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Synthesis and Ceramic Conversion Reactions of Pinacolborane- and Diethylborazine-Modified Poly(vinylsiloxane)s. The Development of a Processable Single-Source Polymeric Precursor to Boron-Modified Silicon Carbide

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The design, synthesis, and properties of two new types of poly(borosiloxane) preceramic polymers, diethylborazine- (PVS−DEB) and pinacolborane-modified (PVS−PIN) poly(vinylsiloxane)s, are reported. The polymers are synthesized in excellent yields by the $RhH(CO)(PPh_3)_3$-catalyzed reactions of poly(vinylsiloxane) (PVS) with either diethylborazine (DEB−H) or pinacolborane (PIN−H). The spectroscopic data for the polymers, along with results of the $RhH(CO)(PPh_3)_3$-catalyzed hydroboration reactions of diethylborazine and pinacolborane with the model compound vinyltris(trimethylsiloxy)silane, are consistent with predominately anti-Markovnikov hydroboration of the polymer vinyl groups by the boranes. The degree of polymer hydroboration is simply controlled by varying the reactant ratios with the compositions of the PVS−DEB polymer ranging from $(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(ViMe_2SiO_{0.5})_{0.17}(DEB(CH_2)_2Me_2SiO_{0.5})_{0.04}$ to $(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(DEB(CH_2)_2Me_2SiO_{0.5})_{0.21}$ and those of the PVS−PIN polymers from $(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(ViMe_2SiO_{0.5})_{0.18}(PIN(CH_2)_2Me_2SiO_{0.5})_{0.03}$ to $(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(PIN(CH_2)_2Me_2SiO_{0.5})_{0.21}$. The borane-modified polymers are soluble and stable in ethers, acetone, methylene chloride, benzene, and pentane. Molecular weight analyses using SEC with refractive index, viscometry, and light-scattering triple detection show significant differences in hydrodynamic volume, molecular weight, radius of gyration, and conformation, which indicate that the PVS−PIN and PVS−DEB polymers adopt a more branched and spherical structure compared to the unmodified PVS. Bulk pyrolysis of the modified resins produced SiOCB ceramic chars with boron contents ranging from 0.3 to 0.7% depending upon the percentage of polymer modification. XRD and TEM studies of the 1800 °C chars of PVS and PVS−PIN showed significant differences in the degree of grain growth and distribution with the boron-modified char showing both a smaller average crystallite size and a more narrow size range. The PVS−PIN polymers were found to be excellent melt-processable, single-source precursors to small-diameter SiOCB fibers.

Introduction

Silicon-based ceramics including silicon carbide, silicon oxycarbide, and silicon nitrides have many desirable properties, such as high strength and resistance to corrosion and temperature, that have enabled their use in many high-performance applications.[3] Since the pioneering work of Yajima,[4] extensive efforts have been devoted to the development of polymeric precursors that can be used to generate these ceramics in fiber form.[5] Precursor-derived small-diameter ceramic fibers are now widely used in continuous-fiber ceramic matrix composites (CMC) intended for operation at high temperatures in both oxidative and inert atmospheres.[6] Most of the current, commercial silicon oxycarbide fibers, such as the NICALON and TYRANNO fibers, are

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still based on polycarbosilane precursors.[7,8] However, the use of a siloxane resin as an alternative precursor could potentially reduce the fiber cost because of the simplicity of the material production process.[9,10] In this regard, Su et al. recently reported the formation of SiOC and SiC ceramic fibers by melt-spinning of either vinyl ether or vinyl-functionalized siloxane resins, followed by a rapid chemical or radiation curing process.[11] Crystalline SiC fiber was obtained upon pyrolysis of the cured green fibers at 1200 °C and densification at 1800 °C.

The introduction of a boron sintering aid by either blending boron-containing materials into the resin before processing or by treating the processed green fibers with a gaseous boron reagent has yielded significant improvements in fiber performance. For example, Dow Corning's Sylramic crystalline SiC fiber is produced by doping silicon oxycarbide fiber with a boron source at high temperature, followed by a densification process.[12] The added boron promotes sintering to yield high-strength, dense crystalline SiC fibers. However, because of the complexity in the fiber-spinning, curing, and subsequent high-temperature conversion process, the production costs for these fibers are generally high, which effectively limit their applications.

The use of a single-source poly(borosiloxane), in which the boron sintering aid is a polymer component, could both reduce the expense of the fibers and yield more homogeneous ceramics. Zank has previously developed poly(borosiloxane)s, with a typical composition of $(PhSiO_{1.5})_{0.60}(BO_{1.5})_{0.2}(ViMe_2SiO_{0.5})_{0.2}$, by incorporating trimethylborate in the siloxane polymerization reactions.[13] Pyrolysis studies then demonstrated that these polymers yielded silicon carbide sintered to high densities. Although these poly(borosiloxane)s may be useful for matrix materials, they were found to be too unstable for the more demanding processing conditions required for the melt-spinning of fibers. Thus, there has been a clear need for new types of processable poly(borosiloxane)s.

In this paper, we report the design, synthesis, and properties of two new types of poly(borosiloxane) polymers, the diethylborazine- and pinacolborane-modified poly(vinylsiloxane)s. Most importantly, these studies have demonstrated that one of these new polymers, the pinacolborane-poly(vinylsiloxane), is the first melt-processable poly(borosiloxane) that can be used as a single-source precursor to small-diameter SiOCB fibers.

Experimental Section

All synthetic manipulations were carried out using standard high-vacuum or inert atmosphere techniques described by Shriver.[14]

Materials. Poly(vinylsiloxane) (PVS), with an empirical formula $(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(ViMe_2SiO_{0.5})_{0.21}$, was obtained from the Advanced Ceramics Program at Dow Corning Corporation and used as received. Vinyltris(trimethylsiloxy)silane was purchased from Gelest Inc. and stored under nitrogen until use. $RhH(CO)(PPh_3)_3$ and $Cp_2Ti(CO)_2$ were purchased from Pressure Chemical Co. and Strem, respectively, and used as received. Cp_2TiMe_2 was prepared according to literature procedure.[15] Pinacolborane (PIN−H) was purchased from Aldrich Chemical Co. and stored under nitrogen until use. Diethylborazine (DEB−H) was prepared as previously described.[16] Diethyl ether was distilled from sodium benzophenone ketyl prior to use. Methylene chloride was dried over molecular sieves.

Physical Measurements and Instrumentation. Infrared spectra were obtained on a Perkin-Elmer System 2000 FTIR. Diffuse-reflectance IR spectra (DRIFT) of the polymers were obtained on the same Perkin-Elmer instrument equipped with a diffuse-reflectance attachment. The ^1H NMR spectra at 200.1 and 500.4 MHz were obtained on Bruker AF-200 and Bruker AMXII-500 spectrometers, respectively. ^{13}C NMR spectra at 100.4 and 125.8 MHz were obtained on Varian VXR400S and Bruker AMXII-500 spectrometers, respectively. 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. The ^{29}Si NMR spectra at 39.7 and 79.5 MHz were obtained on Bruker AF-200 and Varian VXR400S spectrometers in $CDCl_3$ solutions using a 5 mm switchable probe or a 16 mm Si-free probe, respectively. $Cr(acac)_3$ was added to the samples for the ^{29}Si NMR spectra to ensure quantitative acquisition. The ^{29}Si chemical shifts are referenced to Me_4Si (0.0 ppm) with a negative sign indicating an upfield shift.

GC/MS analyses of the molecular species were performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 5970 Series Mass Selective Detector. Thermogravimetric analyses were obtained on a Texas Instruments SDT 2960 Simultaneous DTA-TGA using an argon gas purge. Thermal mechanical analyses (TMA) were recorded on a Dupont 940 Thermomechanical Analyzer in a nitrogen atmosphere. Elemental analyses were performed at the University of Pennsylvania microanalysis facility (molecular species), the Nesmeyanov Institute of Organoelement Compounds (INEOS), Moscow, Russia (polymers and ceramics), or the Dow Corning analytical facility (ceramics).

Size exclusion chromatography (SEC) with multiangle laser light scattering (MALLS), viscometry, and refractive index (RI) triple detection was performed on a Waters 2690 Alliance System using two Polymer Laboratories Plgel Mixed-D (300 × 7.5 mm, 5 mm, 200−200000 Da exclusion limit) styrene−divinylbenzene columns preceded by a Polymer Laboratories Plgel guard column (50 × 7.5 mm, 5 mm). The columns were thermostated at 30 °C. The detection system consisted of a Viscotek T60 Multiple Detector (Viscosity and Right Angle Light Scattering) and a Viscotek model 125 Differential Laser Refractometer. HPLC-grade THF (Fisher Scientific) was the eluant. The flow rate was 1 mL/min, and a 100 μL injection volume was used (samples typically at 1 wt/vol % concentration).

