Synthesis and Ceramic Conversion Reactions of 9-BBN-Modified Allylhydridopolycarbosilane: A New Single-Source Precursor to Boron-Modified Silicon Carbide

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The design, synthesis, and properties of a new type of poly(borocarbosilane) polymer, 9-borabicyclo[3.3.1]nonane-modified allylhydridopolycarbosilane (AHPCS−9-BBN), that has proven to be an excellent processible single-source precursor to dense silicon carbide ceramics is reported. The polymers were synthesized in high yields by the reaction of allylhydridopolycarbosilane (AHPCS) with 9-borabicyclo[3.3.1]nonane (9-BBN). The spectroscopic data for the AHPCS−9-BBN polymers, along with results of the hydroboration reaction of 9-BBN with the model compound allyldimethylsilane, are consistent with predominantly anti-Markovnikov hydroboration of the polymer allyl groups. The degree of polymer hydroboration was controlled by varying the reactant ratios with the compositions of the modified polymers ranging from $(SiH_2CH_2)_{0.95}(Si(allyl)_2CH_2)_{0.044}(Si(allyl)(CH_2CH_2CH_2\text{-}9\text{-}BBN)CH_2)_{0.006}$ to $(SiH_2CH_2)_{0.95}(Si(allyl)_2CH_2)_{0.012}(Si(allyl)(CH_2CH_2CH_2\text{-}9\text{-}BBN)CH_2)_{0.038}$. The AHPCS−9-BBN polymers are soluble and stable in hydrocarbons and aromatics. Solution properties analysis indicated molecular weight growth and intrinsic viscosity decrease with increasing boron incorporation. Thermal gravimetric analyses showed that the AHPCS−9-BBN polymers have thermal stabilities similar to that of the parent AHPCS polymer and thus maintain the processibility needed for their use as precursors to matrix materials. Bulk pyrolyses at 1600 °C of the AHPCS−9-BBN polymers produced SiCB ceramic chars with boron contents ranging from 0.1 to 0.8% depending upon the degree of polymer modification. XRD studies showed that the 1800 and 2000 °C AHPCS−9-BBN ceramic chars had larger grain sizes than ceramics derived from the parent AHPCS polymer. Most significantly, in agreement with previous studies that have shown that the presence of small amounts of boron (<1%) can enhance SiC sintering, it was found that with increasing temperature the AHPCS−9-BBN-derived ceramics exhibited dramatic increases in their densities compared to those derived from the parent AHPCS.

Introduction

Silicon carbide has many desirable properties, such as high strength and excellent corrosion and temperature stabilities, that have enabled its use in many high-performance applications.[1] Following seminal work by Yajima,[2] extensive efforts have been devoted to the development of new polymeric precursors that can be used to generate silicon carbide materials with enhanced properties and in forms, such as fibers, films, coatings, and matrixes, previously unattainable from powder processing.[3]

The incorporation of <1 wt % boron into SiC ceramics has been shown to significantly improve sintering.[4] This result has spurred interest in the incorporation of boron

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into polymeric precursors to SiC ceramics. In the initial work in this area, boron was introduced by either blending boron-containing materials into polymeric precursors before processing or by treating a processed green ceramic material with a gaseous boron reagent.[5,6] More recently, single-source polymeric precursors to boron-modified silicon carbide have been of interest due to the improved homogeneity of the ceramic, as well as the potentially reduced production costs. A number of different synthetic approaches have been explored to produce such single-source precursors, including (1) polymerization of compounds possessing Si−Cl and B−Cl bonds,[7] (2) incorporating trimethylborate in siloxane polymerization reactions,[8] and (3) hydroboration of unsaturated groups on polysilanes and polysiloxanes.[9,10] We have, in fact, previously used the latter approach to synthesize pinacolborane-modified polyvinylsiloxanes and demonstrated that these PVS−PIN polymers are excellent precursors to both boron-modified SiCO and SiC ceramic fibers.[10] In this paper, we report the synthesis, properties, and ceramic conversion of a new type of preceramic polymeric precursor, 9-borabicyclo[3.3.1]nonane-modified allylhydridopolycarbosilane (AHPCS−9-BBN), and demonstrate that the small amounts of boron incorporated into these polymers and their derived ceramics results in significant increases in ceramic density.

Experimental Section

All synthetic manipulations were carried out using standard high-vacuum or inert atmosphere techniques described by Shriver.[11]

Materials. Allylhydridopolycarbosilane (AHPCS), with a general empirical formula of $(SiH_2CH_2)_{0.95}(Si(allyl)_2CH_2)_{0.05}$, was obtained from Starfire Systems, Inc. and used as received. Allyldimethylsilane was purchased from Gelest Inc., distilled from calcium hydride and stored under nitrogen until use. The 9-borabicylo[3.3.1]nonane (9-BBN) and $BH_3{\cdot}SMe_2$ were purchased from Aldrich Chemical Co. and stored under nitrogen until use. Toluene and diethyl ether were distilled from a sodium benzophenone ketyl prior to use.

Physical Measurements and Instrumentation. The ^1H NMR spectra at 200.1 and 500.4 MHz were obtained on Bruker AF-200 and Bruker AMXII-500 spectrometers, respectively. The ^{13}C NMR spectra at 125.8 MHz were obtained on a Bruker AMXII-500 spectrometer. All chemical shifts were measured relative to internal residual protons from the lock solvents and are referenced to Me_4Si (0.0 ppm). ^{11}B NMR spectra at 64.2 MHz were obtained on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. The ^{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.

Thermal gravimetric analyses of the polymers were obtained on a Texas Instruments SDT 2960 Simultaneous DTA-TGA using an argon gas purge. TGA-MS analyses were performed on the same Texas Instruments DTA-TGA with a Fison Thermolab mass spectral analyzer. Elemental analyses were performed at the University of Pennsylvania's microanalysis facility (molecular species) and the Nesmeyanov Institute of Organoelement Compounds (INEOS), Moscow, Russia (polymers and ceramics).

