane adduct can react with the cyclotrisilazane by undergoing a hydroboration reaction[57,58a] with the vinyl group (reaction 1) and/or by a dehydrocoupling reaction[59] to form boron−nitrogen bonds (reaction 2).

$$H_2C{=}CHR + BH_3{\cdot}NMe_3 \rightarrow H_2B{-}CH_2{-}CH_2R + NMe_3 \quad (1)$$

$$>N{-}H + BH_3{\cdot}NMe_3 \rightarrow >N{-}BH_2 + H_2 + NMe_3 \quad (2)$$

Polymerization results because the $-BH_2$ group can react further with a vinyl group or an N−H on another ring. The occurrence of these reactions to produce PBSa, PBSb, and/or PBSc is supported by ^{13}C, ^{29}Si, and ^{11}B solution and solid-state MAS NMR spectroscopy, FTIR, and elemental analysis.

The ^{13}C solid-state MAS NMR spectrum (Figure 2a) of PBSb indicates a new methylene resonance at 12.1 ppm from a $-CH_2-B$ environment resulting from hydroboration of the vinyl group. In the ^{29}Si solid-state MAS NMR spectrum (Figure 3a), the new peak at −3.2 ppm indicates saturation of the vinyl groups on the Si atoms in the ring and the new peak at 14.8 ppm suggests the formation of B−N bonding with the silazane ring. New ^{11}B peaks are observed at 64.8, 42.5, 32.6, and −8.1 ppm in the ^{11}B solid-state NMR spectrum of PBSb (Figure 4a) as compared with the starting borane adduct. The ^{11}B peak at 64.8 ppm is consistent with both a terminal H_2BC environment and a ring bridging HBC_2 environment,[48] providing further confirmation of the hydroboration reaction. The remaining peaks in the ^{11}B MAS NMR spectrum provide evidence of B−N bonding in the polymer; the peak at 47.5 ppm is consistent with both HBCN and C_2BN environments[48,60,61], while the small peak at 32.6 ppm suggests a BN_3 and/or a HBN_2 environment.[48,60,61] The sharp peak at −8.1 ppm in the ^{11}B NMR spectra is consistent with tetrahedrally coordinated B, as would be found in an adduct between BH_3 and an amine.[58b,60] Since the peak at −8.1 ppm does not match the solid-state MAS ^{11}B chemical shift of borane−trimethylamine adduct (−15.9 ppm), the peak at −8.1 ppm most likely arises from an adduct with the silazane ring. We speculate that it is this adduct which is the precursor to the trigonal, nitrogen-bonded boron environments observed in the ^{11}B MAS NMR spectrum.

The FTIR spectrum of PBSa (Figure 5b) further supports the hydroboration and dehydrocoupling reactions since the intensity of the vinyl C−H stretches (3048 cm^{-1} and 1595 cm^{-1}), relative to the alkyl C−H stretch (2850−3000 cm^{-1}), is reduced and a new peak at 1330 cm^{-1} indicates the formation of B−N bonding. Additionally, however, another new peak at 2104 cm^{-1} is observed in the spectrum of PBSb, which is consistent with an Si−H stretch. Sneddon et al. also reported observation of an Si−H peak in the IR spectrum of the polymer obtained from reaction of a cyclotrisilazane with borazine.[25] They speculated that ring opening gave rise to the observed peak. The results of the current study also suggest ring opening—both the borane adduct in this work and Sneddon's borazine contain B−H bonds. Because ring opening results in B−N as well as Si−H bond formation, a ring-opening process is consistent with the observed ^{29}Si and ^{11}B solid-state NMR spectral evidence showing the existence of B−N bonds (Figures 3a, 4a).

Elemental analysis data (Table 1) for PBSa and PBSb show the molar ratio of Si:B in the experimental

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(58) *Comprehensive Organometallic Chemistry, The Synthesis, Reactions, and Structures of Organometallic Compounds*; Wilkinson, G., Ed.; Pergamon Press: New York, NY, 1982; Vol. 7, (a) p 163, (b) p 299.

(59) Stock, A. *Hydrides of Boron and Silicon*; Cornell University Press: Ithaca, 1933; p 92.

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empirical formula is in good agreement with the theoretical ratio, which is based on the stoichiometry of the starting materials and assumes that no dehydrocoupling occurred. The boron content of PBSc, however, falls considerably short of the 1:3 silazane-to-borane molar ratio initially added in the reaction. The elemental analysis data show that PBSc is closer to a 1:2 molar ratio. This is not surprising since boron is in excess for polymerization with a 1:3 molar ratio, but with a 1:2 molar ratio the silazane and borane functionalities are matched.

Having matched functionality for PBSc, in theory, means that all N−H, all B−H, and all vinyl groups have reacted. In reality, of course, all of them would not have reacted. The ^{11}B solid-state NMR spectrum of PBSc shows evidence of ring adduct (−8.1 ppm) and the FTIR spectrum of PBSc shows the presence of B−H bonds (spectra not shown). The ^{13}C solid-state NMR spectrum, however, shows that all vinyl groups have reacted.

