

Amine-Modified Polyborazylenes: Second-Generation Precursors to Boron Nitride

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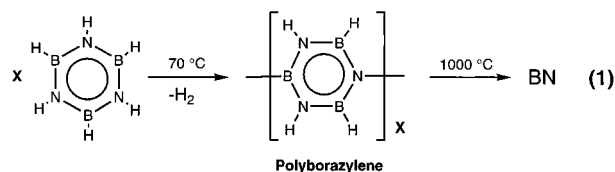
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New second-generation polymeric precursors to BN ceramics have been synthesized in high yield by the reaction of polyborazylene (PB), $[B_3N_3H_{\sim 3.5}]_x$, with diethylamine (DEA), dipentylamine (DPA), and hexamethyldisilazane (HMD). Elemental analyses and the spectroscopic data indicate that the resulting DEA-PB, DPA-PB, and HMD-PB polymers contain boron-bonded amino groups attached to the polyborazylene backbone. Analysis of volatile byproducts of the reaction suggests modification of PB with DEA and DPA occurs primarily through dehydrocoupling reactions, while the reaction with HMD involves amine Si–N bond cleavage with elimination of trimethylsilane. Combined molecular weight/infrared spectroscopy studies show the polymers are modified throughout the molecular weight distribution. Modification with HMD results in increased molecular weights due to cross-linking reactions involving the silazane. The DEA-PB and DPA-PB polymers have lower molecular weights than the starting PB, with the highest amine concentrations in the lower molecular weight fractions, suggesting some backbone scission occurs during polymer modification. The modified polymers show increased solubility in organic solvents compared to the parent PB polymer. Also unlike PB, the DPA-PB polymers become fluid, without weight loss, in the range 75–95 °C. The DPA-PB polymers were melt-spun using a crude ram extruder to yield continuous polymer fibers 30–40 μm in diameter. After a brief air-cure, pyrolysis of the polymer fibers under ammonia yielded $\sim 30 \mu\text{m}$ BN ceramic fibers of good quality, as determined by SEM, DRIFT, XRD, and RBS measurements, as well as oxidation and mechanical studies.

Introduction

Boron nitride has a wide range of attractive properties, including high-temperature stability and strength, a low dielectric constant, large thermal conductivity, hardness, and corrosion and oxidation resistance, leading to a number of potential applications as a structural or electronic material.³ Boron nitride powders may be easily obtained,⁴ but it has proven more difficult to prepare BN in more complex forms, especially fibers and coatings. Thus, there has been intense interest by many research groups on the development of polymeric precursors to BN.^{3a}

We have previously shown that borazine can be readily dehydrocoupling polymerized to give the soluble pre-ceramic polymer, polyborazylene (PB), in excellent yields.⁵



The combined analytical, spectroscopic, and molecular weight data indicate the polymer has a complex structure, related to those of the organic polyphenylenes, with linear, branched-chain and fused-cyclic borazine segments, and typical $M_n = 500\text{--}900 \text{ g/mol}$ and $M_w = 3000\text{--}8000 \text{ g/mol}$. According to its powder X-ray diffraction spectra, the polymer also appears to have a layered structure in the solid state. Further studies have shown that polyborazylene is an important pre-ceramic polymer that converts to boron nitride in

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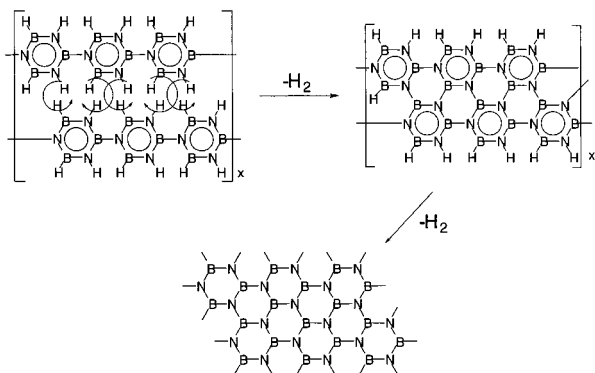


Figure 1. Proposed two-dimensional cross-linking process for the ceramic conversion reaction of polyborazylene.

excellent chemical (89–99%) and ceramic yields (84–93%) by a process involving a two-dimensional cross-linking reaction similar to that shown in Figure 1.

While polyborazylene has proven to be an excellent precursor for the production of boron nitride coatings, films, and shaped materials, the initial polymer-cross-linking reaction depicted in Figure 1 occurs at low temperature and has prevented the use of the polymer in applications requiring melt-processing. Thus, the key to the utilization of this polymer in other more demanding applications, such as the melt-spinning of fibers, is to control the dehydrocoupling reaction that leads to the formation of boron–nitrogen cross-links between the polyborazylene chains. One strategy by which this could be accomplished is to reduce the number of reactive B–H or N–H sites by functionalizing the polymer with suitable substituents. In this way it should be possible to improve both the thermal stability and lower the glass transition temperature (T_g) of the polymer. Indeed, we have previously prepared polyorganoborazylenes,⁶ including both B-ethyl- and B-propyl-substituted polyborazylenes, and found that these polymers have increased thermal stabilities compared to the parent polyborazylene. However, it was not possible to lower the T_g of the polyorganoborazylenes below the onset of cross-linking, and thus, these polymers are not meltable. The polyorganoborazylenes also have the added disadvantage that because of the inefficient elimination of the alkyl groups during the ceramic conversion process, carbon is retained in the BN ceramics derived from these polymers. Given these problems, investigations of alternative approaches for the formation of functionalized polyborazylenes with enhanced properties were initiated.⁷ Herein, we now report the high-yield syntheses and properties of new types of amine-substituted polyborazylene polymers that have proven to be excellent BN precursors for applications that require stable melts.

Experimental Section

All synthetic manipulations were carried out using standard high-vacuum or inert-atmosphere techniques as described by Shriver.⁸

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Materials. Borazine was prepared by the reaction of NaBH₄ and (NH₄)₂SO₄,⁹ and purified through a –63, –78, and –196 °C trap series, with only the material in the –78 °C trap used in the experiments. Dipentylamine (DPA), diethylamine (DEA), and hexamethyldisilazane (HMD) were distilled from CaH₂ before use. Glyme was freshly distilled from sodium benzophenone ketyl. Diethylborazine was prepared as recently reported.⁶

Physical Measurements and Instrumentation. Diffuse-reflectance IR spectra (DRIFT) were recorded on a Perkin-Elmer 1760 Fourier transform spectrophotometer equipped with a diffuse-reflectance attachment. ¹¹B NMR spectra were obtained at 64.2 MHz, and ¹H NMR were obtained at 200.1 MHz on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. All ¹¹B chemical shifts are referenced to BF₃·O(C₂H₅)₂ (0.0 ppm) with a negative sign indicating an upfield shift. All ¹H chemical shifts were measured relative to internal residual protons from the lock solvents and are referenced to Me₄Si (0.0 ppm). High-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. GC/MS analyses were performed on a Hewlett-Packard 5890 gas chromatograph equipped with a 5970 Series mass-selective detector. The composition of each component was established both by its observed *m/e* cutoff and by comparison of the calculated and observed isotope patterns in the parent and/or fragment envelopes.

Thermogravimetric analyses were obtained on a Perkin-Elmer TGA 7 thermogravimetric analyzer using an argon gas or breathing air purge. TGA/MS studies were performed on a Seiko Instruments Model 320 TG/DTA with a Fison Thermalab mass spectral analyzer. X-ray powder diffraction spectra were obtained on a Rigaku Geigerflex X-ray powder diffractometer. X-ray diffraction studies on single BN ceramic fibers were carried out on a MSC/R-AXIS IIC area detector employing graphite-monochromated Mo K α radiation. Ruthenium backscattering spectroscopy (RBS) measurements were obtained on a NEC Model 5SDH Pelletron tandem accelerator operating at 5.1 MeV. Mechanical studies of BN fibers were performed at Dow Corning Corp. on an Instron 1122 Mechanical Analyzer. Scanning electron microscopy was performed on a JEOL 6300 electron microscope.