Ceramic conversions at 1200 and 1600 °C were carried out in mullite pyrolysis tubes using a Lindberg model 54434 furnace equipped with a Eurotherm temperature controller. Argon gas (99.999% pure), passed through a LabClear oxygen scavenger, was used as the purge gas. Pyrolyses at 1800 and 2000 °C were carried out in a carbon resistance Astro furnace. Temperatures were monitored with an Ircon Modeline Plus optical pyrometer. Densities of ceramic materials were measured by flotation in halogenated hydrocarbons. Transmission electron micrographs were obtained on a Phillips 400 TEM.

The X-ray powder diffraction spectra were collected on a Rigaku Geigerflex automated X-ray powder diffractometer using Cu Kα radiation and a graphite monochromator. The average crystallite size of the ceramic powders was estimated by the Scherrer equation.[12]

Molecular Weight Analysis. Molecular weight distribution averages were determined using a model 150-CV size-exclusion chromatograph (SEC) (Waters Chromatography Inc.) equipped with a model PD2040 dual-angle light scattering detector (Precision Detectors Inc.). The SEC was operated at 35 °C with a three-column set of PL gel mixed-bed styrene−divinylbenzene columns (Polymer Laboratories Inc.). The SEC system was equilibrated in anhydrous toluene that served as both the chromatographic mobile phase and the polymer solvent. Polymer solutions were prepared at a nominal concentration of 5 mg/mL and an injection volume of 400 μL was used. The flow rate was determined gravimetrically as 0.9 mL/min.

The signals from the SEC system's differential refractive index (DRI) 90° and 15° light scattering (LS) detectors were acquired using the program PrecisionAcquire (Precision Detectors Inc.), and static light-scattering-based molecular weight distribution averages were calculated using the program Discovery 32 (Precision Detectors Inc.). The light-scattering detector calibration constant and the inter-detector delay volume used in the calculations were determined from the DRI and LS detector responses for a nearly monodisperse polystyrene calibrant (Pressure Chemical Co., $M_p = 90\,000$ g/mol, $M_w/M_n < 1.04$). The specific refractive index increment, dn/dc, of analyzed polymers was determined from the polymer's DRI response following calibration of the DRI detector with a standard polystyrene reference material, SRM 706a (NIST), of known dn/dc (0.11 mL/g) in toluene. Static light-scattering molecular weights were corrected for angular dissymmetry by extrapolation to zero scattering angle using the output of both 15° and 90° light-scattering detectors. Reported molecular weight distribution averages are mean values of duplicate

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Table 1. Synthesis of the AHPCS−9-BBN Polymers

sample	AHPCS (g, mmol allyl)	9-BBN (g, mmol)	reaction time (h)	yield (g, %)
AHPCS−9-BBN-1	9.86, 20.51	0.125, 1.02	18	9.79, 98
AHPCS−9-BBN-2	7.74, 16.10	0.17, 1.39	21	7.52, 95
AHPCS−9-BBN-3	7.72, 16.06	0.27, 2.21	24	7.75, 97
AHPCS−9-BBN-4	8.89, 18.49	0.44, 3.61	18	9.12, 98
AHPCS−9-BBN-5	7.00, 14.56	0.66, 5.41	14	7.35, 96

determinations and were reproducible to within ±5% for M_w and ± 10% for M_n and M_z.

Intrinsic viscosity distribution averages were determined by universal calibration. Molecular weights used to generate the universal calibration curve were obtained from light-scattering molecular weights at each chromatographic data point of the broad molecular weight SRM 706a polystyrene standard. The corresponding intrinsic viscosities for the polystyrene calibrant were obtained using previously reported[13,14] values for Mark−Houwink coefficients of polystyrene in toluene at 34 °C, as shown in eq 1.

$$[\eta]\ (\mathrm{dL/g}) = 9.7 \times 10^{-5}\ M_w^{\ 0.753} \qquad (1)$$

Reaction of Allylhydridopolycarbosilane (AHPCS) and BH_3·SMe_2. Under an inert atmosphere, a two-neck, round-bottom flask equipped with a Teflon stirbar, septum, and high-vacuum stopcock was charged with 0.78 g (corresponding to 3.0 mmol of allyl groups) of AHPCS. The flask was evacuated and 20 mL of dry Et_2O was added. The flask was warmed to 0 °C and backfilled with nitrogen. A 0.3 mL (3.0 mmol) sample of BH_3·SMe_2 was added dropwise via syringe at 0 °C. Some gas evolution was observed. The reaction mixture was allowed to warm to room temperature. After 3 h the polymer became viscous, and after 8 h it had formed a gel.

Reaction of AHPCS and 9-Borabicyclo[3.3.1]nonane (9-BBN). All reactions were carried out according to the following general procedure. Under an inert atmosphere, a two-neck, round-bottom flask equipped with a Teflon stirbar, septum, and high-vacuum stopcock was charged with AHPCS and 9-BBN. Specific reaction conditions are listed in Table 1. After evacuating the flask for 30 min to degas the polymer, approximately 30 mL of dry toluene was added by vacuum transfer. The reaction mixture was stirred for 14−21 h at room temperature and monitored by ^{11}B NMR spectroscopy until the 9-BBN resonance at 28 ppm disappeared.

Upon completion of the reaction, the solvent was removed under vacuum yielding a viscous yellow liquid that was soluble in common organic solvents including aliphatic and aromatic hydrocarbons. Anal. found: AHPCS−9-BBN-1, Si, 55.9%; C, 33.3%; H, 8.5%; B, 0.1%; AHPCS−9-BBN-2, Si, 54.6%; C, 34.7%; H, 8.5%; B, 0.4%; AHPCS−9-BBN-3, Si, 52.0%; C, 29.1%; H, 8.3%; B, 0.3%; AHPCS−9-BBN-4, Si, 53.7%; C, 33.4%; H, 8.9%; B, 0.5%; AHPCS−9-BBN-5, Si, 50.6%; C, 37.3%; H, 9.6%; B, 0.8%. For polymer AHPCS−9-BBN-5: ^{11}B NMR (64.2 MHz, C_6D_6, ppm), 89.0, 57.4; ^1H NMR (200.1 MHz, C_6D_6, ppm), 5.8 (br, allyl), 5.0 (br, allyl), 4.1 (br, $Si\mathit{H}_2CH_2$), 3.8 (br, $Si\mathit{H}_3C$), 1.8 (br, 9-BBN), 1.7 (br, 9-BBN), 1.2 (br, $Si\mathit{CH}_2$-$CH{=}CH_2$), 0.8 (CH_2), −0.1 (br, $SiH_2\mathit{CH}_2$). Similar NMR spectra were recorded for each of the polymers with the intensities of the peaks varying according to the 9-BBN content. The polymer compositions and molecular weights analyses are summarized in Table 2 and 3.

