to Ag^+ and the dissolution probably involves a slow attack of Ag(II), generated in solution, on the surface $\equiv Cr-S_2O_8^{2-}$ complexes.

The value of $k'_{\max}$ is in fact a composite number:

$$k'_{\max} = k^{\text{int}}_{\max}\Gamma_{\text{sat}} \qquad (18)$$

The variations observed in Table I may arise from different surface densities at saturation (Γ_{sat}) or from inherent different reactivities ($k^{\text{int}}_{\max}$). The most important conclusion is that the order of $k'_{\max}$ values does not reflect the actual ability of different reagents to dissolve chromium oxide. For instance, the highest tabulated value, which is for BrO_3^-, is in fact an extrapolated figure, not achievable in practice, whereas the maximum rate is easily obtained with Ce(IV) (Figure 3).

For the set of reagents that react by similar mechanisms (except for $S_2O_8^{2-} + Ag^+$), the aggressiveness toward Cr_2O_3 is related more to K_S than to $k_{\max}$. The precursor formation seems to be as important on the surface of the oxide as in homogeneous solutions.

The acid dependence of the dissolution rate (Figure 5) results from the acid influence of K_S and $k_{\max}$. A detailed analysis would require the measurement of this dependence at various oxidant concentrations, especially where saturation rates cannot be achieved. Only in the case of Ce(IV) can the effects of acidity on K_S and $k_{\max}$ be solved. As stated, K_S is expected to decrease with increasing acid concentration, and the right branch in Figure 5B is due to this effect. The descending branch in alkaline media must be attributed to the requirement of protons to bring about dissolution, i.e., the influence on $k_{\max}$. The latter data can be fitted, within the error margins, by either first- or second-order rate laws on $[H^+]$. In the standard surface complexation approach,[3] this dependency is explained by identifying a peculiar surface complex, among the many that may form, as the reactive species. Thus, the sensitivity of $k_{\max}$ to pH is explained not as the change in the rate of dissolution but as the change in surface speciation; it is then further assumed that the reactive species dissolves at a rate that is pH independent. Following this line of reasoning, the effect of pH on K_S suffices to explain all our experimental results. There are other well-documented examples, in which the reactivity of surface complexes seems to be pH independent; there is no evidence, however, that this is a general feature and, furthermore, the surface density of anions at the "maximum" coverage usually is a function of the pH.[32,33] A pH dependence of $k^{\text{int}}_{\max}$ and/or Γ_{sat} may be embodied in the results.

In the redox chemistry of aqueous Cr(III) → Cr(VI) species, the barriers are seemingly associated with the kinetic stage Cr(IV) $\rightleftarrows$ Cr(V), at which a change in the coordination number takes place; it is tempting to conclude that the same stage controls the dissolution behavior.

Acknowledgment. M.A.B. and P.J.M. are members of CONICET. Funding has been partially supported by CONICET, by Engelhard Corp., Edison, NJ, and by NSF Grant CHE-9108420.

Registry No. Cr_2O_3, 1308-38-9; Ce, 16065-90-0; MnO_4^-, 14333-13-2; BrO_3^-, 15541-45-4; $S_2O_8^{2-}$, 15092-81-6; Ag^+, 14701-21-4.

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(32) Blesa, M. A.; Maroto, A. J. G.; Morando, P. J. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2345.

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Preparation, Characterization, and Pyrolysis of $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ Polymers: A New Route to Boron Nitride

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Polymers of type $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ have been prepared by reaction of decaborane(14) with various diamines, including $H_2NCH_2CH_2NH_2$, $Me_2NCH_2CH_2NMe_2$, $HN(CH_2CH_2)_2NH$, and $N(CH_2CH_2)_3N$ in diethyl ether solution. The polymers, all white solids, were characterized by elemental, thermogravimetric, and thermomechanical analysis and molecular weight determinations. The synthesis and characterization of copolymers and end-capped oligomers are also described. Pyrolysis of such polymers in a stream of argon to 1000 °C gave boron carbonitride in high yield. Pyrolysis in a stream of ammonia gave almost carbon-free boron nitride. Heating of these amorphous ceramics to 1500 °C gave a crystalline material. The pyrolysis mechanism involves early conversion of the covalent polymer, by proton transfer from boron to nitrogen, to a nonvolatile diammonium salt of the $[B_{10}H_{10}]^{2-}$ anion. These polymers serve as low-loss binders for ceramic powders and as precursors for ceramic monoliths. Short (5 cm) fibers could be drawn from syrups of such polymers in DMF; subsequent pyrolysis gave ceramic fibers.

