Communications

Dipentylamine-Modified Polyborazylene: A New, Melt-Spinnable Polymeric Precursor to Boron Nitride Ceramic Fibers

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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.[1−3] Seminal studies by Economy,[4] Paciorek,[5] Paine,[6] and Kimura[7] have clearly shown that polymeric precursors can achieve the formation of such fibers but have, in addition, demonstrated the need for new "second-generation" preceramic polymers with improved processing and ceramic-conversion properties. In this communication, we report the synthesis and preliminary fiber-spinning studies of a new polymer, dipentylamine-modified polyborazylene, **DPAPB**, that has now proven to be an attractive melt-spinnable polymeric precursor to boron nitride fibers.

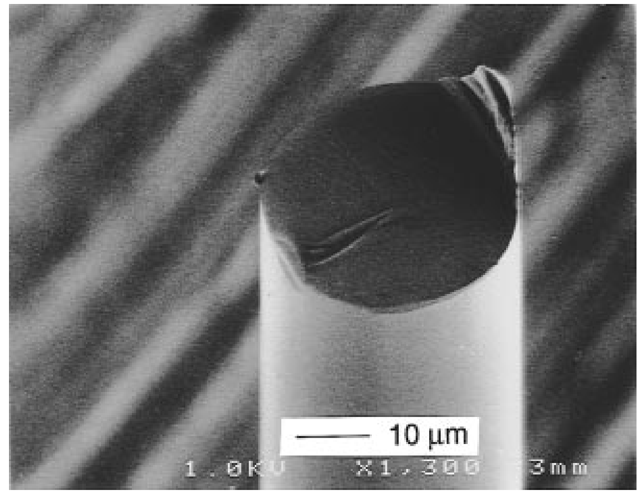
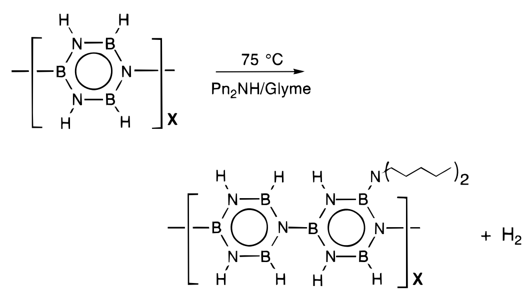


Figure 1. Scanning electron micrographs of a **DPAPB** polymer fiber.

In a typical reaction, the **DPAPB** polymer was synthesized by reacting 2.55 g of polyborazylene, $[B_3N_3H_{\sim 4}]_x$,[8] with 25 mL of dipentylamine dissolved in 25 mL of glyme for 192 h at 75 °C in vacuo. Upon completion of the reaction, vacuum evaporation of the volatile components left 4.58 g (91% yield based on the composition below) of a clear polymeric material:



Elemental analysis[9] of the modified polymer and measurements of the hydrogen evolved during the reaction are consistent with a $[(B_3N_3H_{3.5})(NPn_2)_{0.49}]_x$ composition. The ^{1}H NMR, ^{11}B NMR, and DRIFT spectra[10] suggest a polymer structure composed of a polyborazylene backbone containing boron-bonded dipentylamine substituents.

In contrast to the parent $[B_3N_3H_{\sim 4}]_x$ polymer,[8] **DPAPB** shows solubility in hydrocarbons and, most significantly, becomes fluid without weight loss when heated

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(9) Anal. Calcd for $(B_3N_3H_{3.5})(NPn_2)_{0.49}$: B, 20.98%; N, 31.63%; C, 38.08%; H, 9.31%. Anal. Found: B, 20.73%; N, 32.20%; C, 36.13%; H, 9.22%.
(10) **DPAPB:** ^{1}H NMR (δ, 200 MHz, THF-d_8), 6.2−3.6 (br, BH and NH), 2.90 (br, CH_2), 1.44 (br, CH_2),1.31 (br, CH_2), 0.91 (br, CH_3); ^{11}B NMR (δ, 64.2 MHz, THF-d_8) 34−23 ppm (br); DRIFT: 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}.