Reaction of Allyldimethylsilane and 9-BBN. A two-neck round-bottom flask equipped with a Teflon stirbar, septum, and high-vacuum stopcock was charged with 0.24 g (1.97 mmol) of 9-BBN. The flask was then moved to a vacuum line where it was evacuated and 3 mL of dry toluene was added by vacuum transfer. The flask was then back-filled with nitrogen and 0.19 g (1.90 mmol) of allyldimethylsilane was added via syringe under nitrogen. According to analysis by ^{11}B NMR, after 17 h of stirring at room temperature no 9-BBN remained. The solvent was vacuum-evaporated to give 0.38 g (1.70 mmol, 88.4% yield) of 1-(9-BBN)-3-[$(CH_3)_2HSi$]C_3H_6. ^{11}B NMR (64.2 MHz, C_6D_6, ppm) 88.9; ^1H NMR (500.4 MHz, C_6D_6, ppm) 4.28 (m, SiH), 1.97 (m, 9-BBN), 1.95 (s, 9-BBN), 1.81 (m, 9-BBN), 1.61 (t, $Si\mathit{CH}_2CH_2CH_2B$), 1.33 (m, $SiCH_2\mathit{CH}_2$-CH_2B), 0.79 (t, $SiCH_2CH_2\mathit{CH}_2B$), 0.21 (s, $SiMe_2$); ^{13}C NMR (125.8 MHz, C_6D_6, ppm) 33.61 (t, 9-BBN), 32.81 (s, 9-BBN), 31.56 (s, CH_2B), 23.79 (t, 9-BBN), 19.96 (t, CH_2), 18.32 (t, $SiCH_2$), −4.10 (q, $SiMe_2$). IR data (NaCl plates, cm^{-1}) 2912 (vs), 2839 (vs), 2110 (vs), 1694 (w), 1580 (w), 1447 (m), 1412 (w), 1366 (m), 1334 (m), 1248 (s), 1205 (w), 1169 (w), 1128 (w), 1112 (w), 1040 (m), 972 (m), 886 (s).

Table 2. AHPCS−9-BBN Polymer Compositions

sample	% modification	% B	polymer composition
AHPCS	0	-	$Si_{1.0}C_{1.25}H_{4.30}\,(O_{0.20})^a$
AHPCS−9-BBN-1	5.0	0.1	$Si_{1.0}C_{1.39}H_{4.21}B_{0.005}\,(O_{0.07})^a$
AHPCS−9-BBN-2	8.6	0.4	$Si_{1.0}C_{1.49}H_{4.33}B_{0.020}\,(O_{0.06})^a$
AHPCS−9-BBN-3	13.8	0.3	$Si_{1.0}C_{1.31}H_{4.47}B_{0.015}\,(O_{0.35})^a$
AHPCS−9-BBN-4	19.5	0.5	$Si_{1.0}C_{1.45}H_{4.64}B_{0.022}\,(O_{0.12})^a$
AHPCS−9-BBN-5	37.2	0.8	$Si_{1.0}C_{1.73}H_{5.31}B_{0.040}\,(O_{0.06})^a$

[a] Estimated maximum oxygen impurity based on differences from total analysis.

Table 3. Solution Properties of Functionalized AHPCS

polymer	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	d*n*/d*c* (mL/g)	$[\eta]_w$ (dL/g)
AHPCS	36,800	170,800	1,007,000	0.052	0.035
AHPCS−9-BBN-1	184,600	549,200	2,424,500	0.046	0.017
AHPCS−9-BBN-2	260,700	820,000	6,106,000	0.028	0.006
AHPCS−9-BBN-3	151,400	473,200	2,333,500	0.041	0.016

Table 4. Polymer to Ceramic Conversions and Compositions to 1600 °C

sample	char yield (%)	grain size[a] (nm)	% B	ceramic composition[b]
AHPCS	58.9	12	-	$Si_{1.0}C_{1.19}\,(O_{0.19})^b$
AHPCS−9-BBN-1	80.7	10	0.1	$Si_{1.0}C_{1.29}B_{0.004}\,(O_{0.07})^b$
AHPCS−9-BBN-2	83.8	9	0.5	$Si_{1.0}C_{1.31}B_{0.022}\,(O_{0.11})^b$
AHPCS−9-BBN-3	79.3	10	0.4	$Si_{1.0}C_{1.19}B_{0.015}\,(O_{0.24})^b$
AHPCS−9-BBN-4	84.9	10	0.7	$Si_{1.0}C_{1.42}B_{0.032}\,(O_{0.10})^b$
AHPCS−9-BBN-5	75.9	23	0.8	$Si_{1.0}C_{1.48}B_{0.034}\,(O_{0.04})^b$

[a] SiC grain size was estimated from the powder X-ray diffraction peaks. [b] Estimated maximum oxygen impurity based on differences from total analysis.

Ceramic Conversion Reactions. For pyrolyses at 1200 and 1600 °C, an aliquot of the polymer was weighed under inert atmosphere into a graphite crucible that was then transferred into a tube furnace flushed with argon. The sample was heated under argon to 1200 or 1600 °C at 10 °C/min and held at temperature for 1 h before cooling to room temperature. Anal. found for 1600 °C chars: AHPCS, Si, 61.8%; C, 31.5%; AHPCS−9-BBN-1, Si, 62.6%; C, 34.6%; B, 0.1%; AHPCS−9-BBN-2, Si, 60.0%; C, 33.6%; B, 0.5%; AHPCS−9-BBN-3, Si, 60.6%; C, 30.8%; B, 0.4%; AHPCS−9-BBN-4, Si, 59.3%; C, 36.0%; B, 0.7%; AHPCS−9-BBN-5, Si, 59.9%; C, 37.9%; B, 0.8%. Additional properties of these ceramics are presented in Table 4.