Ceramic conversions at 1200 °C were carried out in a Lindberg model 54434 furnace equipped with Eurotherm

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Table 1. Metal-Catalyzed Reactions of DEB−H and PIN−H with Vinyltris(trimethylsiloxy)Silane (1)

reactants (mmol)	catalyst (mmol, mol %)[a]	reaction time (h)	% conversion	total turnovers	isolated yield (mmol, %)	product ratios
1/DEB−H						**2**:**3**
1.39/1.46	0.069, 4.7[b]	65	93	18	1.2, 86	34:1
0.53/1.54	0.082, 5.3[b]	9	100	6	0.45, 85	35:1
1/PIN−H						**4**:**5**
1.92/1.95	0.017, 0.9[b]	8	100	108	1.83, 95	1[e]
0.81/0.86	0.005, 0.6[b]	7	99	157	0.79, 97	1[e]
2.67/2.58	0.005, 0.2[b]	57	73	400	2.0, 78	1[e]
0.59/3.44	0.006, 0.2[b]	8	97	93	0.54, 93	1[e]
4.09/4.46	0.060, 1.3[c]	4	95	57	3.4, 82	7.6:1
1.74/1.80	0.034, 1.9[d]	8	94	44	1.5, 86	2.1:1

[a] Mol % of catalyst relative to the borane. [b] $RhH(CO)(PPh_3)_3$. [c] $Cp_2Ti(CO)_2$. [d] Cp_2TiMe_2. [e] **4** was the only product.

Table 2. Synthesis of the PVS−DEB and PVS−PIN Polymers

polymer	PVS/ borane (g)	catalyst (mmol, mol %)[a]	reaction time (h)	turn-overs	yield (g, %)
PVS−DEB-1	4.93/0.35	0.050, 2.1	16	51	3.9, 74
PVS−DEB-2	5.05/0.88	0.130, 2.0	11	49	3.0, 51
PVS−DEB-3	5.00/1.79	0.260, 2.0	>140	50	2.0, 53
PVS−PIN-1	6.01/0.21	0.021, 1.3	2.0	78	5.82, 94
PVS−PIN-2	6.00/0.41	0.033, 1.0	1.0	97	5.90, 92
PVS−PIN-3	6.01/1.05	0.086, 1.1	0.75	95	2.84, 83
PVS−PIN-4	22.12/7.41	0.290, 0.5	120	167	24.68, 84

[a] Mol % catalyst relative to the borane.

temperature controllers. Pyrolysis at 1800 °C was carried out in a carbon resistance Astro furnace. Carbon, hydrogen, and nitrogen analyses of the ceramics were carried out at Dow Corning on a Perkin-Elmer 2400 Analyzer. The silicon and boron analyses were performed by first digesting the ceramic samples with sodium peroxide using the Leco FX-503 flux fusion device. The fused samples were then analyzed using the Perkin-Elmer Optima 3000 DV-ICP (inductively coupled plasma). Densities were measured by flotation in halogenated hydrocarbons. Transmission electron micrographs were obtained on a Phillips 400 TEM. Scanning electron micrographs were obtained on a Cambridge T-300.

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.[17]

Reaction of Vinyltris(trimethylsiloxy)silane (1) and DEB−H: Synthesis of 1-(DEB)-1-[$(Me_3SiO)_3Si]C_2H_4$ (2) and 1-(DEB)-2-[$(Me_3SiO)_3Si]C_2H_4$ (3). A two-neck flask equipped with a Teflon stir bar, septum, and high-vacuum stopcock was charged with 0.063 g (0.068 mmol) of $RhH(CO)(PPh_3)_3$. The flask was then moved to a vacuum line and evacuated, and 3 mL of dry CH_2Cl_2 was added by vacuum transfer. At room temperature, the catalyst dissolved to produce a clear, yellow solution. Both 0.45 g (1.4 mmol) of **1** and 0.20 g (1.5 mmol) of DEB−H were added separately via syringe under nitrogen. According to ^{11}B NMR spectra, after 65 h of stirring at room temperature no DEB−H remained. The mixture was then filtered through a 2 in. plug containing layers of Florisil and neutral, decolorizing carbon. The solvent was then vacuum-evaporated from the filtrate to give 0.56 g (1.2 mmol, 80% yield) of a mixture of 1-(DEB)-1-[$(Me_3SiO)_3Si]C_2H_4$ (**2**) and 1-(DEB)-2-[$(Me_3SiO)_3Si]C_2H_4$ (**3**) in a 1:35 ratio determined by GC/MS and ^1H NMR analysis. For the isomeric mixture: ^{11}B NMR (64.2 MHz, C_6D_6, ppm) 36.0; ^1H NMR (500.4 MHz, C_6D_6, ppm) 4.75 (br, N*H*), 1.21 (m), 1.08 (t), 0.95 (q), 0.83 (t, DEB $CH_2C\mathit{H}_3$), 0.71 (q, DEB, $C\mathit{H}_2CH_3$), 0.35 ($OSiMe_3$, 1,1-isomer), 0.32 ($OSiMe_3$, 1,2-isomer); ^{13}C NMR (125.8 MHz, C_6D_6, ppm, 25 °C) 66.31, 15.76, 9.29 (DEB), 9.12 (DEB), 7.84, 7.43, 2.12 ($OSiMe_3$); ^{29}Si NMR (39.7 MHz, C_6D_6/$Cr(acac)_3$, ppm) 7.7 (s, $OSiMe_3$), −62.6 (s, $SiCH_2CH_2DEB$).

Reaction of 1 and PIN−H: Synthesis of 1-(PIN)-2-[$(Me_3SiO)_3Si]C_2H_4$ (4). Analogous to the previous reaction, 0.62 g (1.9 mmol) of **1** and 0.25 g (2.0 mmol) of PIN−H were reacted in 3 mL of CH_2Cl_2 in the presence of 0.015 g (0.017 mmol) of $RhH(CO)(PPh_3)_3$. The reaction mixture was monitored via ^{11}B NMR spectroscopy and stirred at room temperature until completion at 8 h. The reaction mixture was then washed with deionized water and extracted with Et_2O. The ether extract was then filtered through a Florisil and carbon plug, and the solvent was vacuum-evaporated. To separate any remaining catalyst from the modified siloxane, the product was distilled under vacuum at 100 °C, to give 0.84 g (1.9 mmol, 96% yield) of clear, colorless liquid. Analysis by GC/MS confirmed a single product. For 1-(PIN)-2-[$(Me_3SiO)_3Si]C_2H_4$ (**4**): ^{11}B NMR (64.2 MHz, C_6D_6, ppm) 34.2; ^1H NMR (500.4 MHz, C_6D_6, ppm) 1.13 (m, CH_2), 1.06 (s, PIN, CH_3), 0.87 (m, CH_2), 0.18 (s, $OSiMe_3$); ^{13}C NMR (125.8 MHz, Tol-*d*^{8}, ppm, −78 °C) 82.84 (s, PIN, C), 24.91 (q, PIN, CH_3), 7.71 (t, CH_2), 4.40 (s, CH_2PIN), 1.97 (q, $OSiMe_3$); ^{29}Si NMR (39.7 MHz, C_6D_6/$Cr(acac)_3$, ppm) 7.6 (s, $OSiMe_3$), −63.6 (s, $SiCH_2CH_2PIN$). IR data (NaCl plate) 2959 (s), 2901 (m), 1370 (s), 1321 (s), 1251 (s), 1149, (s), 1055 (vs), 967 (w), 843 (vs), 713 (m), 687 (m) cm^{-1}. Anal. Found: C, 44.4%; H, 9.9%. Calcd: C, 45.0%; H, 9.6%.

Reaction of 1 and PIN−H Catalyzed by $Cp_2Ti(CO)_2$ or Cp_2TiMe_2. Using methods similar to those described above, 1.32 g (4.1 mmol) of **1** and 0.57 g (4.5 mmol) of PIN−H were reacted in the presence of 0.014 g (0.060 mmol) of $Cp_2Ti(CO)_2$ at 45 °C for 4 h. Workup yielded 1.57 g (3.5 mmol, 82% yield) of a mixture of **1**, 1-(PIN)-1-[$(Me_3SiO)_3Si]C_2H_4$ (**5**) , and 1-(PIN)-2-[$(Me_3SiO)_3Si]C_2H_4$ (**4**) in a 0.5:1:7.6 ratio determined by GC/MS and ^1H NMR analysis.

An analogous reaction of 0.24 g (0.74 mmol) of **1** and 0.14 g (1.0 mmol) of PIN−H in Et_2O solution in the presence of 0.0073 g (0.035 mmol) of Cp_2TiMe_2 at 50 °C for 16 h yielded 0.33 g (0.6 mmol, 87% yield) of a mixture of **1**, 1-(PIN)-1-[$(Me_3SiO)_3Si]C_2H_4$ (**5**), and 1-(PIN-2-[$(Me_3SiO)_3Si]C_2H_4$ (**4**) in a 0.2:1:2 ratio determined by GC/MS and ^1H NMR analysis.