Introduction

There is much current interest in boron-containing ceramics: boron nitride, boron carbide, and metal borides. In particular, recent efforts have been focused on boron nitride.[1] A variety of methods exists for the preparation of hexagonal boron nitride powder, and this material is an article of commerce.[1] A new direction in ceramics processing, the pyrolysis of processable (i.e., soluble or fusible) polymers ("preceramic polymers"[2]), which has been applied

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(1) For a recent, comprehensive review on boron nitride, see: Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73.

(2) (a) Wynne, K. J.; Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 297. (b) Rice, R. W. *Am. Ceram. Bull.* **1983**, *62*, 889. (c) Baney, R. H. *Chemtech* **1988**, 739.

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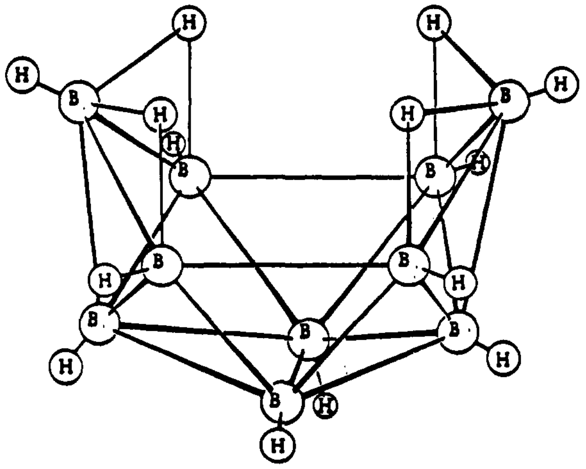


Figure 1. Structure of decaborane(14).

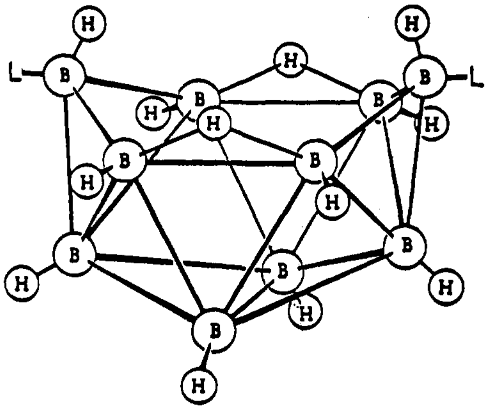


Figure 2. Structure of a $B_{10}H_{12}\cdot 2$ Lewis base adduct.

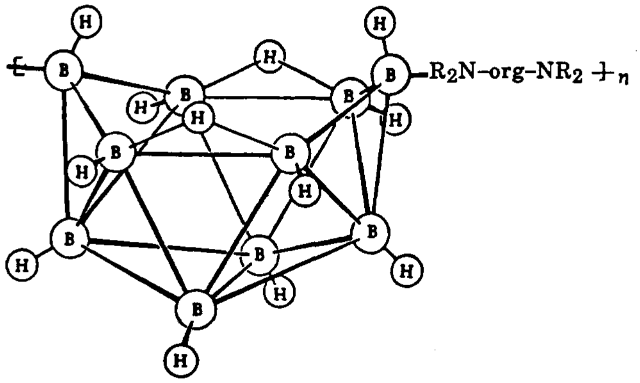
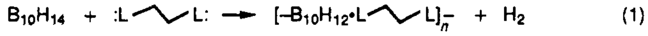


Figure 3. $B_{10}H_{12}$·diamine polymer.

principally to the preparation of silicon-containing ceramics,[3] also has been of interest in connection with boron nitride. Preceramic polymers find their main application in the preparation of ceramic fibers, coatings, and matrices, all of which are used in the fabrication of composites, and as binders used in the consolidation and shaping of ceramic powders. High thermal stability, high thermal shock resistance, resistance to molten metals, and other useful properties have led to an interest in boron nitride fibers, in particular,[1,4] although BN coatings and polymers whose pyrolysis gives BN for use as binders for BN powder also may be considered as worthwhile goals.