For pyrolyses at 1800 and 2000 °C, 1600 °C ceramic chars were weighed into a graphite crucible and transferred into an Astro graphite furnace which was then evacuated. The samples were heated under vacuum to 1800 or 2000 °C at 10 °C/min and held at temperature for 1 h before cooling to room temperature. Anal. found for 1800 °C chars: AHPCS, Si, 65.3%; C, 31.1%; AHPCS−9-BBN-2, Si, 61.9%; C, 31.2%; B, 0.3%; AHPCS−9-BBN-3, Si, 60.0%; C, 36.6%; B, 0.3%; AHPCS−9-BBN-5, Si, 53.8%; C, 34.6%; B, 0.7%. Anal. found for 2000 °C chars: AHPCS, Si, 57.7%; C, 39.1%; AHPCS−9-BBN-

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Table 5. Polymer to Ceramic Conversions and Compositions to 1800 °C

sample	char yield (%)	grain size[a] (nm)	% B	ceramic composition[b]	density (g/cm^3)
AHPCS	53.0	93	-	$Si_{1.0}C_{1.11}(O_{0.10})^b$	2.54
AHPCS−9-BBN-2	76.3	93	0.3	$Si_{1.0}C_{1.18}B_{0.010}(O_{0.19})^b$	2.54
AHPCS−9-BBN-3	74.0	119	0.3	$Si_{1.0}C_{1.43}B_{0.012}(O_{0.07})^b$	2.75
AHPCS−9-BBN-5	69.8	119	0.7	$Si_{1.0}C_{1.51}B_{0.032}(O_{0.36})^b$	2.75

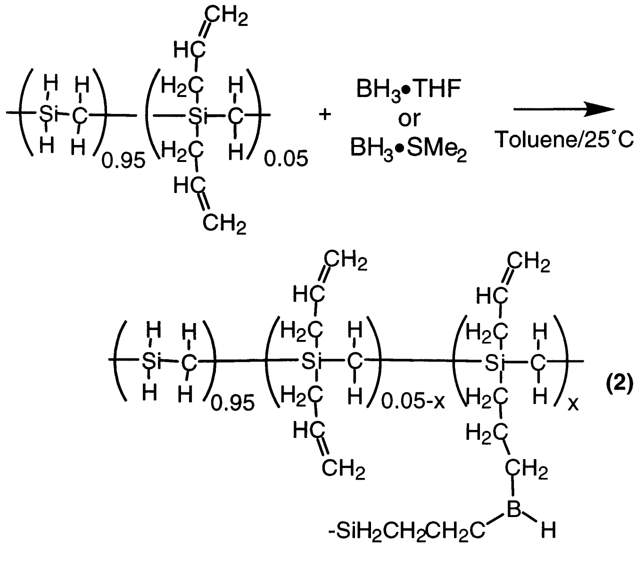
[a] The SiC grain size was estimated from the powder X-ray diffraction peaks. [b] Estimated maximum oxygen impurity based on differences from total analysis.

1, Si, 58.5%; C, 39.6%; B, 0.1%; AHPCS−9-BBN-2, Si, 56.3%; C, 42.4%; B, 0.1%; AHPCS−9-BBN-3, Si, 47.4%; C, 50.6%; B, 0.1%; AHPCS−9-BBN-4, Si, 37.3%; C, 43.4%; B, 0.1%; AHPCS−9-BBN-5, Si, 45.1%; C, 52.3%; B, 0.2%. Additional properties of these ceramics are presented in Tables 5 and 6.

Results and Discussion

Allylhydridopolycarbosilane (AHPCS) is a highly branched polymer with a general empirical formula of $[(H_3SiCH_2)_a(SiH_2CH_2)_b(Si(allyl)_2CH_2)_c(SiH(CH_2)_2)_d(Si(CH_2)_3)_e]$.[15] The polymer converts to SiC upon pyrolysis in high yield, with a C:Si ratio of nearly 1:1, and is a well-established precursor to SiC ceramic matrix materials.[16]

The allyl substituents on the AHPCS polymer provide both a source of latent reactivity for curing of the polymer after forms have been made, and a potential reactive site for polymer modification with borane reagents. Indeed, our initial studies of the hydroboration reactions of the AHPCS allyl groups with $BH_3{\cdot}THF$ and $BH_3{\cdot}SMe_2$ both led to boronated polymers, but these polymers were extensively cross-linked and, therefore, no longer processible (eq 2).

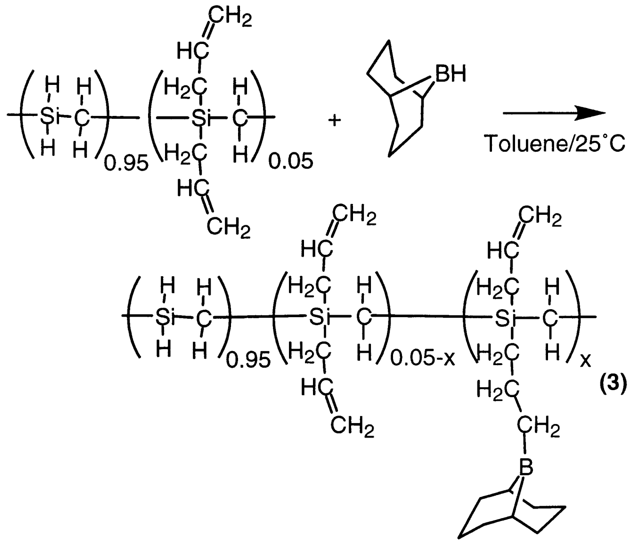

(2)