Reaction of Poly(vinylsiloxane) (PVS) and Diethylborazine (DEB−H). All reactions were carried out by charging PVS and $RhH(CO)(PPh_3)_3$, in the proportions indicated in Table 2, into a two-neck flask equipped with a Teflon stir bar, septum, and high-vacuum stopcock. The flask was then moved to a vacuum line and evacuated, and 20 mL of dry CH_2Cl_2 was added by vacuum transfer. At room temperature, the catalyst and polymer dissolved to produce a clear, yellow solution. DEB−H was then added to the stirring reaction mixture via syringe under nitrogen. Within 15 min at room temperature the color of the reaction mixture changed from yellow to dark orange-brown. The reaction was monitored via ^{11}B NMR spectroscopy until the resonances of DEB−H at 36 and 30 ppm were completely converted to a single resonance at 36 ppm.

The reaction mixture was then filtered through a 2 in. plug containing layers of Florisil and neutral, decolorizing carbon. The solvent was vacuum-evaporated and the product further dried for 12 h in vacuo to give white to light yellow solids. The details of individual reactions are given in Table 2. The polymers softened to a melt in the range of 0−80 °C (Table 3) and were soluble in common organic solvents, including ethers and hydrocarbons. Anal. Found: PVS−DEB-1, C, 41.2%; H, 5.6%; B, 1.3%; Si, 28.1%; N, 1.5%; PVS−DEB-2, C, 41.1%; H,

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Table 3. PVS−DEB and PVS−PIN Polymer Compositions

polymer	T_g[a] (°C)	composition
PVS	118	$(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(ViMe_2SiO_{0.5})_{0.21}$
PVS−DEB-1	76	$(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(ViMe_2SiO_{0.5})_{0.17}(DEB(CH_2)_2Me_2SiO_{0.5})_{0.04}$
PVS−DEB-2	41	$(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(ViMe_2SiO_{0.5})_{0.10}(DEB(CH_2)_2Me_2SiO_{0.5})_{0.11}$
PVS−DEB-3	7	$(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}$ $(DEB(CH_2)_2Me_2SiO_{0.5})_{0.21}$
PVS−PIN-1	106	$(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(ViMe_2SiO_{0.5})_{0.18}(PIN(CH_2)_2Me_2SiO_{0.5})_{0.03}$
PVS−PIN-2	82	$(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(ViMe_2SiO_{0.5})_{0.15}(PIN(CH_2)_2Me_2SiO_{0.5})_{0.06}$
PVS−PIN-3	56	$(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(ViMe_2SiO_{0.5})_{0.09}(PIN(CH_2)_2Me_2SiO_{0.5})_{0.12}$
PVS−PIN-4	44	$(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(PIN(CH_2)_2Me_2SiO_{0.5})_{0.21}$

[a] Determined by TMA.

Table 4. Polymer Molecular Weights

sample	M_w[a]	M_n[b]	M_z[c]	M_w/M_n	R_{gw}[d] (nm)	M−H *a*[e]	d*n*/d*c*[f]
PVS	39000	11700	89400	3.33	3.75	0.403	0.080
PVS−DEB-1	61000	12900	171000	4.73	4.44	0.406	0.079
PVS−DEB-2	91500	15800	288500	5.79	5.24	0.390	0.078
PVS−DEB-3	28500	8490	69100	3.36	3.25	0.367	0.076
PVS	37700	13300	93 800	2.84	3.65	0.392	0.080
PVS−PIN-1	53200	15800	159000	3.37	4.15	0.394	0.079
PVS−PIN-2	48400	16000	126800	3.03	4.00	0.387	0.077
PVS−PIN-3	73900	22300	216400	3.31	4.63	0.384	0.070
PVS−PIN-4	54000	18800	137500	2.87	4.20	0.373	0.073

[a] Weight average molecular weight. [b] Number average molecular weight. [c] *Z* average molecular weight. [d] The weight average radius of gyration. [e] The Mark−Houwink *a* parameter. [f] The refractive index increment.

5.6%; B, 3.2%; Si, 25.2%; N, 1.8%; PVS−DEB-3, C, 41.3%; H, 6.5%; B, 5.2%; Si, 23.2%; N, 5.3%. For polymer PVS−DEB-1: ^{11}B NMR (64.2 MHz, C_6D_6, ppm) 36.0; ^1H NMR (200.1 MHz, C_6D_6, ppm) 7.86 (br, Ph), 7.15 (br, Ph), 6.15 (br, vinyl), 5.88 (br, vinyl), 4.62 (br, NH), 0.96 (br), 0.84 (br,), 0.28 (br, $OSiMe_3$); ^{13}C NMR (100.4 MHz, $CDCl_3$, ppm) 138.81 (d, $Si\mathit{CH}{=}CH_2$), 134.16 (d, phenyl), 131.86 (d, phenyl), 129.84 (s, phenyl), 127.34 (d, phenyl), 11.55 (t, CH_2), 9.84, 8.23 (DEB, $\mathit{C}H_2CH_3$), −0.45 (q, $Si\mathit{C}H_3$), −3.05 (s, $\mathit{Me}_2(PINCH_2CH_2)SiO_{0.5}$); ^{29}Si NMR (79.5 MHz, $C_6D_6/Cr(acac)_3$, ppm) 12.0 (Si-DEB), −2.1 (Si-vinyl), −57.3 ($Me(MeO)SiO_{1.0}$), −66.5 ($MeSiO_{1.5}$), −72.1 ($Ph(MeO)SiO_{1.0}$), −79.2, −81.0 ($PhSiO_{1.5}$). DRIFT data for PVS−DEB-1 (KBr): 3637 (w), 3051 (s), 2963 (s), 1958 (m), 1888 (m), 1822 (m), 1595 (s), 1430 (m), 1271 (m), 1048 (s), 699 (m) cm^{-1}. Similar NMR and IR spectra were recorded for each of the polymers with the intensities of the peaks varying according to the DEB content.

Reaction of Poly(vinylsiloxane) (PVS) and Pinacolborane (PIN−H). Using methods similar to those described above, PVS and $RhH(CO)(PPh_3)_3$, in the proportions indicated in Table 2, were dissolved in 20 mL of CH_2Cl_2 to produce a clear, yellow solution. PIN−H was then added to the stirring reaction mixture via syringe under nitrogen. Within 15 min at room temperature the color of the reaction mixture changed from yellow to dark orange-brown. The reaction was monitored via ^{11}B NMR spectroscopy until the doublet resonance of PIN−H at 28 ppm was completely converted to a singlet resonance at 34 ppm.

The reaction mixture was then washed with deionized water and extracted with Et_2O. The ether extract was filtered through a 2 in. plug containing layers of Florisil and neutral, decolorizing carbon. The solvent was vacuum-evaporated and the product further dried for 12 h in vacuo to give white to light yellow solids. The polymers softened to a melt in the range of 44−106 °C (Table 3) and were soluble in common organic solvents, including ethers and hydrocarbons. The data for individual reactions are given in Table 2. Anal. Found: PVS, C, 42.6%; H, 4.9%; Si, 30.5%; PVS−PIN-1, C, 44.4%; H, 5.4%; B, 0.3%; Si, 28.8%; PVS−PIN-2, C, 44.8%; H, 5.4%; B, 0.6%; Si, 27.8%; PVS−PIN-3, C, 44.5%; H, 6.0%; B, 1.3%; Si, 25.1%; PVS−PIN-4, C, 45.8%; H, 6.0%; B, 1.7%; Si, 23.4%. For polymer PVS−PIN-2: ^{11}B NMR (64.2 MHz, C_6D_6, ppm) 34.0; ^1H NMR (200.1 MHz, C_6D_6, ppm) 7.84 (br, Ph), 7.16 (br, Ph), 6.13 (br, vinyl), 5.84 (br, vinyl), 3.45 (m, CH_2), 1.06 (s, PIN), 0.21 (br, $OSiCH_3$); ^{13}C NMR (100.4 MHz, $CDCl_3$, ppm, 25 °C) 138.95 (d, $SiCH{=}CH_2$), 134.04 (d, phenyl), 131.65 (d, phenyl), 129.70 (s, phenyl), 127.23 (d, phenyl), 83.51 (s, PIN, $\mathit{C}(CH_3)_2$), 25.82 (q, PIN, $\mathit{C}H_3$), 10.47 (t, $\mathit{C}H_2$, J_{CH}127), 3.82 (t, $\mathit{C}H_2$, J_{CH} 117), −0.45 (q, $Si\mathit{C}H_3$, J_{CH} 116), −3.05 (s, $\mathit{Me}_2(PINCH_2CH_2SiO_{0.5})$; ^{29}Si NMR (79.5 MHz, $CD_3Cl/Cr(acac)_3$, ppm) 10.2 (Si-vinyl), −2.3 ($SiCH_2CH_2PIN$), −57.0 ($Me(MeO)SiO_{1.0}$), −66.0 ($MeSiO_{1.5}$), −71.8 ($Ph(MeO)SiO_{1.0}$), −78.5, −80.8 ($PhSiO_{1.5}$). DRIFT data for PVS−PIN-2 (KBr): 3074 (s), 3050 (s), 2966 (s), 1959 (w), 1889 (w), 1824 (w), 1595 (s), 1430 (s), 1407 (m), 1370 (m), 1321 (m), 1271 (s), 1130−1026 (br, s), 786 (s), 696 (s) cm^{-1}. Similar NMR and IR spectra were recorded for each of the polymers with the intensities of the peaks varying according to the PIN content.