The polymerization of PBS precursors by hydroboration offers an alternate approach to the formation of Si−N−B polymers by H_2 elimination from an initially formed adduct, as proposed by Seyferth and Plenio.[24] These researchers speculated that adducts, first formed between BH_3 and cyclosilazane oligomers, react with loss of H_2 through a borazane intermediate (with intact silazane rings) to form a borazine via ring-opening of the silazane rings. Our work shows that the predominant pathway for polymerization of PBS precursors is through hydroboration of the vinyl groups, although boron−nitrogen bonding also occurs. Since polymerization can occur through hydroboration as well as through dehydrocoupling, significant cross-linking can occur and polymerization is not hindered by steric interactions of the silazane ring.

The thermal conversion of PBSb in a nitrogen atmosphere to ceramic products was followed using solid-state MAS ^{13}C, ^{29}Si, and ^{11}B NMR spectroscopy. After heating to 220 °C in N_2, ^{13}C, ^{29}Si, and ^{11}B NMR spectroscopy provide evidence that saturation of the vinyl group and B−N bond formation has occurred along with loss of the ring adduct. The ^{13}C NMR spectrum (Figure 2b) shows loss of vinyl functionality at 141.9 and 131.0 ppm and an increase in methylene functionality at 12.1 ppm from additional hydroboration of the vinyl groups, or possibly from thermally induced radical polymerization of the vinyl groups. The ^{29}Si NMR spectrum of the polymer after heating to 220 °C in N_2 (Figure 3b) similarly shows that the number of silazane rings with unreacted vinyl groups (−15.9 ppm) has decreased and the number of silazane rings with saturated vinyl groups (−3.2 ppm) has increased substantially. The ^{29}Si NMR spectrum also shows a slight increase in B−N bonding to the silazane ring (14.8 ppm). The ^{11}B NMR spectrum of the 220 °C PBSb product (Figure 4b) further corroborates that additional hydroboration and B−N bond formation occurred through heating. The ^{11}B spectrum shows a major broad peak centered at 50.9 ppm, which is consistent with both a C_2BN and a HBCN environment. Both of these environments may result from cross-linking of the polymer through additional hydroboration, as well as B−N bonding, but are also consistent with a ring-opening reaction. The other major change that has occurred in the ^{11}B NMR spectrum by heating the sample to 220 °C is the loss of ring adduct (−8.1 ppm). Elimination of H_2 from the adduct, as a result of heating, would produce a covalent B−N bond. The reduction in intensity of the borane−silazane ring adduct is therefore consistent with the subsequent increase of trigonal boron−nitrogen-bonded environments.

The ^{13}C, ^{29}Si, and ^{11}B spectra obtained for PBSb after heating to 350 and 600 °C in N_2 provide evidence that saturation of the vinyl groups is complete by 350 °C and B−N bonds continue to form. In the ^{13}C NMR spectra, the vinyl peaks are no longer observed after heating to 350 °C, and the saturated methylene groups are still present at 12.1 and 3.2 ppm, even after heating to 600 °C. An additional peak appears as a shoulder in the ^{13}C NMR spectra of the 350 and 600 °C products (6.5 and 7.0 ppm, respectively). This peak most likely results from the methylene resonance ($-CH_2-B-N$) that is produced as B−N bonds are formed. The ^{29}Si NMR spectra of the 350 and 600 °C products show that by 350 °C, the original cyclotrisilazane resonance at −15.9 is no longer present. The only silicon environments are those in which the vinyl groups are saturated (−3.2 ppm) and those in which a boron−nitrogen bond has formed with the nitrogen atom in the ring (14.8 ppm). The ^{11}B spectra of the 350 °C and 600 °C products show that the major resonance has shifted slightly upfield from 50.9 ppm in the 220 °C product to 48.0 ppm in the 350 °C and 600 °C products. This region in the ^{11}B spectrum is still consistent with a C_2BN or a HBCN environment. Clearly resolved in the spectrum of the 350 °C product is a major peak at 36.5 ppm, which is consistent with a BN_3 environment or a HBN_2 environment.

The 1:1 molar ratio of silazane ring to borane adduct in PBSb supplies three B−H bonds per three vinyl groups, yet in addition to hydroboration, B−N bond formation occurs as well. The silazane-to-borane ratio in PBSb, however, does not supply enough boron to account for the saturation of all vinyl groups and the B−N bond formation that occurs as a result of heating PBSb in N_2.

The increase in the amount of B−N bonding as PBSb is heated may occur because of the reversibility of hydroboration.[62] Dehydroboration, followed by dehydrogenation, may result in the formation of additional B−N bonds during pyrolysis in N_2. If dehydroboration occurs, the vinyl groups would be restored, but the ^{13}C solid-state NMR spectra show that by 350 °C the vinyl groups are absent. At these temperatures, though, the vinyl groups are likely to undergo a thermally induced, radical polymerization, resulting in saturation of the vinyl groups.