On the basis of our previous studies of the syntheses and properties of new processible boron-modified polysilazanes[17] and poly(vinylsiloxanes),[10] we expected, however, that the AHPCS polymers modified with a monofunctional hydroboration reagent, such as 9-borabicyclo[3.3.1]nonane (9-BBN),[18,19] would retain their solubilities and processibility. Indeed, such AHPCS−9-BBN polymers were readily obtained by the reaction of AHPCS and 9-BBN in toluene solutions. The degree of polymer substitution was controlled by varying the initial reactant ratio of 9-BBN to polymer−allyl groups, as shown in Table 1. Depending on the amounts of 9-BBN of employed, between 5 and 37% of the available AHPCS−allyl groups were modified to produce AHPCS−9-BBN polymers (Table 2) with compositions ranging from $(SiH_2CH_2)_{0.95}(Si(allyl)_2CH_2)_{0.044}(Si(allyl)(CH_2CH_2CH_2\text{-}9\text{-}BBN)CH_2)_{0.006}$ (AHPCS−9-BBN-1) to $(SiH_2CH_2)_{0.95}(Si(allyl)_2CH_2)_{0.012}(S(allyl)(CH_2CH_2CH_2\text{-}9\text{-}BBN)CH_2)_{0.038}$ (AHPCS−9-BBN-5). These compositions correspond to the incorporation of between 0.1 and 0.8 wt % boron into the polymers. Typical reactions required, according to ^{11}B NMR analysis, ~20 h at room temperature for complete consumption of the 9-BBN. The resulting polymers were moderately air stable and soluble in aliphatic and aromatic hydrocarbons. The more highly substituted polymers were found to be more sensitive to exposure to air and moisture.

Table 6. Polymer to Ceramic Conversions and Compositions to 2000 °C

sample	char yield (%)	grain size[a] (nm)	%B	ceramic composition[b]	density (g/cm^3)
AHPCS	36.1	131	-	$Si_{1.0}C_{1.58}(O_{0.08})^b$	2.56
AHPCS−9-BBN-1	54.1	131	0.1	$Si_{1.0}C_{1.58}B_{0.005}(O_{0.05})^b$	2.83
AHPCS−9-BBN-2	54.5	131	0.1	$Si_{1.0}C_{1.76}B_{0.005}(O_{0.04})^b$	2.87
AHPCS−9-BBN-3	40.8	171	0.1	$Si_{1.0}C_{2.50}B_{0.005}(O_{0.08})^b$	2.93
AHPCS−9-BBN-4	45.3	209	0.1	$Si_{1.0}C_{2.72}B_{0.008}(O_{0.90})^b$	2.87
AHPCS−9-BBN-5	37.8	272	0.2	$Si_{1.0}C_{2.71}B_{0.010}(O_{0.10})^b$	2.98

[a] SiC grain size was estimated from the X-ray powder diffraction peaks. [b] Estimated maximum oxygen impurity based on differences from total analysis.


(3)

The spectroscopic data obtained for the AHPCS−9-BBN polymers strongly support the structure shown in

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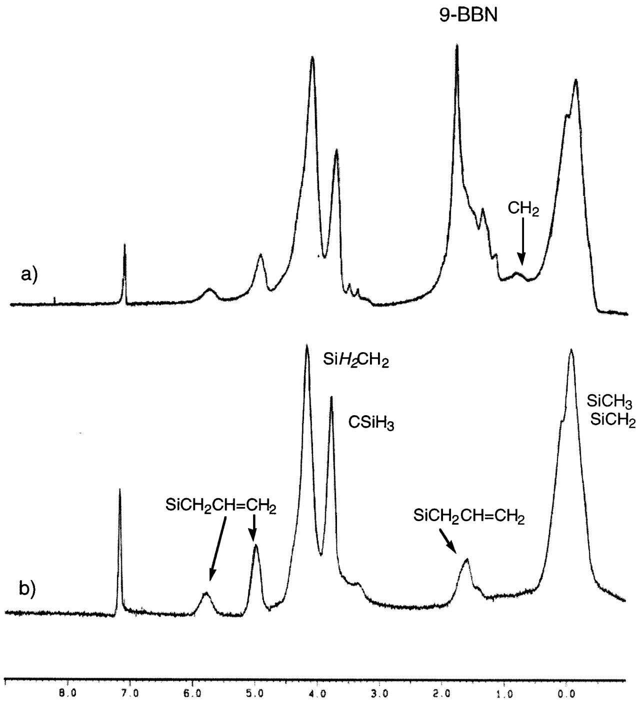
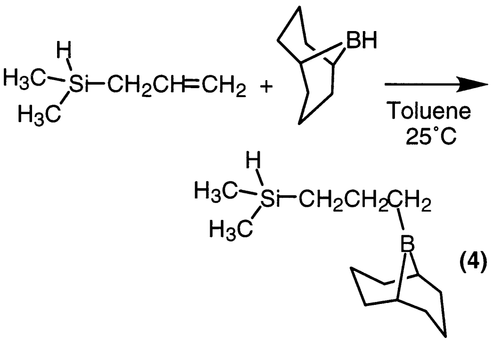


Figure 1. ^{1}H NMR spectra of (a) AHCPS−9-BBN-5 and (b) AHPCS.

eq 3 resulting from the allyl-hydroboration. Thus, the FTIR spectra showed a decreasing intensity of the allyl carbon−carbon double bond stretching frequency (~1620 cm^{-1}) with increasing polymer modification. Likewise, as can be seen in the example in Figure 1, when compared to the spectrum obtained from AHPCS, the ^{1}H NMR spectra of the AHPCS−9-BBN polymers showed, in addition to the 9-BBN resonances (1.2−1.8 ppm), a decrease in the ratio of the integrated intensities of the allyl−proton resonances (5.8 and 5.0 ppm) relative to the Si−H resonances (4.2 and 3.8 ppm). In all cases, these ratios correlated well with both the initial reactant ratios and the degree of modification of the final product that was established by elemental analysis. The AHPCS−9-BBN ^{1}H NMR spectra are also consistent with those obtained from the 1-(9-BBN)-3-[$(CH_3)_2HSi$]C_3H_6 product that is obtained from the reaction of 9-BBN with allyldimethylsilane (eq 4). In agreement with the established[18,19,20] regioselectivity of 9-BBN and borane, these spectra indicate predominately anti-Markovnikov addition with the 9-BBN unit added to the terminal carbon.