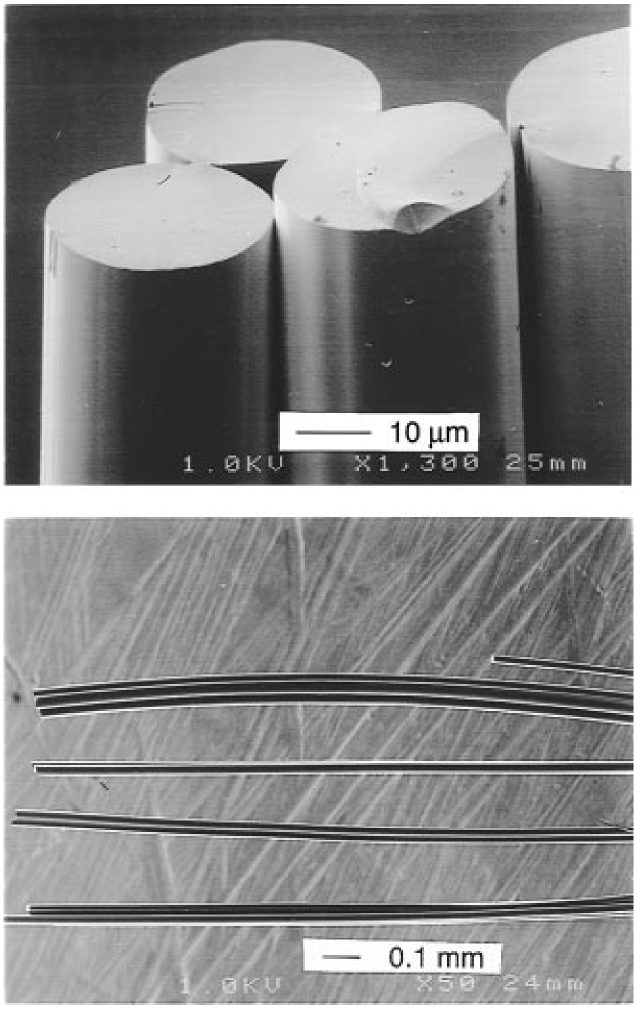

Figure 2. Scanning electron micrographs of **DPAPB**-derived BN ceramic fibers sintered at 1000 °C.

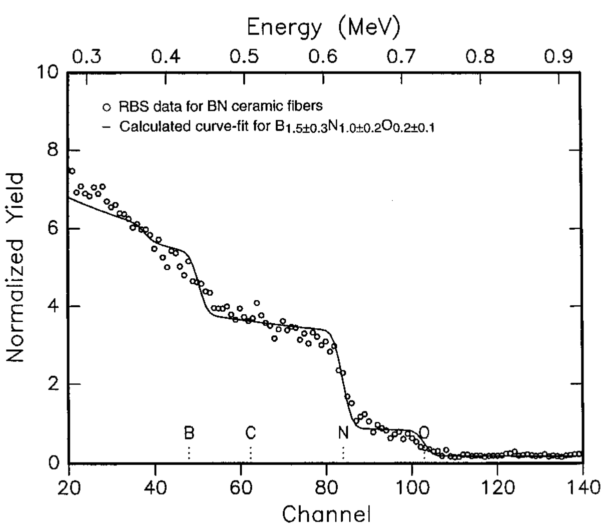

Figure 3. Rutherford backscattering spectrograph of **DPAPB**-derived BN ceramic fibers sintered at 1000 °C.

between 75 and 95 °C.[11] Although the parent polyborazylene is an excellent precursor to boron nitride,[8] upon heating it cross-links before melting, preventing its use in the melt-spinning of BN fibers. In **DPAPB**, as demonstrated by Kimura's earlier studies[7] of laurylamine-containing poly(aminoborazines), the substitution of some of the reactive B−H hydrogens of the borazine ring of the $[B_3N_3H_{\sim4}]_x$ polymer with dipentylamine groups both lowers the melting temperature and retards the cross-linking reaction, thereby making **DPAPB** an excellent candidate for melt-spinning.

As shown in the scanning electron micrograph (Figure 1), high-quality **DPAPB** polymer fibers were achieved by extruding polymer melts from a crude ram extruder built from a 2 mL syringe, equipped with a 20-gauge needle, 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.[7] Despite the crude melt-spinning apparatus, the polymer fibers were flexible, uniform, and free of voids.

Pyrolysis of the cured polymer fibers under ammonia to 1000 °C produced clear, flexible boron nitride fibers of ∼30 μm diameter. SEM micrographs (Figure 2) also show that these ceramic fibers are smooth, uniform, and