Elemental analyses were performed at the Nesmeyanov Institute of Organoelement Compounds (INEOS), Moscow, Russia. Analyses were performed in duplicate and percentages are reported as the average of the two assays. Densities were measured by floatation in halogenated hydrocarbons.

Molecular Weight Analysis. Molecular weight distribution averages and weight-average intrinsic viscosity were determined by size-exclusion chromatography employing in-line viscometric detection (SEC/VISC). Chromatograms were obtained with a Model 150-CV SEC/VISC system (Waters Chromatography Inc.) operated at 35 °C.

The resulting Mark–Houwink relationship for polystyrene in THF at 35 °C was

$$[\eta] = 1.2175 \times 10^{-4} M^{0.712} \quad (2)$$

where M is the peak molecular weight of the calibrant.

A third-order polynomial was least-squares fitted to the log hydrodynamic volume versus retention volume data. From this universal calibration curve, hydrodynamic volume at each chromatographic data point, ϕ_i , was determined. Intrinsic viscosity at the corresponding data point, $[\eta]_i$, was calculated from the combined outputs of the VISC and DRI detectors following previously described¹⁰ methodology. Prior to these calculations, DRI and VISC chromatograms were corrected to account for the retention volume delay between the two detectors and band broadening due to axial dispersion. The delay volume and band broadening parameters were deter-

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Table 1. Synthesis and Polymer Composition

polymer	PBZ/amine/glyme (g/mL/mL)	time (h) at 75 °C	yield (g, %)	composition ^a
PB				(B _{3.0} N _{3.2} H _{~3.5-4})
PB-Δ	3.98/0/32	120	3.96, 100	(B _{3.0} N _{3.3} H _{~3.5-4})
DEA-PB-1	4.98/40/0	60	7.05, 98	(B _{3.0} N _{3.2} H _{~3.5-4})[NEt ₂] _{0.50}
DPA-PB-1	5.02/20/20	1	5.88, 85	(B _{3.0} N _{3.6} H _{~3.5-4})[NPn ₂] _{0.16}
DPA-PB-2	4.97/20/20	15	6.82, 98	(B _{3.0} N _{3.0} H _{~3.5-4})[NPn ₂] _{0.23}
DPA-PB-3	5.01/20/20	60	7.16, 94	(B _{3.0} N _{3.3} H _{~3.5-4})[NPn ₂] _{0.26}
DPA-PB-4	5.03/20/20	120	7.94, 98	(B _{3.0} N _{3.0} H _{~3.5-4})[NPn ₂] _{0.33}
DPA-PB-5	2.55/25/25	192	4.58, 97	(B _{3.0} N _{3.1} H _{~3.5-4})[NPn ₂] _{0.47}
HMD-PB-1	4.98/10/30	120	6.23, 100	(B _{3.0} N _{3.0} H _{~3.5-4})[N(SiMe ₃) _{0.88}] _{0.29}

^a See Experimental Section for elemental analyses.

mined by the program TRISEC (Viscotek Inc.) using chromatograms for the polystyrene calibrants. Concentrations at each chromatographic data point, c_i , were obtained from the DRI peak height, h_i , and the mass of polymer injected, m :

$$c_i = m(h_i)/(v_i) \sum h_i \quad (3)$$

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

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

$$M_i = \phi_i/[\eta]_i \quad (4)$$

Molecular weight distribution averages, M_n , M_w , M_z , and the weight-average intrinsic viscosity, $[\eta]_w$, were calculated by using the appropriate summations of M_i , $[\eta]_i$, and c_i across a chromatogram. Reported molecular weight and intrinsic viscosity averages are mean values of two determinations.

Data acquisition and reduction were provided by either a micro pdp 11/23+ computer (Digital Equipment Co.) or a 486 desktop computer. Data acquisition performed with the 11/23+ computer employed a modified version of program MOLWT3 (Thermo Separations Inc.). Data acquisition performed by the 486 desktop computer employed the program TRISEC (Viscotek Corp.). Universal calibration and molecular weight calculations made with the MOLWT3-acquired data employed customized software. The same calculations performed with TRISEC-acquired data employed calculation modules in the TRISEC software package.

Compositional Heterogeneity Analysis. The variation of composition across a polymer molecular weight distribution was determined by infrared spectroscopic analysis of collected SEC fractions. The approach employed generally followed methods previously described^{11,12} for the characterization of copolymer compositional heterogeneity. The use of this technique is, to the best of our knowledge, the first reported application to the analysis of compositional heterogeneity in inorganic polymers.

Specific conditions used in the present study were as follows: a Model LC-Transform (Lab Connections Inc.) was placed in-line with the SEC/VISC system and used to deposit eluting polymer fractions onto a Ge disk rotating at a constant angular speed of 10°/min. The deposition was performed by splitting off 15% of the eluting solution stream and devolatilizing the stream with a 20 psi flow of He heated to 51 °C. The fractions were deposited around the circumference of the Ge disk as a continuous polymer film. The chromatographic conditions used with the LC-transform were identical with those used for SEC/VISC molecular weight analysis described above. The offset between VISC, IR, and DRI chromatograms was determined with a monodisperse polystyrene standard by overlaying the polymer's Gramm-Schmidt reconstructed IR chromatogram and the corresponding VISC and DRI chromatograms.

Composition analysis was provided by a Model 800 FT-IR spectrophotometer (Nicolet Instrument Co.) which was used to measure the relative change in functional group content along the polymer film. Spectra were collected with a resolution of 4 cm⁻¹. The sample disk was rotated clockwise at 10°/min as dictated by the deposition conditions described above.

Preparation of Polyborazylene (PB). Polyborazylene was prepared by the literature method.^{5,9b} In a typical preparation of the polymer used in this study, borazine (56.57 g, 0.703 mol) was vacuum transferred into a 500 mL stainless steel reaction vessel, equipped with a stirbar and high-pressure stainless steel valve. The vessel was then submerged in a 70 °C oil bath for 48 h. The vessel was then cooled to -196 °C and attached to a vacuum line, and the evolved hydrogen removed. Any unreacted borazine was removed by vacuum evaporation at room temperature for 36 h. The polyborazylene was then removed from the reactor under an inert atmosphere as a white solid (49.06 g). Anal. Found for PB: B, 40.24%; N, 55.20%; H, 4.44%. The polymer was soluble in THF and glyme and exhibited spectroscopic properties and molecular weights similar to those previously reported.^{5,9}

Reaction of Polyborazylene (PB) with Diethylamine (DEA). In a typical reaction, a 4.98 g sample of PB was charged under an argon atmosphere into a 100 mL one-piece glass vessel equipped with a high-vacuum stopcock and stirbar. The addition of 40 mL of DEA via syringe completely dissolved the polymer. The vessel was then evacuated and sealed. The mixture was heated in an oil bath as summarized in Table 1. The vessel was then cooled to -196 °C, attached to a vacuum line, and the evolved hydrogen removed. Any volatile materials were then vacuum distilled from the flask at 25 °C for 18 h. Vacuum-line fractionation of these volatile products showed only unreacted DEA (-78 °C trap). The DEA-PB-1 polymer was removed from the vessel under an inert atmosphere and isolated as a moisture sensitive, white solid (7.05 g, 98% yield). Anal. Found for DEA-PB-1: B, 26.65%; N, 42.72%; C, 20.07%; H, 7.33%. NMR data for DEA-PB-1: ¹H NMR (δ , 200 MHz, THF-*d*₆) 6.0–3.6 (br, B–H and N–H), 3.0–1.9 (CH₂), 1.4–0.6 (CH₃); ¹¹B NMR (δ , 64.2 MHz, THF-*d*₆) ~32, ~28 ppm (br). In some samples, a quartet resonance at -13.5 ppm was also observed suggesting the formation of BH₃·NHEt₂. IR data for DEA-PB-1: 3440 (s) (N–H), 3240 (w), 2970 (s) (C–H), 2940 (s) (C–H), 2920 (s) (C–H), 2500 (s) (B–H), 2370 (m), 2330 (sh, m), 1640 (sh, m), 1450 (vs, br) (B–N), 1100 (m), 1060 (sh, m), 1010 (sh, w), 910 (s) (B–N), 760 (sh, m), 680 (s) cm⁻¹. The polymer was soluble in THF but only sparingly soluble in benzene. Upon heating, the polymer initially softens, but within minutes it begins to decompose with loss of hydrogen gas to produce a gel. Additional polymer properties are listed in Tables 1 and 2.