Ceramic Conversions Reactions. In a typical procedure, an aliquot of the resin was weighed into a graphite crucible and transferred into a tube furnace. The furnace was then evacuated to <20 Torr and backfilled with argon. Under a purge of argon, the sample was heated to 1200 °C at 10 °C/min and held at temperature for 1 h before cooling to room temperature. Anal. Found: PVS, Si, 34.9%; C, 37.0%; PVS−DEB-1, Si, 34.0%; C, 37.9%; B, 0.8%; N, 0.4%; PVS−DEB-2, Si, 33.3%; C, 37.9%; B, 1.8%; N, 1.6%; PVS−PIN-1, Si, 37.3%; C, 36.4%; B, 0.2%; PVS−PIN-2, Si, 35.5%; C, 36.2%; B, 0.4%; PVS−PIN-3, Si, 35.9%; C, 35.9%; B, 0.5%; PVS−PIN-4, Si, 34.9%; C, 35.1%; B, 0.6%. Additional properties of these ceramics are presented in Table 5.

For pyrolyses at 1600 °C, aliquots of resin were weighed into a graphite crucible and transferred into a tube furnace. The furnace was purged under argon for 1.5 h before the sample was heated to 1600 °C at a rate of 10 °C/min and then held at temperature for 1 h, before cooling to room temperature. Anal. Found: PVS, Si, 61.0%; C, 33.6%; PVS−DEB-1, Si, 59.5%; C, 31.5%; B, 1.6%; N, 0.5%; PVS−DEB-2, Si, 56.5%; C, 31.2%; B, 3.0%; N, 2.1%; PVS−PIN-2, Si, 62.55%; C, 32.2%; B, 0.7%. Additional properties of these ceramics are presented in Table 6.

For pyrolyses at 1800 °C, aliquots of resins were weighed into a graphite crucible and transferred into an Astro graphite furnace. The furnace was then evacuated and backfilled with argon. Under a purge of argon, the samples were heated to 1800 °C at a rate of 10 °C/min and then held at temperature for 1 h, before cooling to room temperature. Anal. Found: PVS, Si, 72.6%; C, 33.18%; PVS−PIN-1, Si, 70.1%; B, 0.2%; PVS−PIN-2, Si, 67.0%; C, 35.7%; B, 0.4%; PVS−PIN-3, Si, 68.4%; C, 34.2%; B, 0.3%; PVS−PIN-4, Si, 67.7%; C, 33.0%; B, 0.5%. Additional properties of these ceramics are presented in Table 7.

Formation of Ceramic Fibers from PVS−PIN and PVS−PIN/PVS Blends. Fiber melt-spinning was carried out

Table 5. Polymer Ceramic Conversions and Compositions to 1200 °C

polymer	char yield (%) 1200 °C	yield (%) TGA 1100 °C	%B	ceramic composition[a]
PVS	78.9	84		$Si_{1.0}C_{2.48}O_{1.42}$
PVS−DEB-1	76.5	82	0.8	$Si_{1.0}C_{2.60}O_{1.52}B_{0.06}N_{0.03}$
PVS−DEB-2	75.2	76	1.8	$Si_{1.0}C_{2.66}O_{1.36}B_{0.14}N_{0.10}$
PVS−PIN-1	78.8	81	0.2	$Si_{1.0}C_{2.28}O_{1.22}B_{0.02}$
PVS−PIN-2	71.4	78	0.4	$Si_{1.0}C_{2.38}O_{1.38}B_{0.03}$
PVS−PIN-3	62.8	69	0.5	$Si_{1.0}C_{2.34}O_{1.35}B_{0.04}$
PVS−PIN-4	49.4	61	0.6	$Si_{1.0}C_{2.35}O_{1.48}B_{0.04}$
PVS−PIN-2 fiber			<0.5	$Si_{1.0}C_{2.31}O_{1.31}B_{0.03}$
blend fiber			0.2	$Si_{1.0}C_{2.15}O_{1.18}B_{0.01}$

[a] Oxygen content determined by difference.

Table 6. Polymer Ceramic Conversions and Compositions to 1600 °C

polymer	char yield (%)	grain size[a] (nm)	%B	ceramic composition[b]
PVS	42.9	33		$Si_{1.0}C_{1.29}O_{0.16}$
PVS−DEB-1	40.1	39	1.6	$Si_{1.0}C_{1.24}B_{0.07}N_{0.02}O_{0.22}$
PVS−DEB-2	39.8	35	3.0	$Si_{1.0}C_{1.29}B_{0.14}N_{0.07}O_{0.23}$
PVS−PIN-2	37.9	35	0.7	$Si_{1.0}C_{1.20}B_{0.03}O_{0.12}$

[a] The SiC grain size was estimated from the X-ray powder diffraction peaks. [b] Oxygen content determined by difference.

Table 7. Polymer Ceramic Conversions and Compositions to 1800 °C

polymer	char yield (%)	grain size[a] (nm)	%B	ceramic composition
PVS	42.5	152		$Si_{1.0}C_{1.07}$
PVS−PIN-1	40.7	77	0.2	$Si_{1.0}C_{1.00}B_{0.01}$
PVS−PIN-2	36.0	76	0.4	$Si_{1.0}C_{1.25}B_{0.01}$
PVS−PIN-3	28.3	65	0.3	$Si_{1.0}C_{1.17}B_{0.01}$
PVS−PIN-4	23.9	65	0.5	$Si_{1.0}C_{1.14}B_{0.02}$

[a] The SiC grain size was estimated from the X-ray powder diffraction peaks.

using a custom-designed apparatus composed of an extruder and a motor-driven drum for continuous fiber take-up. Prior to melt-spinning, a toluene solution of the PVS−PIN samples was stirred with a mercapto-functionalized silica gel (Dow Corning)[18] for 12 h in order to remove any trace amounts of rhodium catalyst that might have remained in the samples. The solvent was then vacuum-evaporated to yield a solid resin. Samples were then placed in the extruder and equilibrated at the melt temperature. The melt-spinning was typically carried out between 140 and 220 °C, depending on the glass transition temperature of the particular resin. Once equilibrated, the polymers were extruded through a 381 μm orifice of a spinneret. The resulting fiber was taken up continuously on a spool. The average diameter of the green fibers was between 18 and 30 μm. The green fibers were then cured with electron beam radiation (40−100 Mrad) under the protection of a nitrogen atmosphere using an Energy Science, Inc. (ESI) electron beam machine. The cured green fibers were next charged into a graphite boat and transferred into a Lindberg tube furnace. The furnace was evacuated to <20 Torr and backfilled with argon. Under a purge of argon, the sample was heated to 1200 °C at 3 °C/min and held at temperature for 1 h before cooling to room temperature. In a typical experiment, a 1.016 g sample of cured siloxane PVS−PIN-2 fibers produced 0.642 g of black ceramic fibers (63.2% yield). Anal. Found: C, 36.0%; Si, 36.4%; B <0.5%.

In another experiment, a 2.5 g sample of PVS−PIN-4 was blended with 10.0 g of PVS resin in hexane. The solid material obtained by vacuum evaporation of the solvent was melt-spun between 180 and 200 °C into 18−30 μm diameter fibers and cured with electron beam radiation under protection of a nitrogen atmosphere. Pyrolysis of a 0.329 g sample of the cured fibers heated to 1200 °C at 3 °C/min and held at temperature for 1 h before cooling to room temperature yielded 0.224 g of black ceramic fibers (68% yield). Anal. Found: C, 35.37%; Si, 38.5%; B, 0.2%.

Results and Discussion

The PVS precursor resin that was used in this study was prepared by co-condensation of $PhSi(OMe)_3$, $MeSi(OMe)_3$, and $(Me_2Vi)_2O$ as reported previously.[19] The as-synthesized material was obtained as a soft solid and was precipitated by addition of a toluene solution to a large excess of methanol to remove oligomers. As determined by microanalytical and proton NMR analysis, the purified material had a composition that is consistent with a $(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(ViMe_2SiO_{0.5})_{0.21}$ formulation. The typical softening point for the purified resin was in the temperature range 50−140 °C, depending upon the amount of oligomers removed from the bulk of the material.

The vinyl substituents of the PVS polymer used in this study are an important component since they allow for cure of the polymer once a shaped material is formed, as well as provide a reactive site for potential functionalization by boron reagents. Hydroboration reactions of polymer vinyl groups, employing reagents such as $BH_3{\cdot}THF$ and $BH_3{\cdot}SMe_2$, have, in fact, already been utilized as a method of attaching boron-containing groups to a variety of preceramic polymers.[20] Similar reactions of PVS with $BH_3{\cdot}THF$ and $BH_3{\cdot}SMe_2$ also led to vinyl hydroboration, but the resulting boronated polymers were either too chemically reactive or extensively cross-linked (and therefore intractable) for real applications.