Since the Si:B ratio is largely unchanged in each of the ceramic precursors after pyrolysis in N_2 to 1000 °C (Table 2), dehydroboration in N_2 does not appear to result in the loss of boron, only in the increase in the extent of B−N bonding. Dehydroboration that occurs in an NH_3 atmosphere, however, is likely to enhance the formation of amine boranes, which results in the loss of boron from the pyrolyzed product. Elemental analysis

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results from the pyrolysis in NH_3 (Table 3) support this hypothesis.

Any cross-linking that occurs on heating of PBSa is most likely the result of radical polymerization of the vinyl groups since there are more vinyl groups than B−H bonds. Heating PBSc is likely to result in dehydrocoupling from the ring adduct to produce B−N bonds, but dehydroboration, as well as radical polymerization of the vinyl groups, are likely to occur as well. Additionally, it is possible that dehydrocoupling to produce B−B bonds may occur in PBSc because it has the greatest boron content.

Above 600 °C, the B, Si, and C environments dramatically change from those of an organic/inorganic polymeric material to that of an amorphous or nanocrystalline ceramic. This conversion is most notable in the ^{11}B MAS NMR spectrum, which shows a change from an organoborazane environment (N−B−C bonding) to ceramic boron nitride as evidenced by a shift in the ^{11}B NMR peak position from 48.0 to 25.4 ppm. Following annealing at 1600 °C, the major peak sharpens slightly and shifts further to 22.3 ppm, consistent with the formation of turbostratic BN.[49] Similarly, the ^{29}Si NMR spectra at 1000 and 1600 °C show changes in the Si environment—an upfield shift in peak position from that of an organosilazane, to those of SiC and Si_3N_4 ceramic phases. The ^{13}C NMR spectrum of the 1000 °C product shows that total loss of the methyl/methylene functionality has occurred and only graphitic carbon (117.2 ppm)[40] is clearly identifiable, but by 1600 °C no peaks appear in the ^{13}C spectrum.

XRD shows that the ceramic products are amorphous after heating to 1000 °C in N_2 or NH_3, and are poorly crystalline after heating to 1600 °C. By 1800 °C, β-Si_3N_4, β-SiC, and t-BN are observed for the N_2 pyrolyzed PBSc product while α-Si_3N_4 and β-Si_3N_4 are observed for the NH_3-pyrolyzed PBSc product. TEM/SAD techniques also show that a homogeneous distribution of nanocrystallites is produced by the pyrolysis of PBS precursors. The extremely fine grain size, typically less than 50 Å, is likely due to a combination of the atomic-level mixing of the elements in the starting PBS polymers, the retardation of Si_3N_4 crystallization by boron,[13,14,23] and the inhibition of crystallization by intergranular impurities such as carbon.

Conclusion

Poly(borosilazanes) with varying Si:B ratios can be formed by reaction of trimethyltrivinylcyclotrisilazane and borane−trimethylamine adduct. The Si:B ratios in PBSa and PBSb polymers are consistent with the Si:B ratio of the starting materials; however, the targeted 1:3 ratio in the PBSc polymer is actually closer to 1:2. These cross-linked polymers are formed by hydroboration and dehydrocoupling reactions.

The ceramic products obtained after pyrolysis of the PBS precursors depend on the pyrolysis atmosphere, the heating conditions, and the Si/B ratio in the starting precursor. Solid-state NMR spectroscopy of PBSb, XRD of PBSc, and elemental analysis demonstrates that pyrolysis in N_2 results in a SiC/Si_3N_4/C/BN nanocomposite for PBSb and PBSc, with PBSc having the greater boron content (4.42% vs 8.51%). The ceramic product of PBSa pyrolyzed in N_2 is most likely a SiC/Si_3N_4/C/BN nanocomposite as well, although its boron content is the lowest (1.80%) of the three polyborosilazanes pyrolyzed in N_2.

Because pyrolysis in NH_3 results in a substantial loss of boron, the ceramic products of PBSa (0.16% B) and PBSb (0.85% B) pyrolyzed in NH_3 cannot be confidently, or perhaps even accurately, called nanocomposites. These two ceramic products are best described as silicon nitride with a small amount of boron present, most likely in the form of boron nitride.

The product of PBSc pyrolyzed to 1000 °C in NH_3 contains 5.11% B, but the 1800 °C XRD pattern only shows peaks consistent with α-Si_3N_4 and β-Si_3N_4. It is possible that the boron content was reduced even further after heating to 1800 °C or that the BN was not crystalline. Nevertheless, because of the significant boron content after pyrolysis to 1000 °C in NH_3, the ceramic product is presumed to be a Si_3N_4/BN nanocomposite.

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