Reaction of Polyborazylene (PB) with Dipentylamine (DPA). A series of reactions were carried out in which 2.5–5.0 g samples of PB were charged under an argon atmosphere into a 100 mL one-piece glass vessel with a high vacuum stopcock and stirbar. The polymers were dissolved in a 1:1 v:v mixture (8 mL/g of PB) of glyme and DPA. The vessels were then evacuated and sealed. The mixtures were heated in an oil bath as summarized in Table 1. The vessels were then cooled to -196 °C, and attached to a vacuum line, and the evolved hydrogen was removed. Any volatile products were then vacuum distilled from the flasks at 50 °C for 22 h

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Table 2. Polymer Molecular Weights

polymer	M_z (g/mol)	M_w (g/mol)	M_n (g/mol)	M_w/M_n	$[\eta]_w$ (dL/g)
PB	18 750	2700	725	3.72	0.031
PB- Δ	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
DEA-PB-1	4 850	920	430	2.14	0.004
DPA-PB-1	18 800	2355	833	2.83	0.016
DPA-PB-2	32 750	2600	836	3.11	0.009
DPA-PB-3	14 300	1700	756	2.25	0.008
DPA-PB-4	4 310	930	444	2.09	0.008
HMD-PB-1	109 350	6670	1509	4.42	0.024

^a Gel observed.

followed by 70 °C for 2 h. NMR and GC/MS analyses of the volatile products showed only glyme and unreacted DPA. The DPA-PB polymers were removed from the vessels under an inert atmosphere and isolated as moisture-sensitive clear solids. Anal. Found for DPA-PB-1: B, 28.68%; N, 46.56%; C, 17.27%; H, 7.36%. DPA-PB-2: B, 27.98%; N, 39.33%; C, 24.19%; H, 7.52%. DPA-PB-3: B, 26.40%; N, 40.41%; C, 25.61%; H, 7.84%. DPA-PB-4: B, 24.20%; N, 35.13%; C, 29.67%; H, 7.97%. DPA-PB-5: B, 20.73%; N, 32.20%; C, 36.13%; H, 9.22%. NMR data for DPA-PB-5: ¹H NMR (δ , 200 MHz, THF-*d*₆) 6.2–3.6 (br, B–H and N–H), 2.90 (br, CH₂), 1.44 (br, CH₂), 1.31 (br, CH₂), 0.91 (br, CH₃); ¹¹B NMR (δ , 64.2 MHz, THF-*d*₆) ~29 ppm (br). IR data for DPA-PB-5: 3460 (s) (N–H), 2975 (s) (C–H), 2935 (s) (C–H), 2870 (s) (C–H), 2520 (s) (B–H), 2375 (m), 2330 (sh, m), 2280 (sh, w), 1430 (vs, br) (B–N), 1375 (s), 1264 (m), 1200 (m), 1140 (m), 915 (s), 770 (sh, m), 690 (s) cm⁻¹. Each of the polymers had similar NMR and IR spectra with the intensities of the peaks varying according to the amine content. Increasing the DPA content also led to improved solubility and meltability. For example, while PB is insoluble in benzene, DPA-PB-4 was partially soluble and DPA-PB-5 was very soluble. DPA-PB-4 and DPA-PB-5 could be melted without visible decomposition. Additional properties of the modified polymers are listed in Tables 1 and 2.

Reaction of Polyborazylene (PB) with Hexamethyl-disilazane (HMD). In a typical reaction, a 4.98 g sample of PB was charged under an argon atmosphere into a 100 mL one-piece glass vessel with a high-vacuum stopcock and stirbar. The polymer was dissolved in 40 mL of a 3:1 v/v mixture of glyme and HMD. The vessel was then evacuated and sealed. The mixture was heated in an oil bath as summarized in Table 1. The vessel was then cooled to -196 °C and attached to a vacuum line, and the evolved hydrogen was removed. Any volatile materials were then vacuum distilled from the flask at 50 °C for 22 h followed by 70 °C for 2 h. Vacuum line fractionation and NMR and GC/MS analysis of these volatile materials showed glyme and unreacted HMD (-78 °C trap) and trimethylsilane (1.22 g, 16.5 mmol; -196 °C trap). The HMD-PB polymer was removed from the vessel under an inert atmosphere and isolated as a moisture sensitive white solid (6.23 g). Anal. Found for HMD-PB-1: B, 31.30%; N, 45.04%; C, 10.18%; H, 6.03%. NMR data for HMD-PB-1: ¹H NMR (δ , 200 MHz, THF-*d*₆) 6.0–3.5 (br, B–H and N–H), 0.09 (br, Si–CH₃); ¹¹B NMR (δ , 64.2 MHz, THF-*d*₆) 30.9 ppm (br). IR data for HMD-PB-1: 3440 (s) (N–H), 2970 (s) (C–H), 2930 (m) (C–H), 2510 (s) (B–H), 2400 (sh, m), 1420 (vs, br) (B–N), 1280 (s), 1050 (w), 1010 (sh, w), 910 (s) (B–N), 860 (s), 780 (s, sh), 680 (s) cm⁻¹. The polymer was soluble in THF but only sparingly soluble in benzene. Upon heating HMD-PB-1 did not soften before decomposition. Polymer molecular weights are given in Table 2.

Control Experiments. A control experiment to determine any thermally induced molecular weight changes in the starting PB was carried out by charging a 3.98 g sample of PB under an argon atmosphere into a 100 mL one-piece glass vessel with a high-vacuum stopcock and stirbar. The flask was evacuated, and 32 mL of glyme was vacuum transferred into the flask. The vessel was then sealed and heated in an oil bath as described in Table 1. The vessel was then cooled to -196 °C and attached to a vacuum line, and the evolved

hydrogen was removed. Any volatile materials were vacuum distilled from the flask at 25 °C for 6 h, followed by 50 °C for 2 h. The white solid material (3.96 g) was then removed from the vessel under an inert atmosphere. Anal. Found for PB- Δ : B, 35.54%; N, 50.84%; C, 2.83%, H, 4.64%. The material showed signs of gelation and could not be fully dissolved in THF. Therefore, molecular weights could not be determined.

Reaction of Diethylborazine (DEB) with Dipentylamine (DPA). DEB (50 mg, 0.04 mmol) and DPA (500 mg, 3.2 mmol) were charged under an argon atmosphere into a NMR tube equipped with a vacuum stopcock (Chemglass part UP 9703-044). The tube was placed in a 75 °C oil bath for 190 h. Analysis of the reaction mixture by ¹¹B NMR and GC/MS showed mostly unreacted DEB and DPA, as well as 2,4-diethyl-6-(dipentylamino)borazine. DEB-DPA: ¹¹B NMR (64.2 MHz), 35.8 (s), 25.9 (s); cutoff *m/e*: 292 (2%), 235 (100%, P–C₄H₉). Smaller amounts (<30% of the amount of DEB-DPA) of material consistent with the formula BH₃·DPA (cutoff *m/e*: 170 (71%), 43 (100%)) and DEB-NH-DEB, (cutoff *m/e*: 287 (55%), 44 (100%)) were also observed by GC/MS in the reaction mixture.

Bulk Ceramic Conversion Reactions. Bulk polymer pyrolyses were carried out in a Lindberg 54000 series tube furnace with a Eurotherm 818P temperature control unit. Argon gas (99.999% pure) passed through a LabClear (No. DGP-250-R1) oxygen scavenger, or ammonia (anhydrous grade), were used as the purge gases. Alumina pyrolysis tubes were dried by heating to 1000 °C and cooled under argon.