Likewise, the AHPCS−9-BBN polymers and 1-(9-BBN)-3-[$(CH_3)_2HSi$]C_3H_6 each exhibit a singlet resonance in their ^{11}B NMR spectra at similar chemical shifts (88 and 88.9 ppm, respectively) that can be assigned to the 9-BBN boron added to their allyl-groups. The AHPCS−9-BBN polymers also exhibited a resonance signal with lower intensity (5%) at 58.1 ppm. The chemical shift of this peak suggests the presence of borate esters, which could be produced by reaction of the 9-BBN with either small amounts of Si−OH groups present in the polymer network or with atmospheric O_2.[19]



(4)

Solution Properties. Representative multiple-detector size exclusion chromatography results for AHPCS and AHPCS−9-BBN polymers are shown in Figure 2. Bimodal differential refractive index (DRI) chromatograms were found for the AHPCS and AHPCS−9-BBN (1−3) polymers, as shown in Figure 3. Intensity normalization using the major component peak maximum at 28.3 min revealed only small differences in the intensity of the minor component at 23.5 min for the parent AHPCS polymer, AHPCS−9-BBN-1, and AHPCS−9-BBN-3 (solid lines in Figure 3). For AHPCS−9-BBN-2 (open circles in Figure 3), the intensity of the 23.5 min peak was significantly reduced relative to the mode peak at 28.3 nm.

In contrast to the relatively small differences among the DRI chromatograms for the polymers other than the AHPCS−9-BBN-2 functionalized material, significant chromatographic differences were apparent in the corresponding 90° light scattering (LS) chromatograms as shown in Figure 4. Functionalization produced intense modes that eluted earlier than the parent AHPCS polymer's peak at 22 min. Given the intensity of the light scattering from these components, very high molecular weight species were produced during functionalization. However, the weak DRI response at elution times corresponding to these components (Figure 3) indicate that they represent less than 5 to 10 wt % of each polymer's mass.

The qualitative picture of functionalization producing a small fraction of very high molecular weight species was confirmed quantitatively by calculations of light-scattering-based molecular weight distribution averages summarized in Table 3. Molecular weight distribution averages for 9-BBN-modified polymers were consistently higher than the molecular weights for the AHPCS parent polymer. The presence of a very high molecular weight, early-eluting fraction in each functionalized polymer was indicated by the *z*-average molecular weight, which exceeded 2×10^6 g/mol for all of these polymers. The apparent trend toward higher molecular weight with increasing 9-BBN content was reversed in the case of the AHPCS−9-BBN-1 and AHPCS−9-BBN-3 polymers. The reason for this deviation was not apparent in the SEC/LS data. However, the change in polymer composition due to functionalization was verified by the consistent decrease in the specific refractive index increment, d*n*/d*c*, (Table 3) as a function of increasing boron level.

As seen in Table 3, the weight-average intrinsic viscosity ($[\eta]_w$) for functionalized polymers also showed a dependence on the degree of functionalization. The initial value of $[\eta]_w = 0.035$ dL/g for the AHPCS parent

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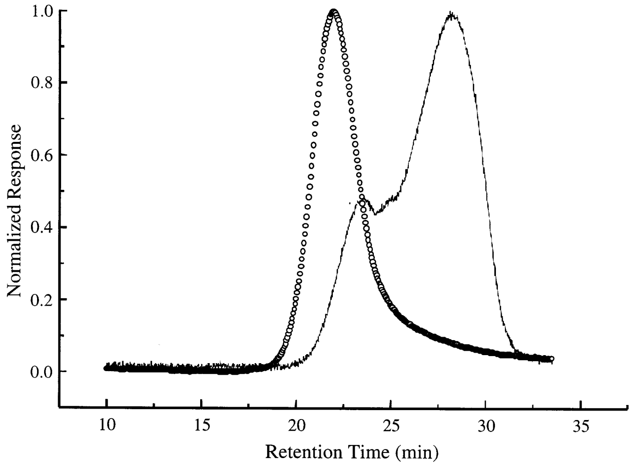

Figure 2. Normalized size-exclusion/light scattering chromatograms for AHPCS. The differential refractive index (DRI) chromatogram is given by the solid line and the 90° light-scattering chromatogram is represented by open circles.

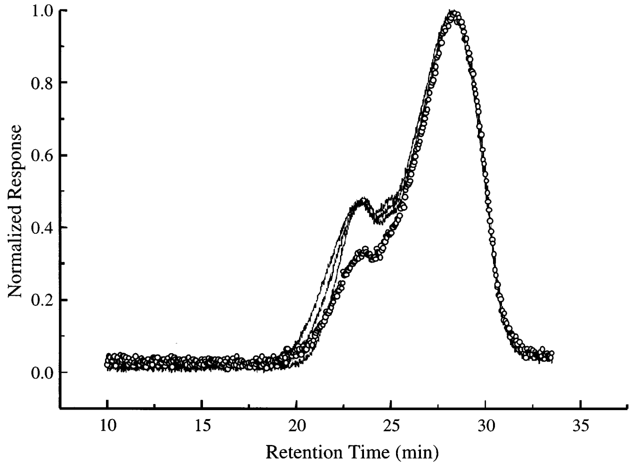

Figure 3. Normalized DRI chromatograms for AHPCS, AHPCS−9-BBN-1, AHPCS−9-BBN-3 (solid lines), and AHPCS−9-BBN-2 (open circles).

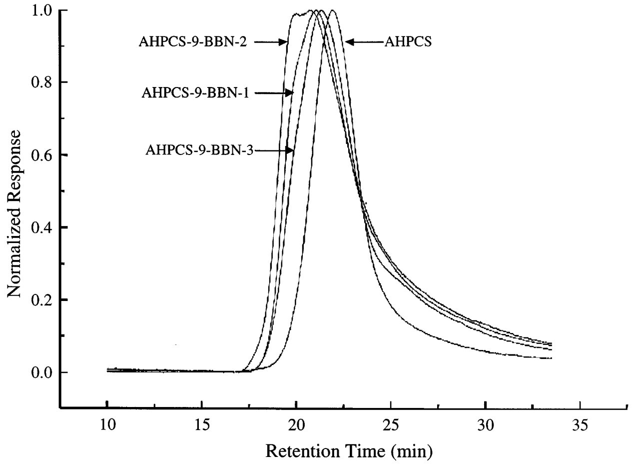

Figure 4. Normalized 90° LS chromatograms for AHPCS and AHPCS−9-BBN series.

polymer decreased to a minimum value of 0.006 dL/g for the AHPCS−9-BBN-2 polymer. The trend noted in $[\eta]_w$ as a function of the degree of modification is the product of large molecular weight increases producing little corresponding increase in polymer hydrodynamic volume. The combined molecular weight and intrinsic viscosity results suggest that the small amount of a very high molecular weight fraction apparent in all 9-BBN-modified polymers corresponds to a low level of partially cross-linked, soluble AHPCS chains, possibly microgelled AHPCS.