On the basis of our previous studies of the design of poly(borosilazane) precursors for SiNCB materials,[21] we expected that poly(vinylsiloxane)s functionalized with the monofunctional boranes, pinacolborane and diethylborazine, would be much more stable, thus allowing more demanding processing conditions, such as melt-spinning. But, initial experiments showed that neither pinacolborane nor diethylborazine is sufficiently reactive by itself to hydroborate the polymer vinyl groups. Thus, it was first necessary to develop methods to activate these boranes for reactions with silyl-olefins.

We,[16,22] and others,[23] have previously shown that a variety of transition metal complexes can catalyze the hydroboration reactions of both polyboranes and organoboranes. Therefore, the use of such catalysts to activate silyl−vinyl groups for hydroboration with both diethylborazine (DEB−H) and pinacolborane (PIN−H) was explored. Initial investigations tested catalyst activity for hydroborations with the compound vinyltris(trimethylsiloxy)silane (**1**) as a model for the polymer.

Metal-Catalyzed Reactions of Vinyltris(trimethylsiloxy)silane (1) with Diethylborazine and Pi-

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[18] Burns, G. T.; Deng, Q.; Hahn, J. H.; Reggio, G. L.; Su, K. U.S. Patent 6,013,187, 2000.

[19] Burns, G. T.; Taylor, R. B.; Xu, Y.; Zangvil, A.; Zank, G. A. *Chem. Mater.* **1992**, *4*, 1313−1323.

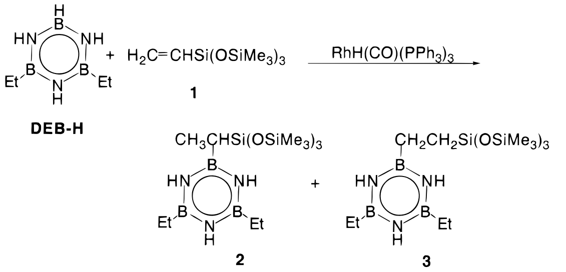
[20] See, for example: (a) Riedel, R.; Kienzle, A.; Szabó, V.; Mayer, J. *J. Mater. Sci.* **1993**, *28*, 3931−3938. (b) Aldinger, F.; Weinmann, M.; Bill, J. *Pure Appl. Chem.* **1998**, *70*, 439−448 and references therein.

[21] Wideman, T.; Cortez, E.; Remsen, E. E.; Zank, G. A.; Carroll, P. J.; Sneddon, L. G. *Chem. Mater.* **1997**, 9, 2218−2230.

[22] Pender, M.; Wideman, T.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1998**, *120*, 9108−9109 and previous papers in this series.

[23] See, for example: (a) Beletskaya, I.; Pelter, A. *Tetrahedron* **1997**, *53*, 4957−5026. (b) Burgess, K.; Ohlmeyer, M. *J. Chem. Rev.* **1991**, *91, 1179−1191.*

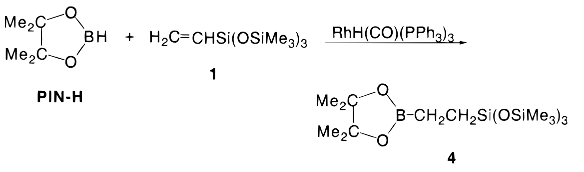
nacolborane. We had previously shown that the complex RhH(CO)$(PPh_3)_3$ has a high activity for catalyzing olefin−borazine hydroborations with a wide variety of olefins.[16] Similar activities were observed for reactions of DEB−H and **1**. As outlined in eq 1 and Table 1, the reactions employed 5 mol % catalyst (with respect to DEB−H) and yielded a 1:35 mixture of 1-(DEB)-1-$[(Me_3SiO)_3Si]C_2H_4$ (**2**) and 1-(DEB)-2-$[(Me_3SiO)_3Si]C_2H_4$ (**3**). These reactions were slow at room temperature and required an excess of DEB−H in order to achieve complete hydroboration of **1**.



(1)

The ^{11}B and ^1H NMR data for **2** and **3** are similar to those that have been previously reported[16] for alkylated diethylborazine derivatives and support the formulations shown in eq 1.

An analogous reaction between **1** and PIN−H employing 0.85 mol % RhH(CO)$(PPh_3)_3$ catalyst yielded a single product **4** (eq 2). The reactions were conveniently monitored by ^{11}B NMR and were stopped when the doublet resonance of the starting PIN−H (28 ppm) reagent was completely converted to the singlet resonance of the product (34 ppm). The higher activity of the RhH(CO)$(PPh_3)_3$-catalyzed reactions with PIN−H relative to those with DEB−H allowed much lower catalyst concentrations and shorter reaction times. For example, quantitative hydroboration of **1** was obtained by reacting equal amounts of **1** and PIN−H in the presence of only 0.85 mol % catalyst for 8 h at room temperature. This corresponds to 116 catalyst turnovers during the 8 h reaction period.

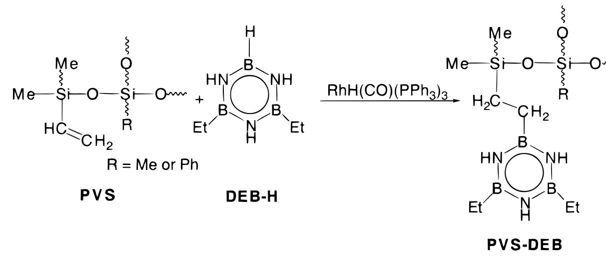


(2)

The reactions with PIN−H were also more selective than those with DEB−H yielding, according to GC/MS, only one product. The NMR data for **4** are consistent with exclusive anti-Markovnikov addition to **1** to yield the 1-(PIN)-2-$[(Me_3SiO)_3Si]C_2H_4$ structure. Thus, in addition to the resonances arising from the pinacol and trimethylsilyl methyls, the ^1H NMR spectrum shows multiplet resonances each of intensity 2 centered at 1.11 and 0.88 ppm attributed to the two CH_2 groups. Likewise, the ^{13}C NMR spectrum at −78 °C shows resonances corresponding to the quarternary and methyl carbons of PIN, along with a triplet at 7.71 ppm and singlet (broadened owing to its attachment to boron) at 4.40 ppm ascribed to the CH_2 and CH_2B groups, respectively. In addition to the resonance arising from $OSiMe_3$, the ^{29}Si NMR spectrum also showed a resonance at −63.6 ppm, instead of the vinyl-silicon resonance at −78.0 ppm that was observed for **1**.

Several other complexes, including Cp_2ZrHCl, RhCl(CO)$(PPh_3)_2$, and $CpNi(PPh_3)_3Cl$,[24] have previously been reported to catalyze pinacolborane olefin hydroborations; however, we observed little or no activity for these complexes when they were employed in reactions of pinacolborane and **1**. Catalytic activity was observed for the $Cp_2Ti(CO)_2$ and Cp_2TiMe_2 complexes, which have previously been reported to catalyze catecholborane olefin hydroborations,[25] but both complexes were much slower than those employing the RhH(CO)$(PPh_3)_3$ catalyst and were not selective, yielding mixtures of the Markovnikov and anti-Markovnikov products. Reaction data for these catalysts are reported in Table 1. The high activities and selectivities of the RhH(CO)$(PPh_3)_3$-catalyzed reactions of **1** led us to explore its use to catalyze the reactions of both DEB−H and PIN−H with PVS.

Synthesis and Characterization of PVS−DEB Polymers. The PVS−DEB polymer syntheses were carried out in CH_2Cl_2 solutions and typically employed ∼5 mol % catalyst. The degree of polymer modification could be readily controlled by varying the DEB−H to PVS reactant ratios, as shown in Tables 2 and 3. A variety of modified polymers were obtained, including PVS−DEB-3, $(MeSiO_{1.5})_{0.42}(PhSiO_{1.5})_{0.37}(DEB(CH_2)_2Me_2SiO_{0.5})_{0.21,}$ in which complete hydroboration of the polymer vinyl groups was achieved. All PVS−DEB polymers were soluble and stable in ethers, acetone, methylene chloride, benzene, and pentane. As can also be seen in Table 3, there was a significant decrease in the polymer T_g's with increasing modification.



(3)

The spectroscopic data obtained for the PVS−DEB polymers strongly supports the structure shown in eq 3 resulting from the anti-Markovnikov hydroboration of the polymer silyl−vinyl groups. For example, their IR spectra clearly show a decrease in the carbon−carbon double-bond stretch (1595 cm^{-1}) with increasing modification. Their ^{11}B NMR spectra show a broad singlet resonance similar to those of the model compounds **2** and **3** at a chemical shift characteristic of trialkylborazines.[16] In their ^1H NMR spectra, the vinyl resonances decrease in intensity with increased modification, and this decrease is accompanied by the growth of the DEB −NH and ethyl resonances. A comparison of the integrated intensities of the phenyl and vinyl ^1H NMR resonances in the PVS−DEB polymers correlates well with the degree of modification established by elemental analysis. With increasing modification, the ^{13}C NMR

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(24) Pereira, S.; Srebnik, M. *J. Am. Chem. Soc.* **1996**, *118,* 909−910.

(25) He, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118,* 1696−1702.