Polymer samples of 1–2 g were weighed into alumina or BN boats under argon and quickly transferred into the pyrolysis tube. After purging the system for 1 h with the pyrolysis gas, the samples were heated at 10 °C/min to the final temperature, as described in Table 3. After pyrolysis, all manipulations of ceramics were carried out in the air. 1200 °C, Argon: Anal. Found for DEA-PB-1.1: B, 35.18%; N, 52.47%; C, 1.80%; H, 0.29%; HMD-PB-1.1: B, 38.47%; N, 53.78%; Si, 3.47%; C, 1.42%; H, 1.07%; DPA-PB-1.1: B, 38.57%; N, 52.33%; C, 4.23%; H, 0.88%; DPA-PB-2.1: B, 36.07%; N, 50.43%; C, 3.44%; H, 1.19%; DPA-PB-3.1: B, 38.49%; N, 50.55%; C, 3.74%; H, 0.87%; DPA-PB-4.1: B, 38.78%; N, 52.36%; C, 2.28%; H, 0.81%; 1200 °C, Ammonia: DPA-PB-3.2: B, 38.20%; N, 54.38%; C, 2.22%; H, 0.36%; DPA-PB-4.2: B, 40.17%; N, 51.72%; C, 0.00%; H, 0.78%; DPA-PB-5.1: B, 40.96%; N, 54.46%; C, 0.00%; H, 0.73%; PB.1: B, 36.15%; N, 55.03%; C, 0.00%; H, 0.48%. 1400 °C, Ammonia: DPA-PB-4.3: B, 35.53%; N, 54.03%; C, 0.00%; H, 0.74%; 1600 °C, Ammonia: DPA-PB-4.4: B, 38.59%; N, 53.64%; C, 1.11%; H, 0.66%. The DRIFT spectra of all ceramics showed absorptions characteristic of boron nitride. All ceramics had a density of ~1.8 g/cm³. Additional information about pyrolysis conditions and ceramic properties are provided in Table 3.

Results and Discussion

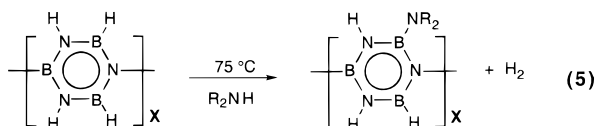
Polymer Synthesis and Characterization. As summarized in Table 1, PB readily reacts with secondary amines to yield modified polymers in high yields. While reactions with DEA did not need a solvent,

Table 3. Polymer Ceramic Conversion Reactions

ceramic	purge gas	final temp (°C)/hold time (h)	ceramic conversion (wt %)	composition ^a	color
DEA-PB-1.1	Ar	1200/2	63.3	B _{1.00} N _{1.15} C _{0.05} H _{0.09}	black
HMD-PB-1.1	Ar	1200/2	74.8	B _{1.00} N _{1.08} Si _{0.03} C _{0.03} H _{0.30}	gray
DPA-PB-1.1	Ar	1200/2	73.4	B _{1.00} N _{1.05} C _{0.09} H _{0.24}	black
DPA-PB-2.1	Ar	1200/2	64.7	B _{1.00} N _{1.08} C _{0.09} H _{0.35}	black
DPA-PB-3.1	Ar	1200/2	62.5	B _{1.00} N _{1.01} C _{0.09} H _{0.24}	black
DPA-PB-4.1	Ar	1200/2	57.4	B _{1.00} N _{1.04} C _{0.06} H _{0.22}	black
DPA-PB-4.2	NH ₃	1200/2	60.3	B _{1.00} N _{1.10} C _{0.00} H _{0.21}	gray
DPA-PB-4.3	NH ₃	1400/2	60.4	B _{1.00} N _{1.17} C _{0.00} H _{0.22}	gray
DPA-PB-4.4	NH ₃	1600/2	58.4	B _{1.00} N _{1.07} C _{0.03} H _{0.18}	gray
DPA-PB-5.1	NH ₃	1000/12	50.2	B _{1.00} N _{1.15} C _{0.05} H _{0.09}	light gray
DPA-PB-3.2 ^b	NH ₃	1000/12	62.1	B _{1.00} N _{1.03} C _{0.00} H _{0.20}	white
PB	NH ₃	1000/12	93.2	B _{1.00} N _{1.18} C _{0.00} H _{0.14}	white

^a See Experimental Section for elemental analyses. ^b Polymer samples were ground to a fine powder before pyrolysis.

reactions of PB with less polar amines required a polar, aprotic solvent, such as glyme, to dissolve the polymer.

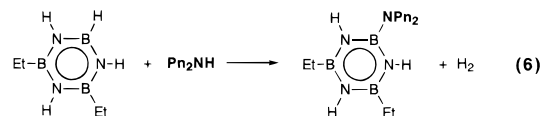


In a typical reaction, 2.55 g of PB and 25 mL of DPA dissolved in 25 mL of glyme were heated for 192 h at 75 °C in vacuo. Upon completion of the reaction, vacuum evaporation of the volatile components left 4.58 g (97% yield) of a moisture-sensitive, clear polymeric solid, DPA-PB-5, which by elemental analyses had a (B_{3.0}N_{3.1}H_{~3.5-4})[NPn₂]_{0.47} composition. The degree of modification and polymer composition could be controlled by varying the reaction time. For example, when samples of PB were reacted with dipentylamine under similar conditions for only 15 h, the amine content of the resulting DPA-PB-1 polymer, as determined by elemental analyses, decreased to (B_{3.0}N_{3.6}H_{~3.5-4})[NPn₂]_{0.16}. The highly modified polymers, such as DPA-PB-4 and DPA-PB-5, also showed increased solubility in organic solvents compared to the parent PB polymer. For example, while PB is soluble only in ethers, DPA-PB-4 was partially soluble and DPA-PB-5 very soluble in benzene.

The combined spectroscopic studies, model reactions, and analysis of volatile byproducts of the polymer-modification reactions indicate the reaction of the PB polymer with the secondary amines proceeds primarily through the formation of boron–nitrogen bonds, with the amines then becoming appended to the intact polyborazylene backbone. In the case of the DEA-PB and DPA-PB polymers, hydrogen was evolved in a nearly 1:1 molar ratio with the amine being incorporated into the polymer (as determined by elemental analysis) suggesting modification of the polymer proceeds primarily through dehydrocoupling of the amine N–H with the polyborazylene B–H. These conclusions are also supported by the spectral data for these polymers. Thus, with increasing modification the IR spectra of the DPA-PB polymers show an increase in the C–H stretch (2950 cm⁻¹) relative to the N–H stretch (3450 cm⁻¹) and a corresponding decrease in the B–H stretch (2500 cm⁻¹). The ¹¹B NMR spectra of the DEA-modified polymers show two overlapping broad resonances, with one centered at 32 ppm and the other at 28 ppm. The latter chemical shift is consistent with that expected for a borazine–boron bound to an elec-

tronegative ring substituent such as nitrogen.¹³ The two resonances were not resolved in the ¹¹B NMR spectra of the DPA-PB polymers. The ¹H NMR spectra showed N–H and B–H resonances characteristic of polyborazylene⁵ in the range of 6.0–3.5 ppm, as well as broad resonances in the 3.0–0.0 ppm region expected for the alkyl groups on the amines.

Additional support for the proposed dehydrocoupling reaction leading to the formation of the DEA-PB and DPA-PB polymers, comes from the reaction of diethylborazine (DEB) with DPA which was found to produce 2,4-diethyl-6-(dipentylamino)borazine (DEB-DPA) as the predominant product. The ¹¹B NMR shift (25.9 ppm) of the amino-substituted boron in DEB-DPA is similar to that observed in the DPA-PB polymers.



Although primary amines are known to induce ring opening of borazine,¹⁴ only small amounts of BH₃·DPA were observed in the above reaction of DPA with DEB. Likewise, only in the case of the DEA and DPA reactions with lower molecular weight samples of PB was there any evidence for the formation of borane adducts (BH₃·DEA and BH₃·DPA) that would be a product of ring-opening reactions. When the PB samples were first precipitated from pentane or when higher molecular weight polyborazylene samples were used, their ¹¹B and ¹H NMR spectra showed no formation of these borane adducts following modification. Likewise, analysis of the volatile materials from the reaction showed only unreacted amine and glyme. Although small amounts of μ-aminobis(2,4-diethylborazine) (DEB-NH-DEB) were also observed in the reaction of DEB with DPA (eq 6), no hydrocarbons arising from cleavage of the amine carbon–nitrogen bonds were detected in the volatile products of the polymer modification reactions with DPA.