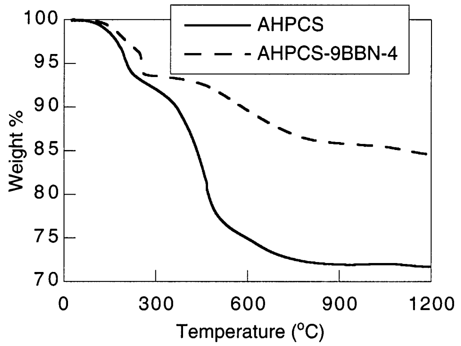

Figure 5. TGA studies to 1300 °C under argon of the AHPCS and AHPCS−9-BBN-4.

Ceramic Conversion Reactions. When pyrolyzed to 1000 °C under argon, AHPCS has been shown to give high yields of amorphous SiC with only a slight excess of carbon. Crystalline β-SiC is produced with minimal mass loss on further heating to 1600 °C.[15a,16a] The TGA study in Figure 5 of the thermal decomposition of AHPCS showed that there was an ~10% weight loss by 300 °C, an additional 13% weight loss by 500 °C, and then a final 6% weight loss between 500 and 800 °C. Weight loss between 800 and 1300 °C was negligible. The TGA trace in Figure 5 for AHPCS−9-BBN-4 is typical of that found for all of the AHPCS−9-BBN polymers. Each showed the onset of thermal decomposition at a temperature (~100 °C) similar to that of AHPCS with a weight loss of 10% by 300 °C. TGA/MS studies (Figure 6a and c) of the AHPCS and AHPCS−9-BBN polymers showed that for both types of polymers the mass losses up to 300 °C are due to H_2 (mass 2, not shown due to scaling of graph), CH_4 (mass 16), and CH_3-CH_3 (mass 30). As shown in Figure 5, over the 300−500 °C region, AHPCS−9-BBN materials exhibited significantly lower weight losses (~2%) than those observed for AHPCS (13%). At temperatures between 500 and 1300 °C the 7% weight loss of the AHPCS−9-BBN materials closely matched that observed for AHPCS. In this high-temperature region (500−1300 °C), the TGA/MS studies (Figure 6) showed that both types of materials had similar gas evolution of H_2 and CH_4. Over the 300−500 °C range, however, significant differences were observed. The AHPCS polymer showed loss of CH_3CH_3, SiH_4 (mass 32), and CH_3SiH_3 (mass 46) fragments (Figure 6a and b), whereas the AHPCS−9-BBN materials did not exhibit significant loss of CH_3-CH_3, nor any loss of SiH_4 and CH_3SiH_3 fragments (Figure 6c). Thus, as a result of the decreased mass lost in the 300−500 °C region, the AHPCS−9-BBN-derived ceramics had higher char yields at 1300 °C (82−85%) compared to that of AHPCS (73%). Regardless of the boron contents, the AHPCS−9-BBN polymers showed little variation in their decomposition profiles and exhibited similar char yields at 1300 °C.

Interrante's earlier studies of hydridopolycarbosilane showed that reactions of the polymer SiH_2 groups help to cross-link the polymer during ceramic conversion, and thereby suppress the loss of polymer fragments, via a process involving the formation of silylene intermediates followed by interchain insertion and rearrangement reactions.[15a,21] The TGA and TGA/MS results discussed above suggest that, in addition to polymer cross-linking which may result from similar reactions of the backbone Si−H groups in AHPCS−9-BBN, reactions of the 9-BBN substituents provide additional polymer cross-linking mechanisms which further reduce polymer fragmentation and volatilization. Possible mechanisms may include Si−H−B bridges between the alkylboranes and Si−H functionalities resulting in intramolecular cross-linking.[22] Additionally, alkyl-substituted 9-BBN compounds and polymers have been shown to decompose, especially in the presence of oxygen, via radical pathways.[23,24] The production and subsequent reactions of such radical species during the thermal decomposition of the AHPCS−9-BBN polymers could, in fact, provide another efficient cross-linking pathway for these polymers.

Bulk Pyrolyses of AHPCS and AHPCS−9-BBN Materials. Bulk pyrolyses of AHPCS−9-BBN samples to 1200 and 1600 °C were carried out under ultrahigh purity argon. Elemental analyses of the 1600 °C chars of the AHPCS−9-BBN-derived ceramics showed boron contents ranging from 0.1% in AHPCS−9-BBN-1 to 0.8% in AHPCS−9-BBN-5 (Table 4), with the relative amounts increasing according to the degree of polymer modification (Table 2). Consistent with the higher char yields observed for the AHPCS−9-BBN-derived materials, their C:Si ratios were slightly higher than those of the AHPCS-derived material.

As can be seen in Tables 5 and 6, the 1800 and 2000 °C AHPC−9-BBN-derived ceramics also showed both higher char yields and somewhat greater C:Si ratios than those found for the comparable AHPCS chars. Boron was again retained in all AHPCS−9-BBN chars, but significant decreases were found in the 2000 °C chars, with all of the materials containing between 0.1 and 0.2% boron regardless of the amount initially in the polymer precursor.

Powder X-ray diffraction studies of the ceramic materials showed that although the 1200 °C chars of all the AHPCS and AHPCS−9-BBN samples were amorphous, the 1600, 1800, and 2000 °C chars contained crystalline β-SiC. As estimated by application of the Scherrer equation on the 111 peak (35.6° 2θ), the 1600 °C chars showed little variation in the average crystallite size as a result of boron-modification, yielding average crystallite sizes of ~10−12 nm (Table 4). At 1800 °C, however, the average crystallite sizes of the AHPCS−9-BBN-3 and AHPCS−9-BBN-5 materials increased to 120 nm, compared to the 93 nm grain size of AHPCS ceramic (Table 5). At 2000 °C, all chars showed, in addition to the β-SiC diffraction peaks, graphite peaks at 26.5° 2θ with relative intensities that appeared to increase with increasing 9-BBN-modification (Figure 7).

