Thermally Induced Borazine Dehydropolymerization Reactions. Synthesis and Ceramic Conversion Reactions of a New High-Yield Polymeric Precursor to Boron Nitride

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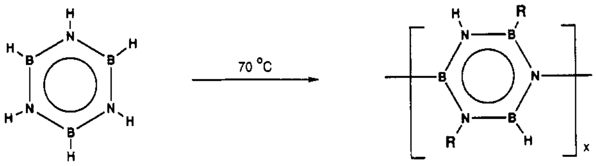
Recent work in our laboratory has focused on the development of new polymeric and molecular precursors to boron-based ceramic materials. For example, we have demonstrated that upon ammonia thermolysis, poly(vinylpentaborane),[3,4] poly(vinylborazine),[4,5] and dibromoborane–dimethyl sulfide[6] may each serve as efficient precursors to boron nitride.[7] In an effort to develop new boron nitride precursors that give improved ceramic yields and/or do not require the use of ammonia during the ceramic conversion step, we have investigated the syntheses of new types of borazine-based polymers. We report herein the simple high-yield synthesis of a new soluble poly(borazylene) polymer that has proven to be an almost ideal chemical precursor to boron nitride.

Small dehydrodimers and oligomers of alkylated borazine have previously been prepared[8-12] primarily by either metathesis or coupling reactions; however, owing to borazine's greater reactivity, these procedures are unsuitable for the generation of analogous species based on the parent $B_3N_3H_6$ compound. The N-B coupled dimer 1:2′-$[B_3N_3H_5]_2$ has been obtained in low yields from the decomposition of liquid borazine at room temperature over several months[13] and from the gas-phase photolytic[14] or pyrolytic[15] reactions of borazine. The latter two studies also reported the formation of insoluble solids that were proposed to have fused borazine polycyclic structures. Several studies[13,16] of the stability of liquid borazine have also reported the formation of white low volatility (perhaps polymeric) solids, but these materials were not identified. Thus, no tractable dehydrocoupled polymers derived from the parent borazine have previously been characterized.

We have now found that simply heating liquid borazine in vacuo at moderate temperatures results in a dehydrocoupling reaction to produce *soluble* polymeric materials in excellent yields (eq 1).



(1)

R = H or Borazinyl

In a typical reaction, 3.15 g of borazine were heated in vacuo at 70 °C in a one-piece 50-mL reaction flask. The reaction was continued with periodic degassing until the liquid became sufficiently viscous that stirring could not be continued (~48 h). The volatile contents of the flask were then vacuum evaporated, leaving a white solid (2.84 g, 90% yield). This material was then completely dissolved in glyme and subsequently precipitated by addition of pentane to give a fine white powder (1.93 g, 61% yield). Elemental analyses of the crude and purified materials are consistent with empirical formulas of $B_{2.7}N_{3.0}H_{3.0}$ and $B_{3.1}N_{3.0}H_{2.7}$, respectively (poly(borazylene) = $B_3N_3H_4$) suggesting the formation of a branched-chain or partially cross-linked structure.[17] Molecular weight studies using size exclusion chromatography/low-angle laser light scattering (SEC/LALLS) indicate that the crude material ($M_w = 4000 \pm 540$, $M_n = 1400 \pm 190$, $M_w/M_n = 2.86$) and the reprecipitated sample ($M_w = 7600 \pm 460$, $M_n = 3400 \pm 210$, $M_w/M_n = 2.23$) show broad molecular weight distributions (MWD). Thus, on the basis of a linear chain model, D_n (number-average degree of polymerization) for these materials ranges from 18 to 43 and D_w (weight-average degree of polymerization) from 51 to 97. Polymerizations carried out for shorter times, for example, for 24 h, showed correspondingly lower molecular weight averages ($M_w = 2100 \pm 330$, $M_n = 980 \pm 150$).[18]

Evidence of chain branching was also found in the LALLS chromatograms of both the crude and recrystallized polymers, where early-eluting high molecular weight components characteristic of highly branched or partially cross-linked chains were observed. In addition, the SEC/LALLS/UV studies[19] showed that polymers in the

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[17] Anal. Calcd for $(B_3N_3H_4)_x$: B, 41.32; N, 53.54; H, 5.14. Found (recrystallized powder): B, 42.33; N, 53.25; C, 1.09; H, 3.49. GPC data: $M_w = 7600 \pm 460$, $M_n = 3400 \pm 210$, $M_w/M_n = 2.23$. IR (diffuse, KBr) 3445 (m), 3230 (br m), 2505 (m), 1450 (br s), 1200 (m), 900 (m), 750 (m), 690 (m) cm^{-1}; ^{11}B NMR (160.5 MHz, THF) 31 ppm (s, vbr). Crude sample: B, 39.62; N, 56.51; H, 4.15; C, <0.5. $M_w = 4000 \pm 540$, $M_n = 1{,}400 \pm 190$, $M_w/M_n = 2.86$.