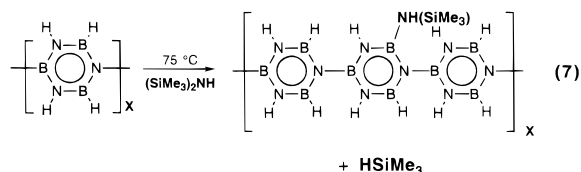
The PB polymer was also found to react readily with hexamethyldisilazane (HMD), but in contrast to the reactions with DEA and DPA, the reaction does not

(13) (a) Gaines, D. F.; Borlin, J. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; pp 245–246. (b) Nöth, H.; Wrackmeyer, B. In *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Springer-Verlag: New York, 1978; pp 188–196.

(14) Gaines, D. F.; Borlin, J. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975; p 257.

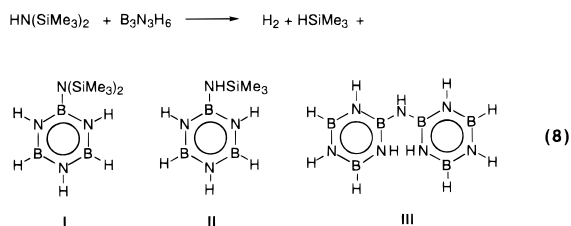
appear to involve dehydrocoupling of the amine and polymer. Thus, in the reaction of HMD with PB to produce HMD-PB-1, hydrogen was produced in only a 1:10 ratio with the amount of amine incorporation into the polymer. This amount of hydrogen is similar to that formed upon heating PB without HMD (to produce PB- Δ) for a comparable time and is consistent with the normal PB cross-linking reaction depicted in Figure 1.

Fractionation of the volatile byproducts from the synthesis of HMD-PB-1, however, showed that significant quantities of trimethylsilane were produced in the reaction. In a typical synthesis of HMD-PB-1 which employed 4.98 g of PB (63.8 mmol of $B_3N_3H_{3.5}$ units), it was found that 1.22 g (16.5 mmol) of trimethylsilane was produced. The formation, as shown in eq 7, of the



HMD-PB-1 polymer, with its analytically determined $(B_{3.0}N_{3.0}H_{3.6})[NH(SiMe_3)]_{0.29}$ composition would require the elimination of ~ 18.5 mmol of trimethylsilane, which is in good agreement with the experimentally observed quantity of evolved $HSiMe_3$.

The above results suggest that reaction of a polyborazylene B-H group with hexamethyldisilazane involves addition to the N-Si bond of the silazane with the elimination of trimethylsilane, as shown in eq 7. These conclusions are also consistent with previous studies¹⁵ of the reaction of borazine with HMD, which was found to produce a number of B-N coupled products, including those (II and III) resulting from trimethylsilane elimination reactions:



Although the ^{11}B NMR spectrum of the HMD-PB-1 polymer showed only one broad peak at ~ 31 ppm, the 1H NMR spectra showed a resonance characteristic of the presence of $-SiMe_3$ groups at ~ 0.09 ppm. The IR spectra show the expected borazynyl N-H (3450 cm^{-1}) and B-H stretches (2500 cm^{-1}) along with a C-H (2950 cm^{-1}) absorption from the pendent HMD groups. Separate N-H absorption bands from the pendent $-NH-SiMe_3$ groups and the polymer N-H groups were, however, not resolved.

It would also be expected that a polymer-bound $NHSiMe_3$ group would be reactive toward a second trimethylsilane elimination reaction with another borazynyl ring on a different polymer chain, to produce an amine cross-linked structure similar to that shown for compound III in eq 8. Indeed, as discussed in the

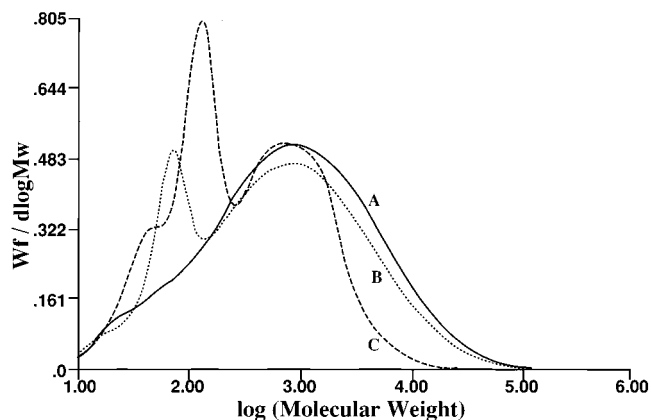


Figure 2. Differential molecular weight distribution for (A) PB, (B) DPA-PB-1, and (C) DPA-PB-4.

next section, molecular weights of the HMD-PB polymers were found to increase significantly upon modification with HMD.

Molecular Weight and Compositional Heterogeneity Analysis. Representative molecular weight distributions for the PB and DPA-PB polymers are shown in Figure 2. The molecular weight distribution for DPA-PB-1 is shifted to lower molecular weight compared to PB and produced an extra low molecular weight mode. The changes apparent in Figure 2 were reflected in molecular weight distribution averages and weight-average intrinsic viscosities listed in Table 2. For example, modification of PB with DPA decreased polymer molecular weight and intrinsic viscosity with increasing reaction time, particularly after 15 h of reaction. When a sample of PB was heated in glyme at $75^\circ C$ for 120 h to yield PB- Δ ; however, an increase in molecular weight was noted, with some material becoming insoluble due to cross-linking.

The trends in molecular weight and intrinsic viscosity point to polymer chain degradation, but no insight into the mechanism of degradation was provided. However, the observation of ring cleavage products in the DEA-PB and DPA-PB polymers, discussed earlier, is consistent with solution properties data.

When the IR chromatogram recorded in the ν_{C-H} region for DPA-PB-1 was overlaid with its DRI chromatogram, direct modification of the polymer by DPA was confirmed by the detection of IR absorbance at all retention volumes of the corresponding DRI chromatogram. However, there were relative intensity differences between IR and DRI chromatograms indicating strong compositional heterogeneity. Greater IR intensity in the lower molecular weight region of the chromatogram pointed to DPA enrichment of lower molecular weight fractions.

A more detailed picture of compositional differences across the polymer's molecular weight distribution was revealed by recording the full IR spectrum of DPA-PB-1 at representative retention volumes indicated in Figure 3 (top). The corresponding IR spectra in Figure 3 (bottom) were dominated by the ν_{B-H} ($2600\text{--}2400\text{ cm}^{-1}$) and the characteristically sharp ν_{N-H} ($3450\text{--}3300\text{ cm}^{-1}$) of the borazine ring in the higher molecular weight regions (A and B) of its DRI chromatogram. The IR spectra of the polymer's lower molecular weight fractions (C and D) yielded ν_{C-H} modes ($2700\text{--}2900\text{ cm}^{-1}$)

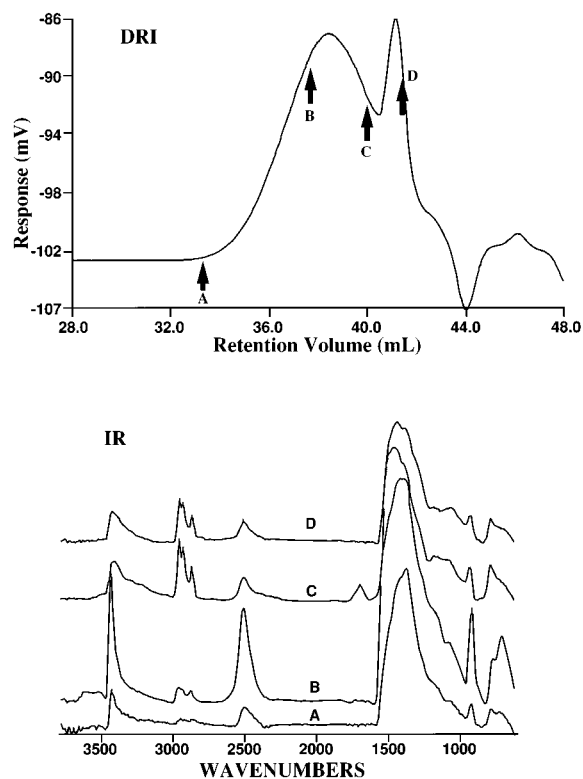


Figure 3. Top: DRI chromatogram of DPA-PB-1. Bottom: IR spectra of DPA-PB-1. Designations (A)–(D) indicate retention volumes at which IR spectra were recorded.

with intensities comparable to those of ν_{B-H} . Other DPA-modified polymers and DEA-PB-1 showed compositional variations similar to those of DPA-PB-1, with changes in the IR spectra reflecting the degree of modification. For example, at the given representative retention volumes indicated in Figure 4 (top), the IR spectra, Figure 4 (bottom), of DPA-PB-5, showed greater ν_{C-H} intensity relative to ν_{B-H} intensities.