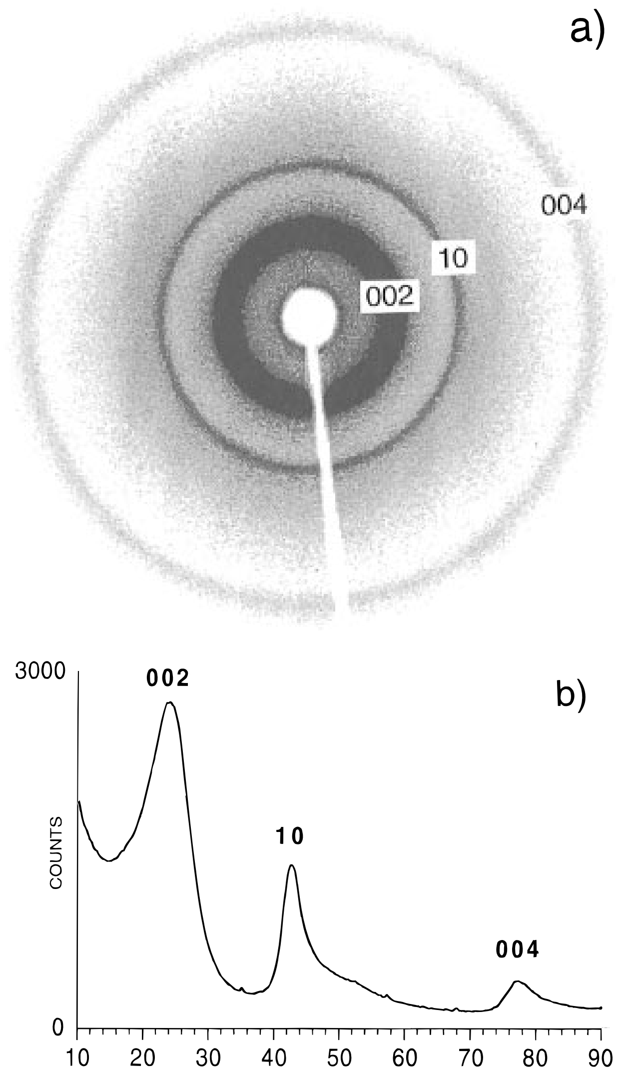

Figure 4. (a) XRD spectrum from a single BN ceramic fiber derived from **DPAPB**.[14] (b) Powder X-ray diffraction spectrum of BN from the bulk pyrolysis of **DPAPB**.

(11) A DSC study of the polymer showed exotherms centered at 90, 177, and 333 °C, with the exotherm at 90 °C attributed to the glass transition (T_g) of the polymer. TGA studies showed decomposition did not begin until 95 °C. Unmodified polyborazylene exhibits a broad endotherm at 125 °C, but does not melt, and loses weight above 80 °C, as described in ref 8.

dense.[12] Surface analysis of the fibers by Rutherford backscattering spectroscopy (Figure 3) indicated a composition of $B_{1.5\pm0.3}N_{1.0\pm0.2}O_{0.2\pm0.1}$ with no detectable carbon.[13] The high boron content and presence of oxygen are consistent with the air cure that should yield a B_2O_3-enriched surface.

X-ray diffraction studies on both single ceramic fibers[14] (Figure 4a) and powders from bulk pyrolyses (Figure 4b)[13] showed diffractions at d = 3.70, 2.12, and 1.24 Å corresponding to the 002, 10, and 004 planes, respectively, of turbostratic BN.[1,2] DRIFT spectra of powdered ceramic fibers showed only absorptions characteristic of boron nitride.[1,2]

Oxidation studies[15] under air of crushed ceramic fibers, as well as BN from bulk **DPAPB** pyrolysis,[13] show the onset of oxidation occurs near 875 °C, which is similar to the oxidation behavior of BN derived from unmodified polyborazylene.[8]

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 10 μm BN fibers reported by Kimura;[7] however, because strengths are strongly dependent on the fiber diameter and processing parameters, significant increases in **DPAPB**-derived BN fiber strengths are expected with the use of a more sophisticated spinning apparatus and higher temperature sintering.[7]

In summary, a new route to BN ceramic fibers has been demonstrated through the use of a melt-spinnable polymer based on a purely poly(borazinyl) backbone. The new method is particularly attractive since the convenient, high-yield syntheses of the $[B_3N_3H_{\sim4}]_x$ polymer[8] and its precursor, borazine,[16] provide efficient routes to the **DPAPB** 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 dialkylamines.

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(12) Densities, measured by floatation in halogenated hydrocarbons, of 1.8 g/cm³ for **DPAPB**-derived BN ceramic fibers are comparable to those for bulk BN from **DPAPB** powder pyrolysis (see ref 13), and for BN derived from unmodified polyborazylene, see ref 8.

(13) When bulk pyrolyses of 1−2 g samples of the **DPAPB** polymers were carried out under ammonia to 1000 °C for 12 h, BN ceramics were produced in greater than 50% ceramic yield and over 98% chemical yield. Anal. Calcd for BN: B, 43.56%; N, 56.44%. Anal. Found: B, 40.96%; N, 54.46%; C, <0.5%; H, 0.73%. Density = 1.8 g/cm³. The **DPAPB**-derived ceramics exhibited similar crystallinity as ceramics obtained from unmodified polyborazylene under similar conditions.

(14) MSC/R-AXIS IIc area detector employing graphite-monochromated Mo Kα radiation.

(15) Performed on a Perkin Elmer TGA 7 at 5 °C/min under breathing air.

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