[18] Molecular weight determinations by SEC/LALLS followed the general guidelines described in: Jordan, R. C. *J. Liq. Chromatogr.* **1980**, *3*, 439–463. Since the poly(borazylenes) were observed to be low molecular weight materials, the most reliable SEC/LALLS molecular weight average is M_w. Number-average molecular weight, M_n, was not accurately determined by SEC/LALLS. Reported M_n were corrected by dividing M_w by M_w/M_n obtained from conventional SEC calibrated with polystyrene standards.

[19] The SEC/LALLS/UV experiments used an ultraviolet absorbance detector in-line with the usual two-detector (LALLS and differential refracive index (DRI)) SEC/LALLS apparatus. A wavelength setting of 230 nm was used to monitor eluting polymer molecules for borazine content. The presence of chain branching was indicated by the lack of overlap between UV and DRI chromatograms.

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high molecular weight end of the MWD, including the high molecular weight component detected by the LALLS detector, had greater UV absorbance per unit mass than those in the lower molecular weight region of the MWD. This heterogeneity with respect to UV absorbance further supports a branched chain structure since the increased absorbance at the high molecular weight end of the MWD is consistent with the greater availability of branching sites.

Although its detailed structure has not been established, the polymer is proposed to be composed primarily of linked borazine rings, analogous to those of the organic poly(phenylene) polymers.[20] Since small amounts of the N:B coupled dimer 1:2′-$(B_3N_3H_5)_2$ are isolated in the volatile materials from the reaction, the polymer is likely to contain N–B linkages between the borazines. Consistent with this interpretation, the ^{11}B NMR spectrum has a broad peak centered in the borazine region at 31 ppm.[21] Also isolated in the volatiles were small amounts of borazanaphthalene; thus it is possible that the polymer also contains some degree of fused-ring structure.

The polymer prepared in the manner described above is soluble in polar solvents such as THF or glyme and appears to be stable for extended periods when stored as a solid at room temperature under vacuum. The polymer is sensitive to water and will decompose over several hours when exposed to moist air.

A number of chemical precursors[22] for the formation of boron nitride have now been reported;[23] however, because of its composition, high-yield synthesis, and solubility, poly(borazylene) would appear to be an almost ideal precursor system. Its ceramic conversion reactions were therefore investigated. Bulk pyrolyses of both the crude and recrystallized polymers were examined under either argon or ammonia to 1200 °C and were found to result in the formation of white boron nitride powders in excellent purities and ceramic yields (85–93%; theoretical ceramic yield, 95%):[24]

$$[B_3N_3H_4]_x \xrightarrow{25\text{–}1200\ ^\circ C} 3BN + 2H_2 \qquad (2)$$

The materials produced at 1200 °C exhibited diffuse reflectance IR spectra consistent with those previously reported for boron nitride[25] and densities (1.7–1.9 g/mL) and X-ray powder diffraction patterns characteristic of turbostratic boron nitride.[26]

Thermogravimetric analysis of the ceramic conversion reaction showed that the polymer follows a well-defined decomposition path in which an initial (2%) weight loss (probably resulting from polymer cross-linking) occurs in a narrow range between 125 and 300 °C, followed by a gradual 4% loss ending by 1100 °C. Thus, poly(borazylene) appears to be an excellent precursor to boron nitride, which, because of its solubility, low-temperature decomposition, and high ceramic and chemical yields, makes it an excellent candidate for the generation of, for example, coatings or fibers of boron nitride. We are presently exploring these possibilities.[27]

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Registry No. Borazine, 6569-51-3; polyborazylene, 39526-51-7; boron nitride, 10043-11-5.

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(24) Anal. Calcd for BN: B, 43.55; N, 56.45. Found (recrystallized sample processed under ammonia to 1200 °C): B, 42.08; N, 54.52; C, <0.5; H, <0.5; XRD, *d*(002) = 3.55. Crude material processed under argon to 1200 °C: B, 40.00; N, 54.79; C, <0.5; H <0.5; XRD, *d*(002) = 3.59. Crude sample under argon to 1450 °C: B, 43.03; N, 56.44; C, <0.5; H, <0.5.

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A Second-Order Nonlinear Optical Poly(organophosphazene)

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The development of polymeric nonlinear optical (NLO) materials is currently an area of intense investigation.[1] Polymeric systems that show second harmonic generation (SHG) have conjugated aromatic molecules with electron-donor and -acceptor moieties in a noncentrosymmetric array. These nonlinear optical molecules can be doped into a glassy polymer matrix[2] or can be covalently attached to

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