Only one modified polymer, HMD-PB-1, exhibited an increase in molecular weight relative to PB (see Table 2). The molecular weight increase was accompanied by a 22.6% decrease in $[\eta]_w$, suggesting chain branching as a possible source of molecular weight growth. The observed byproducts of the polymer modification reaction and the model compound studies described above provide additional support for branching in HMD-PB-1.

The representative retention volumes in Figure 5 (top) of HMD-PB-1 and the corresponding infrared spectra in Figure 5 (bottom) were consistent with amine functionalization. Compositional heterogeneity was also indicated by the increase in ν_{C-H} intensity relative to that of ν_{B-H} as a function of increasing elution volume as seen in fractions (A) and (C).

Fiber Spinning and Ceramic Conversion Reactions. Previous XRD studies of the PB polymer have shown a broad diffraction peak in the $\sim 26\text{--}24^\circ$ 2θ range consistent with the polymer having a layered ($d = \sim 3.4\text{--}3.7$ Å) structure in the solid state similar to that found for boron nitride.⁵ In the DPA-PB polymers (Figure 6), the shift of this peak to lower angles $\sim 20^\circ$ 2θ ($d = \sim 4.4$ Å) is consistent with the steric effect of the DPA pendent groups increasing the distance between polymers. The DPA groups would, therefore, be

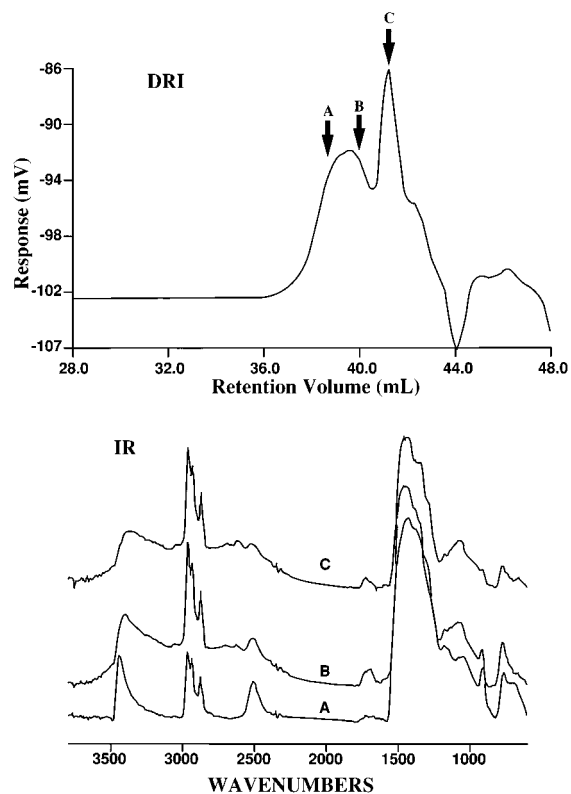


Figure 4. Top: DRI chromatogram of DPA-PB-5. Bottom: IR spectra of DPA-PB-5. Designations (A)–(C) indicate retention volumes at which IR spectra were recorded.

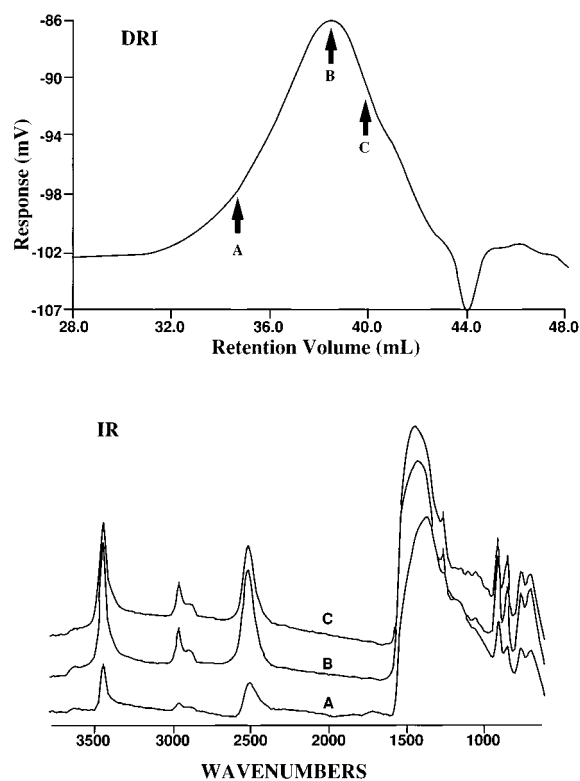


Figure 5. Top: DRI chromatogram of HMD-PB-1. Bottom: IR spectra of HMD-PB-1. Designations (A)–(C) indicate retention volumes at which IR spectra were recorded.

expected to inhibit the polymer cross-linking reaction depicted in Figure 1, not only because there are fewer B–H groups on the polymer but also because two

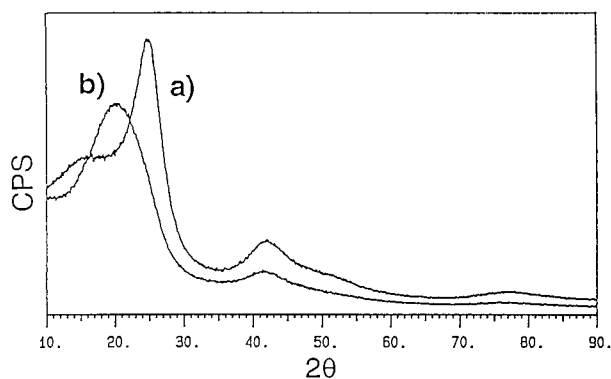


Figure 6. Powder XRD spectra of (a) PB and (b) DPA-PB-4 polymer powders.

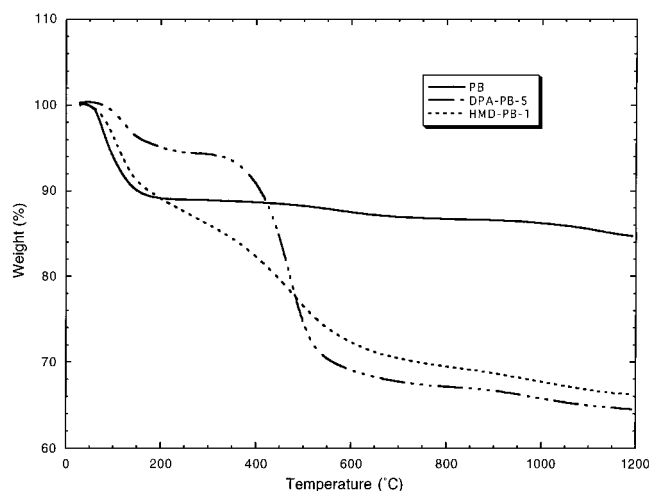


Figure 7. TGA studies to 1200 °C under argon of PB and secondary amine-modified PB.

polymer chains cannot approach each other as efficiently as in the parent PB polymer. In agreement with these conclusions, TGA studies of the DPA polymers showed a reduction in the low-temperature cross-linking reaction, with the onset of weight loss increasing to ~100 °C (Figure 7). On the other hand, TGA studies of the HMD-PB polymers showed that because of the introduction of new cross-linking reactions involving the elimination of trimethylsilane from the pendent NH-SiMe₃ groups, these polymers undergo initial weight losses at lower temperatures (75 °C).