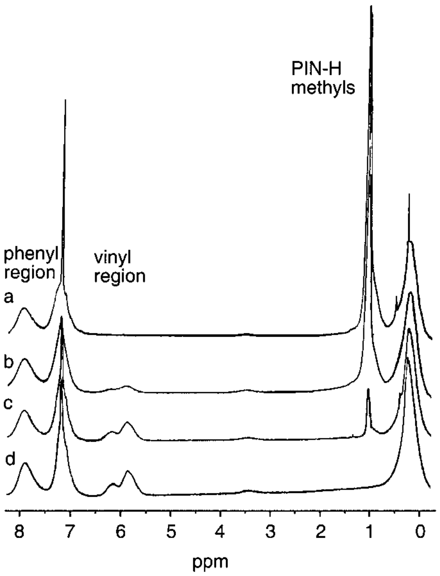


Figure 1. ^1H NMR spectra (200.1 MHz) of (a) PVS−PIN-4, (b) PVS−PIN-3, (c) PVS−PIN-2, and (d) PVS.

spectra show growth of resonances from the DEB-ethyl groups along with a decrease in the PVS vinyl-carbon resonances. One $-CH_2$ resonance was found at 11.55 ppm, but the $-CH_2B$ resonance was not observed. However, such a resonance would be difficult to detect at room temperature because of the broadening effect of its interaction with the quadrupolar boron nuclei. The ^{29}Si NMR spectra show that with increasing modification, the resonance at −2 ppm arising from the $ViSiO_{0.5}$ silicon nuclei disappears, and a new peak corresponding to the silicon of the $DEB(CH_2)_2SiO_{0.5}$ group grows in at 12 ppm. The remaining resonances in the spectra, which correspond to the $MeSiO_{1.5}$, $PhSiO_{1.5}$, $Me(MeO)SiO_{1.0}$, and $Ph(MeO)SiO_{1.0}$ groups, do not change.

Synthesis and Characterization of PVS−PIN Polymers. Consistent with the differences observed for the reactions of DEB−H and PIN−H with the model compound **1**, the $RhH(CO)(PPh_3)_3$-catalyzed reactions of PIN−H with PVS were more active than those of DEB−H, thus allowing lower mole ratios of catalyst and shorter reaction times. For example, while both the PVS−PIN-3 and PVS−DEB-2 have similar degrees of hydroboration, the synthesis of PVS−PIN-3 required only 1 mol % catalyst and was complete in 1 h, whereas the synthesis of PVS−DEB-2 required 11 h with 2 mol % catalyst. As with the PVS−DEB polymers, it was possible to readily control the compositions of the PVS−PIN polymers by simply changing the PIN−H to PVS reactant ratios (Table 3).

The spectroscopic data obtained for the PVS−PIN polymers and the model compound studies strongly support a structure (eq 4) similar to that of the PVS−DEB polymers resulting from the anti-Markovnikov hydroboration of the polymer silyl−vinyl groups by pinacolborane. Thus, the IR spectra of the PVS−PIN polymers again show a decrease in the carbon−carbon double-bond stretch (1595 cm^{-1}) that correlates well with the degree of modification determined by elemental analysis. Likewise, as can be seen in Figure 1, with increasing modification their ^1H NMR spectra show a decrease in the integrated intensity of the vinyl-proton resonances relative to the phenyl resonances that is accompanied by an increase in the pinacolborane methyl resonance. These changes in the ^1H NMR spectra again correlate well with the microanalytical data. Anti-Markovnikov addition is strongly indicated by the ^{13}C NMR spectra, which show, in addition to the methyl and the quaternary carbon resonances of the pinacolborane fragment, two triplets at 10.47 and 3.82 ppm arising from the saturated CH_2 carbons, thus indicating boron substitution at the β-carbon position. As was the case for compound **4**, the ^{29}Si NMR spectra, Figure 2, show that a new resonance at 10.2 ppm has replaced the vinyl-silicon resonance in the starting PVS polymer while the resonances corresponding to the $MeSiO_{1.5}$-$PhSiO_{1.5}$ and $Me(MeO)SiO_{1.0}$ and $Ph(MeO)SiO_{1.0}$ groups remain unchanged. The singlet resonance observed in the ^{11}B NMR spectra of the PVS−PIN polymers is also found at a chemical shift (34 ppm) identical to that found in the model compound **4**.

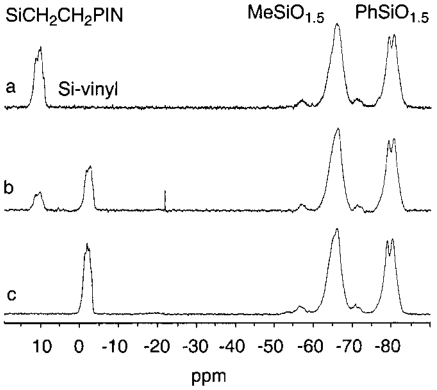
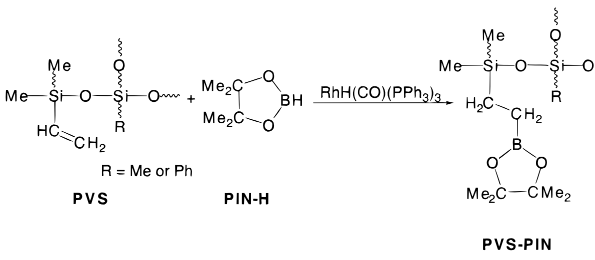


Figure 2. ^{29}Si NMR spectra (79.5 MHz) of (a) PVS−PIN-4, (b) PVS−PIN-2, and (c) PVS.



(4)

The PVS−PIN polymers had similar solubilities, but greater stabilities, than the PVS−DEB polymers. Likewise, as was the case for the PVS−DEB polymers, the softening points of the PVS−PIN polymers decreased significantly according to the degree of modification. Thus, while the starting PVS polymer had a T_g of 118 °C, the modified polymers exhibited a systematic decrease in their T_g's as the degree of modification increased from PVS−PIN-1 (T_g 106 °C) to PVS−PIN-4 (T_g 44 °C).

Molecular Weight Analysis of PVS−DEB and PVS−PIN Polymers. Molecular weight analysis of PVS−PIN polymers was accomplished using SEC with refractive index, viscometry, and light-scattering triple detection. The integration of online viscosity and light-scattering detectors with size exclusion chromatography (SEC) enables the high-precision determination of polymer molecular weight, intrinsic viscosity, and molecular size distributions in a single experiment. Because of the absolute nature of the measurements, no column cali-

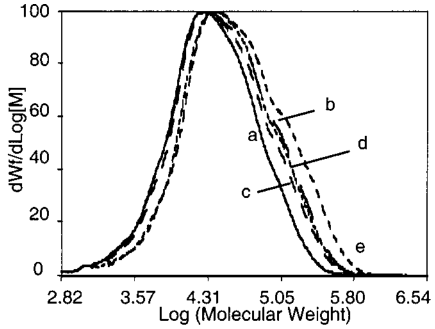


Figure 3. Molecular weight distribution of (a) PVS, (b) PVS−PIN-1, (c) PVS−PIN-2, (d) PVS−PIN-3, and (e) PVS−PIN-4.

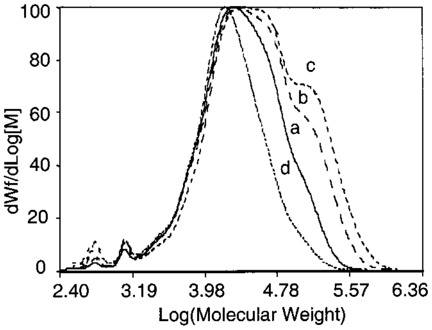


Figure 4. Molecular weight distributions of (a) PVS, (b) PVS−DEB-1, (c) PVS−DEB-2, and (d) PVS−DEB-3.

bration is required and the results are insensitive to variation in SEC experimental conditions. This method is especially suitable for molecular weight determinations of siloxane resins because of their complexity in structure. In SEC with triple-detector capability, the molecular weight information from the light-scattering (LS) detector is combined with the intrinsic viscosity (IV) information from the viscometer detector to determine the polymer molecular size, which is often described as the polymer radius-of-gyration (R_g) values. This combination gives the capability of determining molecular weight and R_g at every elution slice across the entire SEC elution curve. From these results, the dependence of polymer IV and R_g on molecular weight can be used to determine polymer branching and conformational differences between samples.

Consistent with the NMR results for the PVS, PVS−PIN, and PVS−DEB samples, the molecular weight analyses revealed significant differences in hydrodynamic volume, molecular weight, radius of gyration, and conformation after modification. The molecular weights, as determined using light-scattering, radius of gyration, and the Mark Houwink (M−H) "*a*" parameter, of the initial PVS and the PVS−PIN samples are summarized in Table 4. The overlay of molecular weight distributions for PVS and the modified PVS−PIN materials in Figure 3, shows that, as expected, the molecular weights increase following polymer modification by the addition of the PIN groups (molecular weight of each PIN group = 127 g/mol). Likewise, the radius of gyration of the PVS−PIN samples increased to the 4.00−4.63 range, from the initial value of 3.65 for the starting PVS. The unusually high molecular weight and radius of gyration for PVS−PIN-3 is attributed to an unknown side reaction that leads to additional branching or cross-linking in this resin. This conclusion is supported by the increased response in the light-scattering signal at the high molecular weight end.