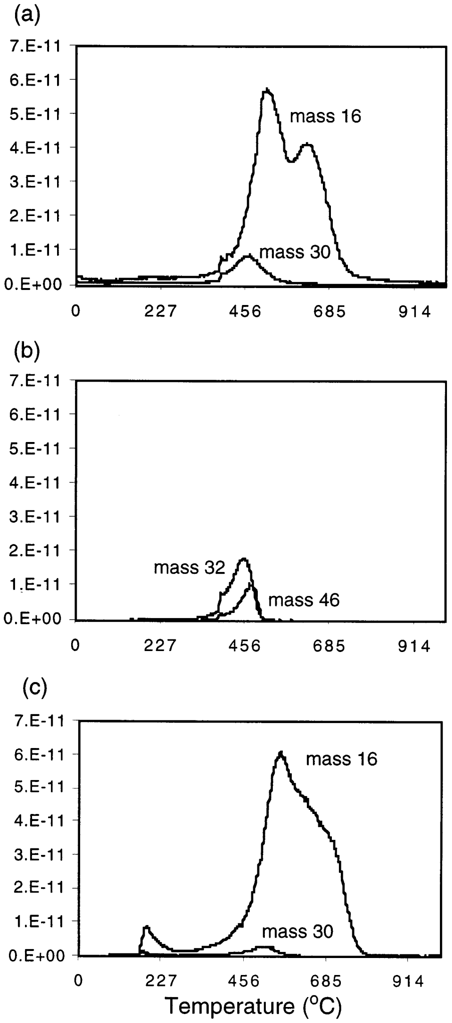

Figure 6. TGA/MS traces for AHPCS (a, b) and AHPCS−9-BBN-5 (c).

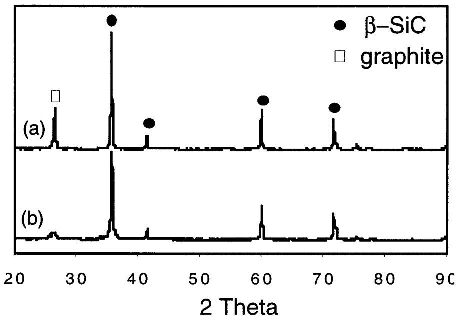

Figure 7. Powder X-ray diffraction results of 2000 °C chars of (a) AHPCS−9-BBN-5 and (b) AHPCS.

However, it should be noted that the 2000 °C pyrolyses, unlike the lower temperature ceramic conversion reactions, were carried out in a graphite crucible and furnace, so carbon contamination from these sources is also possible. The 2000 °C chars exhibited significant differences in their degree of grain growth (Table 6) with the AHPCS char having an average grain size of 131 nm, compared to the 171−272 nm grain sizes observed for the AHPCS−9-BBN ceramics. Although a quantitative study was not undertaken, TEM studies also confirmed the increased grain sizes of the AHPCS−9-BBN materials compared to those of the AHPCS materials.

In agreement with previous studies that have shown that the presence of small amounts of boron (<1%) can

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enhance SiC sintering,[4] it was found that with increasing temperature the AHPCS−9-BBN-derived ceramics exhibited dramatic increases in their densities compared to those derived from the parent AHPCS. As shown in Table 5, the 1600 °C ceramic chars of the AHPCS and AHPCS−9-BBN materials had densities that were similar and in the range of 2.50 ± 0.05 g/cm^3, but the 1800 °C ceramics derived from the AHPCS−9-BBN-3 and AHPCS−9-BBN-5 chars were found to be significantly denser (2.75 ± 0.05 g/cm^3) than those derived from AHPCS (2.54 ± 0.05 g/cm^3). This difference is especially significant because the sintering of SiC does not normally occur until much higher temperatures (1950−2100 °C).[4]

The density differences between the AHPCS- and AHPCS−9-BBN-derived ceramics became even more pronounced at higher temperatures. Thus, as seen in Table 6, the 2000 °C chars of all of the AHPCS−9-BBN ceramics had markedly increased densities, ranging from 2.83 to 2.98 ± 0.05 g/cm^3, compared to that of the AHPCS-derived ceramic, which was 2.56 ± 0.05 g/cm^3. Because the boron contents in the samples ranged from only 0.1−0.2%, it is impossible to establish a correlation between the density and the amount of boron present in the ceramics, but it is perhaps significant that the polymer with the highest boron content, AHPCS−9-BBN-5, produced the highest density ceramic (2.98 g/cm^3). The way in which boron affects the sintering of silicon carbide is complex and still not well understood. Originally, boron was thought to play a thermodynamic role in promoting the sintering of SiC,[4a,d] but, more recently, it has been proposed that boron increases sintering by suppressing the surface diffusion mechanism of solid-state mass transport while supporting bulk diffusion.[4b,c,i,j] Regardless of the mechanism, it is clear in the AHPCS−9-BBN-derived ceramics that the inclusion of a small amount of boron has significantly improved their densification compared to that of the AHPCS-derived ceramic. Thus, in the case of the 2000 °C AHPCS−9-BBN-5 ceramic, the presence of only 0.2% boron resulted in densification to within 92% of theoretical (SiC $d = 3.21$ g/cm^3), whereas the corresponding ceramic obtained from the parent AHPCS ceramic was only 80% dense.

The work described in this paper has demonstrated that boron-modification of the AHPCS polymer can be efficiently achieved by hydroboration reactions of the polymer allyl groups. Furthermore, the use of the monofunctional borane 9-BBN preserves the polymer solubility and processibility. Boron modification of the polymer was found to have two significant effects: First, the ceramic yields of the AHPCS−9-BBN polymers were significantly higher than that of AHPCS due to an additional cross-linking reaction involving the 9-BBN substituent. Second, and more importantly, as a result of the presence of only a small amount of boron, there was a significant increase in the density of the 1800 °C and 2000 °C ceramics derived from the 9-BBN modified materials compared to those of the unmodified ceramics. Thus, in conclusion, AHPCS−9-BBN polymers have proven to be easily synthesized, processible, single-source precursors to silicon carbide ceramics which have significantly higher densities than that which can be obtained from the parent AHPCS precursor.

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