Similar to Kimura's earlier studies¹⁶ of laurylamine-containing poly(aminoborazines), the DEA and DPA pendants were found to lower the glass transition temperatures of the polymers. Thus, while DSC studies of PB have shown only a broad endotherm at ~140 °C attributed to the cross-linking of the polymer, DSC studies of DPA-PB-5 showed the alkyl groups of the pendent DPA groups serve as efficient plasticizers, reducing the T_g of the polymer to 90 °C, which is below the cross-linking temperature observed in the TGA. These results indicated that DPA-modified polymers should be excellent candidates for melt-spinning. In-

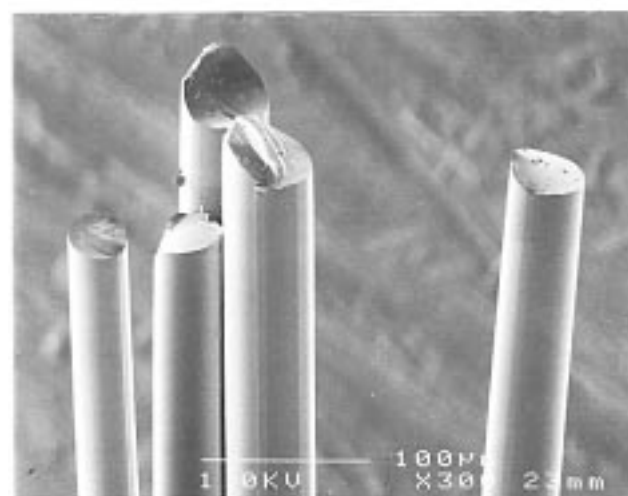
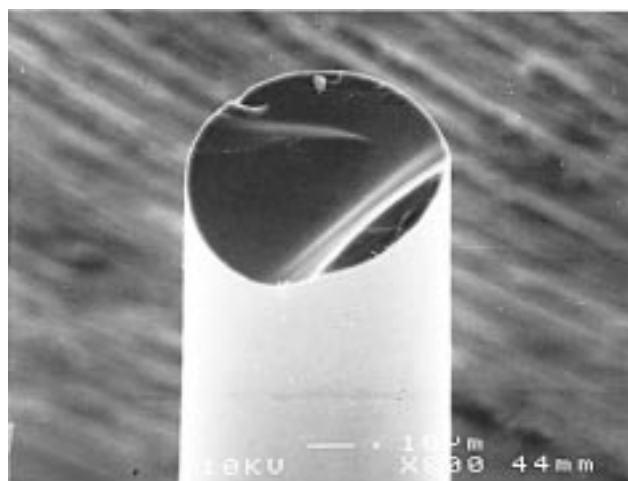
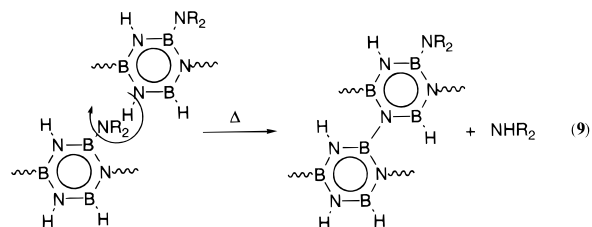


Figure 8. SEM micrographs of DPA-PB-5 polymer fibers.

deed, as shown in the scanning electron micrograph in Figure 8, high-quality, flexible DPA-PB-5 polymer fibers were achieved by extruding polymer melts from a crude ram extruder built from a 2 mL syringe heated at 75–95 °C. Fiber draw-down and take-up at a constant rate of 30 m/min were achieved by a geared motor to form a continuous filament of approximately 30–40 μm in diameter. The fibers were cured by brief exposure to air using the procedure described by Kimura.¹⁶ As shown in the micrograph, the polymer fibers were uniform and free of voids, despite the crude melt-spinning apparatus.

Even when carried out under an argon atmosphere, bulk pyrolyses of DEA-PB and DPA-PB powders to 1200 °C produced ceramics with only 2–4% carbon (Table 3). The amines serve as efficient leaving groups via deamination reactions, such as shown in eq 9, that can occur during the cross-linking of polymer chains.



(16) (a) Kimura, Y.; Kubo, Y.; Hayashi, N. *Comput. Sci. Technol.* **1994**, *51*, 173–179. (b) Kimura, Y.; Kubo, Y. In *Inorganic and Organometallic Polymers II: Advanced Materials and Intermediates*; Wisian-Neilson, P., Allcock, H. R., Wynne, K. J., Eds.; ACS Symposium Series 572; American Chemical Society: Washington, DC, 1993; pp 375–388. (c) Kimura, Y.; Kubo, Y.; Hayashi, N. *J. Inorg. Organomet. Polym.* **1992**, *2*, 231–242.

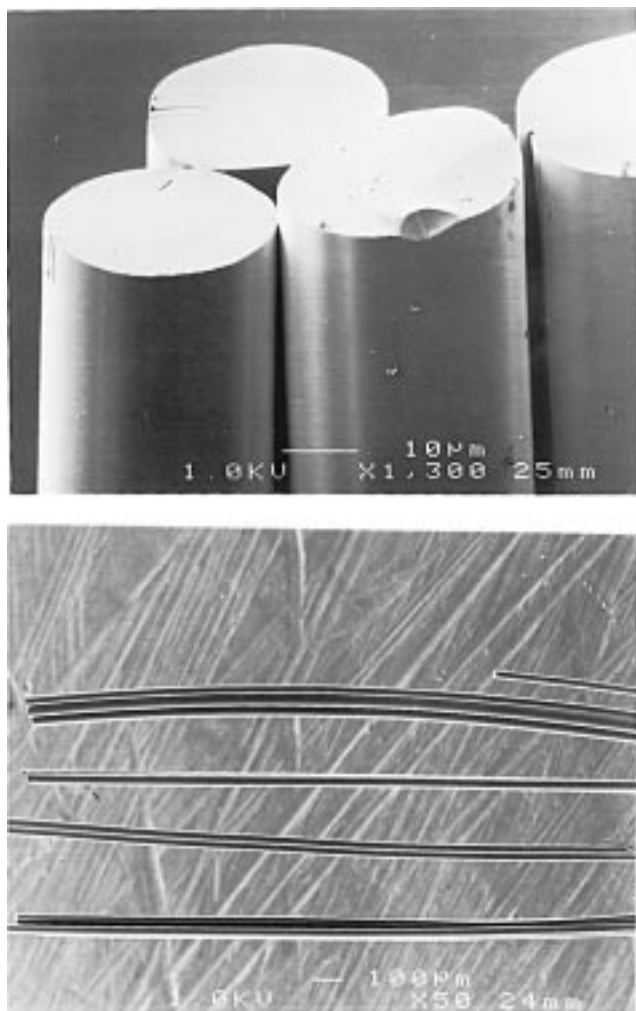


Figure 9. SEM micrographs of DPA-PB-5 derived BN ceramic fibers.

TGA/MS studies of the DEA-PB and DPA-PB polymers indicate the major weight loss in these polymers occurs near 500 °C and is essentially over by 800 °C with the observed ceramic yields being near the values predicted for the loss of the dialkylamine pendants and hydrogen, but with retention of the polyborazylene boron and nitrogen atoms. TGA (Figure 7) and TGA-MS studies of HMD-PB-1 indicate the loss of $(\text{SiMe}_3)_2\text{-NH}$ beginning near 75 °C, followed by loss of HSiMe_3 at ~300 °C. Bulk pyrolysis of HMD-PB-1 under argon to 1200 °C produced a gray ceramic with a slightly lower carbon content (1.4%) than the DEA-PB and DPA-PB derived ceramics (2–4%), but the material also retained a significant amount of silicon (3.5%, Table 3).