The conformation and the extent of branching after chemical modification can be obtained from the Mark Houwink (M−H) *a* parameter. For example, a spherical or rod conformation can be assigned to the polymer when the M−H *a* parameter is 0 or 2.0, respectively. A random coil conformation corresponds to an *a* parameter of 0.7, and for branched materials the *a* parameter falls between 0 and 0.7. As can be seen in Table 4, the PVS starting material has an *a* parameter of 0.392, indicating a highly branched and almost spherical conformation. After chemical modification the *a* parameter decreases further and the extent of decrease appears to be correlated with the percentage of PIN modification. The *a* parameter (0.373) of PVS−PIN-4, in which all the vinyl groups are substituted with pinacolborane, indicates the resin is closer to a spherical structure than is found in the unmodified PVS. The change to a more spherical conformation of the PVS−PIN polymers is consistent with the steric repulsions that might arise upon the attachment of the bulky PIN substituents. Alternatively, the more spherical conformation may result from increased chain branching following modification.

Similar to the PIN-modified resin, the PVS−DEB-modified materials exhibit changes in molecular weight that are related to the concentration of DEB in the modified resin, as indicated by the molecular weight and R_g values in Table 4 and as shown in the molecular weight distribution overlay for this series of resins in Figure 4. A decrease in molecular weight for the resin with the highest DEB loading (PVS−DEB-3) is observed and is perhaps due to some type of chain scission side reaction. All other modified resins with less DEB content show a shift to shorter retention times indicating an increase in molecular weight. The effective incorporation of DEB into the resin structure is supported by the decrease in the refractive index increment (d*n*/dc) for the modified samples as shown in Table 4. In addition, like the PIN-modified resins, after chemical modification the *a* parameter decreases and the extent of decrease appears to be correlated with the percentage of DEB modification. The low values of the Mark Houwink *a* parameters for the PVS−DEB series indicates a similar highly dense spherical conformation.

Ceramic Conversion Reactions. The formation of SiOC ceramics from polysiloxanes, as well as structural characterization of the resulting silicon oxycarbide glass, has been extensively studied since the discovery by Chi[26] that silicon oxycarbide glass could be prepared from organically modified sol−gel precursors.[19,27] One of the great advantages of silsesquioxane precursors to silicon oxycarbide materials is that the composition of the

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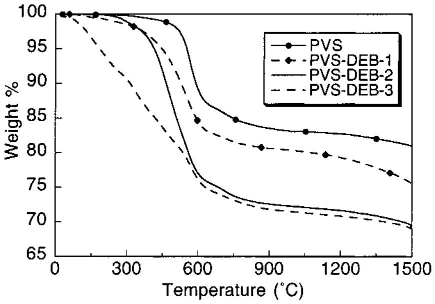

Figure 5. TGA studies to 1500 °C under argon of PVS and the PVS−DEB series.

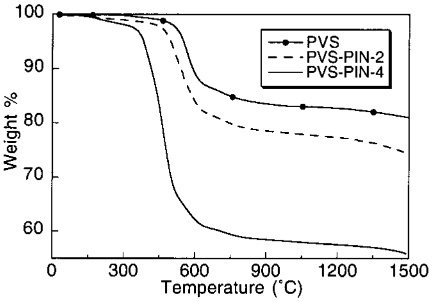

Figure 6. TGA studies to 1500 °C under argon of PVS and the PVS−PIN series.

ceramics can be readily controlled by varying the polymer precursor composition or pyrolysis conditions.[28] The synthesis of silicon oxycarbide materials from various siloxane precursors has been accomplished by heating the precursor at temperatures between 800 and 1400 °C under an inert atmosphere. Higher temperature treatment (>1400 °C) results in chemical decomposition of SiO ceramics accompanied by the loss of oxygen in the ceramics and eventually results in formation of SiC ceramic materials that contain either excess carbon or silicon depending upon the initial siloxane resin composition.

As discussed in the Introduction, previous studies of the PVS polymer used in this paper have demonstrated that upon pyrolysis conversion to silicon oxycarbide and silicon carbide occurs according to eq 5.[19]

$$(\mathrm{RSiO}_{1.5})_n \xrightarrow{1200\ ^\circ\mathrm{C}} \mathrm{C}_x\mathrm{Si}_y\mathrm{O}_z \xrightarrow{1800\ ^\circ\mathrm{C}} y\mathrm{SiC} + (x-y-z)\mathrm{C} + z\mathrm{CO(g)} \quad (5)$$

The TGA traces for the PVS−DEB materials, Figure 5, show that in each case polymer decomposition begins at a significantly lower temperature (<300°) than found for PVS (~400 °C) and that the thermal stabilities of the polymers decrease significantly with increasing modification. Indeed, the most highly modified polymer, PVS−DEB-3, showed an immediate weight loss upon heating suggesting that the DEB substituents are involved in the initial polymer decomposition reaction. Weight losses for the PVS and PVS−DEB samples were complete by 800 °C, with char yields that decrease with increasing DEB modification.

The PVS−PIN polymers were found to have much higher thermal stabilities than the PVS−DEB polymers. Thus, as shown in the TGA traces in Figure 6, the PVS−PIN-2 polymer does not begin decomposition until nearly 350 °C and even the most highly substituted sample, PVS−PIN-4, was stable to over 250 °C. Consistent with a decomposition reaction that includes the cleavage of the $(\mathrm{Me_2C})_2\mathrm{O_2}^-$ fragments of the PIN substituents during the pyrolysis, the ceramic yields for the PVS−PIN polymers are lower than that of PVS and decrease with increasing polymer modification.

Pyrolysis of bulk PVS−DEB samples to 1200 and 1600 °C were carried out under argon. Elemental analyses of the PVS−DEB-derived ceramics showed that there was retention of both boron and nitrogen in the chars (Tables 5 and 6), and that the Si:C:O ratios were similar to those of the PVS chars at comparable temperatures. The amount of boron in both the 1200 and 1600 °C chars for PVS−DEB-1 and PVS−DEB-2 was consistent with the relative amounts of DEB in their corresponding PVS−DEB polymer precursors.

Pyrolyses of bulk samples of the PVS−PIN samples were carried out to 1200 and 1800 °C. Elemental analyses of the resulting ceramics are summarized in Tables 5 and 7 and show that boron is retained in all chars. Consistent with the lower boron contents of the PVS−PIN polymers relative to those of the PVS−DEB materials, the PVS−PIN chars had lower amounts of boron (<0.7%) than those derived from PVS−DEB. Again, the boron contents of the chars varied according to the amount of boron in the precursor polymer and ranged from 0.2% (PVS−PIN-1) to 0.6% (PVS−PIN-4) in both the 1200 and 1800 °C chars. The Si:C:O ratios in each of the 1200 °C ceramics are similar to the PVS-derived ceramic at comparable temperatures. The compositions of PVS−PIN 1800 °C chars are consistent with the loss of oxygen to produce a silicon carbide ceramic with only a slight excess of carbon. This result again indicates that while the boron of the PIN unit is retained in the char, most of the pinacol fragment ($(\mathrm{Me_2C})_2\mathrm{O_2}^-$) is efficiently lost during the ceramic conversion reaction.

As has been pointed out by numerous researchers, increased fracture toughness is key to improving the performance and widening the applications of SiC composites.[29] It has been proposed that one method of achieving improvements in toughness is to both reduce the grain sizes and attain a more uniform grain size distribution in such materials. In this regard, there have been a number of studies[30] demonstrating that boron addition prior to either powder-processing of SiC powders or the ceramic-conversion reaction of SiC preceramic materials affects the nucleation and growth of SiC crystallites and enhances the formation of fine-grained ceramics at high temperatures. For example, for preceramic SiC materials derived from boron-containing polycarbosilanes, Eber and Jones have recently demonstrated[30j] that 1800 °C (1 h) pyrolyzed ceramics contain-

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[28] Bujalski, D. R.; Grigoras, S.; Lee, W.-L.; Wieber, G. M.; Zank, G. A. *J. Mater. Chem.* **1998**, *8*, 1427−1433.

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[30] See, for example, (a) Prochazka, S.; Scanlan, R. M. *J. Am. Ceram. Soc.* **1975**, *58*, 72. (b) Greskovich, C.; Rosolowski, J. H. *J. Am. Ceram. Soc.* **1976**, *59*, 336−343. (c) Suzuki, H.; Hase, T. *J. Am. Ceram. Soc.* **1980**, *63*, 349−350. (d) Stutz, D. H.; Prochazka, S.; Lorenz, J. *J. Am. Ceram. Soc.* **1985**, *68*, 479−482. (e) Negita, K. *J. Am. Ceram. Soc.* **1986**, *69*, C-308−C-310. (f) van Rijswijk, W.; Shanefield, D. J. *J. Am. Ceram. Soc.* **1990**, *73*, 148−149. (g) Passing, G.; Riedel, R.; Petzow, G. *J. Am. Ceram. Soc.* **1991**, *74*, 642−645. (h) Cao, J. J.; MoberlyChan,

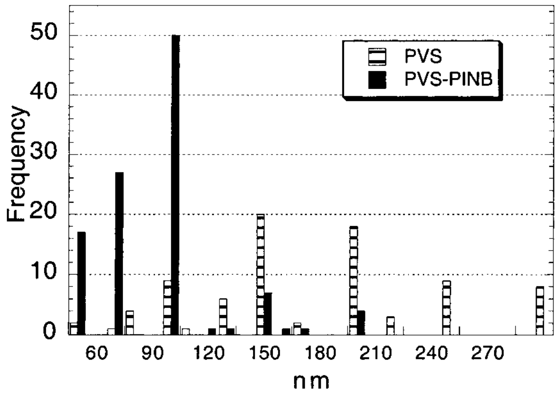

Figure 7. Histogram of the crystal sizes observed in TEM micrographs of 1800 °C PVS and PVS−PIN-2 chars.

ing 0.7% boron have significantly reduced grain sizes and more narrow distributions relative to ceramics derived from non-boron-containing polycarbosilanes pyrolyzed under similar conditions. Our XRD and TEM studies, discussed below, of the microstructures of the PVS−PIN- and PVS-derived ceramics revealed similar differences.

Powder X-ray diffraction studies showed that while the 1200 °C chars of all PVS, PVS−PIN, and PVS−DEB samples were amorphous, their 1600 °C chars each showed the formation of crystalline β-SiC. As estimated using the Scherrer equation,[17] the 1600 °C chars showed no variation in crystallite size as a result of boron modification, with each char having an average crystallite size in the ~33−39 nm range. TEM analysis of these samples also indicated similar average crystallite sizes, ~50 nm, and distributions with a standard deviation of 15 nm for each of the samples. However, in contrast to the results observed for the lower temperature chars, the 1800 °C chars of PVS and PVS−PIN showed significant differences in the degree of grain growth and distribution. Thus, on the basis of the X-ray data, the average crystallite size (Table 7) for each of the four PVS−PIN chars was ~half (~65−77 nm) that found for the PVS-derived ceramic (152 nm). This difference was also confirmed by the comparison TEM studies of the PVS and PVS−PIN-2 1800 °C chars that are summarized in Figure 7. According to the TEM studies, the 1800 °C PVS-derived ceramic had a broad crystallite size distribution, ranging from 50 to 300 nm, with an average size of 175 nm and a standard deviation of 65 nm. In contrast, the 1800 °C PVS−PIN-2-derived ceramic, which contained 0.4% boron, showed a more narrow size range, 50−200 nm, and both a smaller average crystallite size (93 nm) and standard deviation (35 nm). Density measurements showed that the 1600 °C chars of PVS, PVS−PIN-2, and PVS−DEB-1 all had similar densities (2.79 g/cm^3). The 1800 °C chars of PVS−PIN-2 were slightly denser (2.90 g/cm^3) than those derived from PVS (2.81 g/cm^3), but significant differences in the densities of the PVS- and PVS−PIN-derived ceramics would not be expected until higher temperatures.

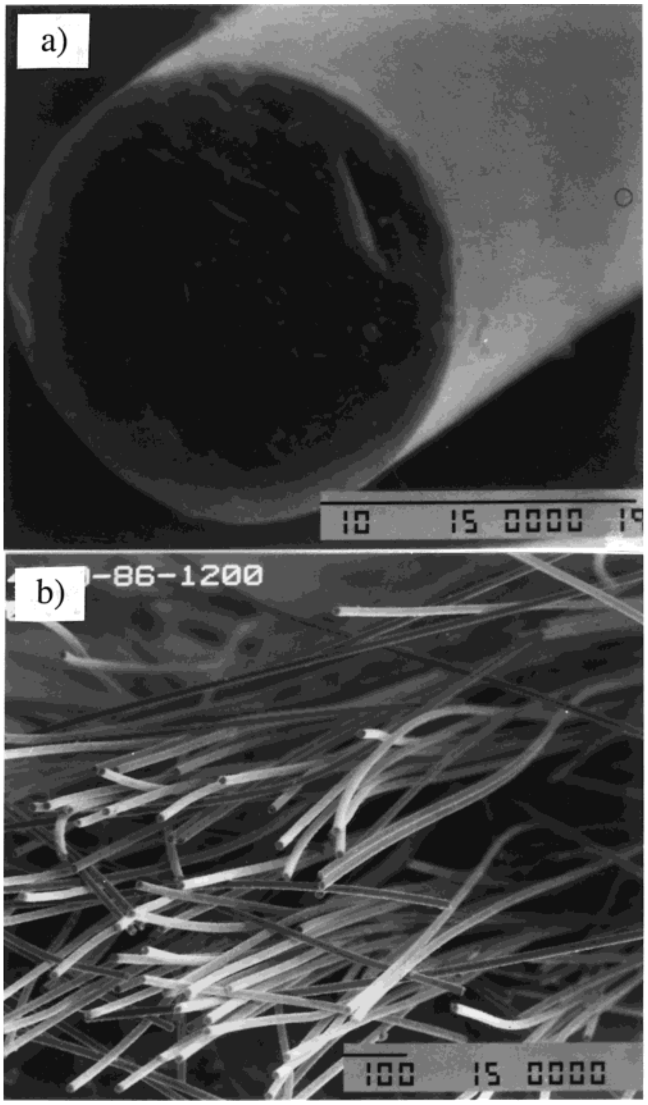

Figure 8. SEM micrographs of SiOCB ceramic fibers at (a) 5000X and (b) 100X magnification.

Formation of Polymer and Ceramic Fibers from Pinacolborane-Modified PVS. The formation of ceramic fibers from siloxane resins has been reported in the literature[9b,10] and, most recently, pursued at the Advanced Ceramics Program, Dow Corning Corporation as an alternate route to SiC and SiOC fibers.[10,11] A typical ceramic-fiber-forming process involves formation of green polymer fibers by a spinning process (melt-spinning or dry-spinning), followed by fiber-curing to make them infusible, and then, finally, formation of the ceramic fiber by high-temperature pyrolysis. Major difficulties in the production of continuous, small-diameter fibers have included both polymer reactivity at the melt-spin temperature and fiber deformation during pyrolysis because of the lack of efficient fiber cure chemistry.[31]

As discussed above, TGA studies of the PVS−PIN polymers indicated no weight loss up to 250 °C. This fact, coupled with their excellent melt stability, indicated that they should be good candidates for the melt-

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spinning of fibers. Indeed, our preliminary studies have now shown that both the PVS−PIN-2 resin and a blend of the PVS−PIN-4 resin with unmodified PVS can be easily melt-spun in the 140−220 °C temperature range into green fibers. Depending upon the exact spinning conditions, green fibers were obtained with diameters in the 18−30 μm range. The green fibers were cured with electron beam radiation to render them infusible. The cured fibers were then pyrolyzed to 1200 °C to yield boron-modified silicon oxycarbide fibers. The char yield (63.2%) of the PVS−PIN-2 fiber was somewhat less than that observed for the pyrolysis of 1200 °C powder PVS−PIN-2 samples (71.4%), but their elemental compositions were nearly identical to those of the powder chars. The char yield of the PVS−PIN-4/PVS blend was somewhat higher (68%) than that obtained from PVS−PIN-2 and yielded a boron-modified SiOC ceramic with a near 1:1 Si:C ratio. As can be seen in the SEM micrographs in Figure 8 of the PVS−PIN-2-derived ceramic fibers, significant shrinkage was observed after pyrolysis with the diameters of the ceramic fibers reduced to the 10−20 μm range, but the fibers were smooth, uniform, and free of voids. Slight adhesion between fibers was found in some cases. These preliminary spinning studies strongly indicate that the PVS−PIN polymers have excellent promise for development as single-source precursors to boron-modified SiOC and, potentially, boron-modified SiC fibers. Further work is now in progress to optimize the melt-spinning and pyrolysis conditions.

Conclusions

The work described in this paper has demonstrated several important points. First, it was shown that the PVS polymer can now be controllably modified with the thermally stable boron-containing pendants, pinacolborane and diethylborazine, using a $RhH(CO)(PPh_3)_3$-catalyzed hydroboration reaction. The rhodium-catalyzed reaction is general and should prove useful for the borane modification of other polymers containing olefinic groups. Second, while both the PVS−PIN and PVS−DEB polymers yield boron-modified SiOC ceramics upon pyrolysis, the PVS−PIN polymers are of particular importance. They are easily prepared from the commercially available pinacolborane and have both the excellent stability and processability that allows them to be readily melt-spun into polymer fibers which can then be converted to boron-modified SiOC fibers upon pyrolysis. Finally, the reduced grain growth and more uniform grain distribution found in the 1800 °C PVS−PIN ceramic chars compared to the ceramics derived from the unmodified PVS again demonstrate the pronounced effect the addition of even small amounts of boron (<1%) can have on ceramic properties. We are now exploring the sintering and mechanical properties of these ceramics at higher temperatures, and the results of these studies will be presented in future publications.

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