Low-carbon-content white BN powders could be readily produced by pyrolyses of the DEA-PB and DPA-PB polymers under ammonia. For example, pyrolyses of DPA-PB-4 held at 1200, 1400, or 1600 °C for 2 h under ammonia produced gray ceramics with carbon contents <1.3% (Table 3), while pyrolyses of a finely ground DPA-PB-3 powder to 1000 °C for 12 h under ammonia, yielded white DPA-PB-3.2 with a composition of $\text{B}_{1.00}\text{N}_{1.03}\text{C}_{0.00}\text{H}_{0.20}$.

Pyrolysis of the cured DPA-PB polymer fibers under ammonia to 1000 °C produced clear, flexible boron nitride fibers of ~30 μm diameter. SEM micrographs (Figure 9) also show that these ceramic fibers are

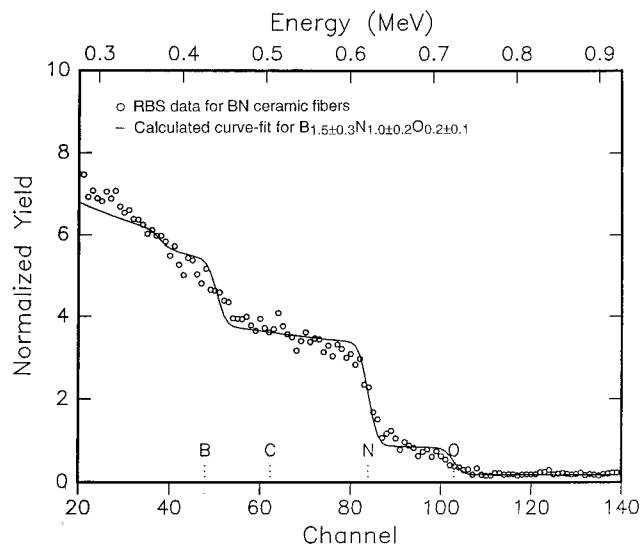


Figure 10. Rutherford backscattering spectrograph of DPA-PB-5 derived BN ceramic fibers sintered at 1000 °C.

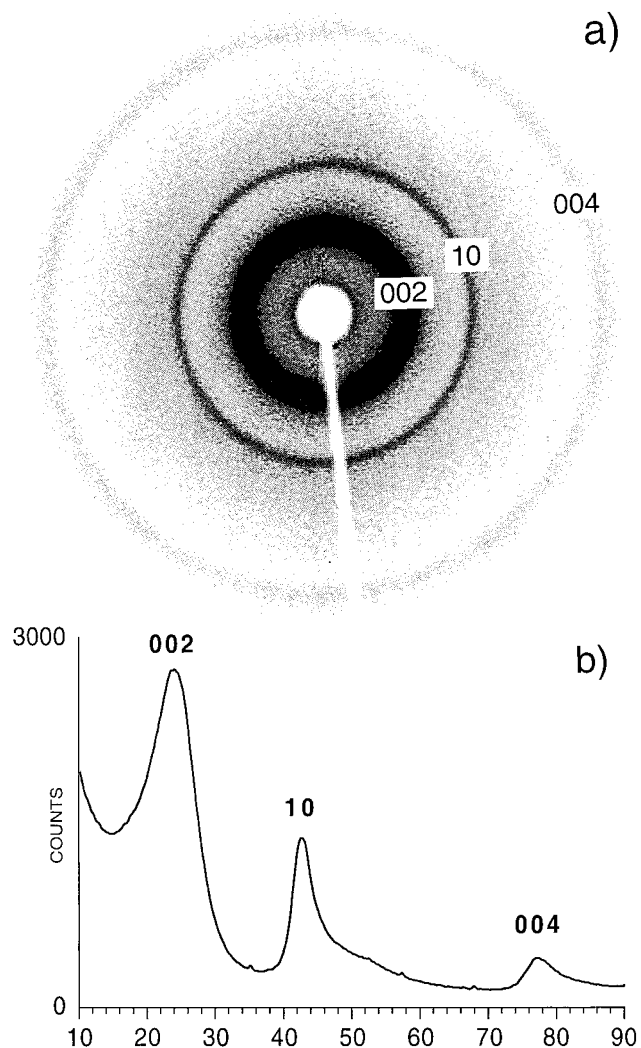


Figure 11. X-ray diffraction spectra of (a) a single DPA-PB-5 derived BN ceramic fiber. (b) DPA-PB-4 powder pyrolyzed under ammonia at 1000 °C for 12 h.

smooth and uniform. Densities, measured by floatation in halogenated hydrocarbons, for DPA-PB-5 derived BN ceramic fibers (of 1.8 g/cm^3) are comparable to those for BN prepared from powders of either DPA-PB-5 or PB

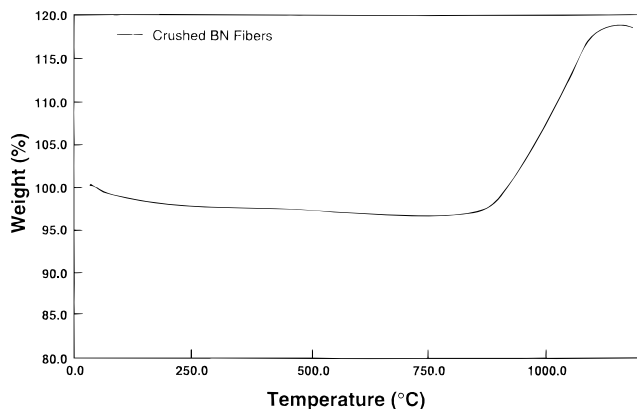


Figure 12. TGA analysis of the oxidation of crushed DPA-PB-5 derived BN fibers under breathing air at 5 °C/min.

powders. Surface analysis of the fibers by Rutherford backscattering spectroscopy (Figure 10) indicated a composition of $B_{1.5\pm 0.3}N_{1.0\pm 0.2}O_{0.2\pm 0.1}$ with no detectable carbon. The high boron content and presence of oxygen are consistent with the air cure that should yield a B_2O_3 -enriched surface.

The X-ray diffraction spectra of a *single* ceramic fiber (Figure 11a) showed characteristic diffractions of the 002, 10, and 004 planes of turbostratic BN and exhibited a degree of crystallinity similar to powder samples of either DPA-PB-4 (Figure 11b) or PB pyrolyzed under the same conditions. DRIFT spectra of powdered ceramic fibers showed only absorptions characteristic of boron nitride.³ As shown in Figure 12, oxidation studies under air of crushed DPA-PB derived ceramic fibers show the onset of oxidation occurs near 875 °C, which is similar to the oxidation behavior of BN derived from the PB polymer.⁵

Preliminary measurements of the mechanical properties of crude 30 μm fibers gave typical tensile strengths of 0.18 GPa and elastic moduli of ~ 14 GPa. These values are lower than the poly(aminoborazine)-derived BN fibers reported by Kimura;¹⁶ however, because strengths are strongly dependent on the fiber diameter and processing parameters, significant increases in DPA-PB derived BN fiber strengths are expected with the use of a more sophisticated spinning apparatus and higher temperature sintering.

Conclusions

Boron nitride ceramic fibers are of technological importance because of their potential uses in the

fabrication of composite materials with enhanced oxidation resistance, thermal stability, infrared and microwave transparency, and/or electrical insulation properties.³ Seminal studies by Economy,¹⁷ Paciorek,¹⁸ Paine,¹⁹ and Kimura¹⁶ have clearly shown that polymeric precursors can achieve the formation of such fibers, but have, in addition, demonstrated the need for new routes to preceramic polymers with improved processing and ceramic-conversion properties. In this paper a new precursor route to BN ceramic fibers has been demonstrated through the use of a melt-spinnable polymer based on a polyborazylene backbone. The new method is particularly attractive since the convenient, high-yield syntheses of the PB polymer,^{5,9b} and its precursor, borazine,⁹ as well as the high yields of the amine-polyborazylene reactions (typically >97%), provide efficient and economical routes to the modified polymers. Furthermore, it is expected that the properties of the polyborazylene polymer may now be systematically tailored for use in different technological applications by modification with the wide variety of available secondary amines.

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