Most approaches to the synthesis of preceramic polymers whose pyrolysis will give BN have involved the use of borazines as starting materials.[1] However, there is another potential starting material for a polymeric precursor for boron nitride: decaborane(14). The first hint of this was provided by Stock and Pohland in 1929, who reported that the tri- and hexammoniates of $B_{10}H_{14}$ decomposed thermally to produce small quantities of crude BN.[5] Decaborane(14) (Figure 1), in fact, is an excellent monomer for the preparation of linear polymers since it reacts with diverse Lewis bases (e.g., amines, phosphines, sulfides, nitriles) to form adducts of type $B_{10}H_{12}\cdot 2L$ (Figure 2) with loss of a mole of dihydrogen.[6] It is obvious that if both Lewis base sites are in the same molecule, a linear polymer will result (eq 1). Decaborane(14)-derived polymers were first reported in 1962,[7,8] and they were studied in some detail by Schroeder et al.[7] We began our study of the applicability of decaborane(14)-derived polymers as precursors for useful ceramic materials with an examination of the pyrolysis of the known[7a,c] polymer $[-B_{10}H_{12}\cdot Ph_2POPPh_2]-_n$ and of the ceramic material thus produced.[9] There were some major problems with this system: (1) The ceramic produced in the pyrolysis of this polymer contained large amounts of free carbon due to the presence of the phenyl substituents on phosphorus. (2) The phosphorus and oxygen content of the ceramic could be reduced to minimal values for powder samples by processing at 1500 °C, but for complete removal of these elements high (ca. 2200 °C) temperatures were required. (3) Although this polymer served well as a low-loss binder for ceramic powders, it was not suitable for the production of ceramic fibers.

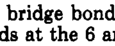


$$B_{10}H_{14} + :L\diagup\diagdown\diagup L: \longrightarrow [-B_{10}H_{12}\cdot L\diagup\diagdown\diagup L]_n^- + H_2 \qquad (1)$$

Since amine adducts of decaborane(14), $B_{10}H_{12}\cdot R_nNH_{3-n}$ ($n = 1, 2, 3$) are well-known and easily prepared,[6] it seemed reasonable to expect that reactions of $B_{10}H_{14}$ with organic diamines would give linear polymers. This was the case, and we report here the results of our studies of such polymers and their pyrolytic conversion to boron-containing ceramics.

Results and Discussion

Preparation and Characterization of $[-B_{10}H_{12}\cdot$diamine$]-_n$ Polymers. $[B_{10}H_{12}\cdot$diamine$]_n$ polymers were prepared from $H_2NCH_2CH_2NH_2$, $Me_2NCH_2CH_2NMe_2$, an 85:15 mixture of $MeHNCH_2CH_2NHMe$ and $MeHNCH_2CH_2NH_2$, $H_2NCH_2CH_2CH_2NH_2$, $HN(CH_2CH_2)_2NH$ (1), and $N(CH_2CH_2)_3N$ (2) by the reaction of



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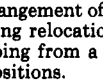

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(3) Seyferth, D. In *Silicon-Based Polymer Science, A Comprehensive Resource*; Zeigler, J. M., Fearon, F. W. G., Eds.; American Chemical Society: Washington, DC, 1990; pp 568–569.

(4) Economy, J.; Lin, R. In *Boron and Refractory Borides*; Matkovich, V. I., Ed.; Springer: New York, 1977; pp 552–564.

(5) (a) Stock, A.; Pohland, E. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 90. (b) Stock, A.; Wiberg, E.; Martini, H.; Nicklas, A. *Ber. Dtsch. Chem. Ges.* **1932**, *65*, 1711.

(6) For a review, see: *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Niedenzu, K., Buschbeck, K.-C., Ed.; Springer, Berlin, 1979; Vol. 54, pp 151–165. There is no polyhedral rearrangement of boron atoms in this reaction, the only structural change being relocation of B–H–B three-center, two-electron bridge bonds on going from a nido to an arachno structure with ligands at the 6 and 9 positions.

(7) (a) Schroeder, H.-J.; Reiner, J. R.; Heying, T. L. *Inorg. Chem.* **1962**, *1*, 618. (b) Schroeder, H.-J.; Reiner, J. R.; Knowles, T. A. *Inorg. Chem.* **1963**, *2*, 393. (c) Reiner, J. R.; Schroeder, H.-J. US Patent 3,141,856, 1964. (d) Schroeder, H.-J. US Patent 3,155,630, 1964.

(8) Parshall, G. W. US Patent 3,035,949, 1962.

(9) (a) Seyferth, D.; Rees, W. S., Jr.; Lightfoot, A.; Haggerty, J. S. *Chem. Mater.* **1989**, *1*, 54. (b) Rees, W. S., Jr.; Seyferth, D. *Ceram. Eng. Sci. Proc.* **1988**, *9*, 1009. (c) Lightfoot, A.; Rees, W. S. Jr.; Haggerty, J. S. *Ceram. Eng. Sci. Proc.* **1988**, *9*, 1021.

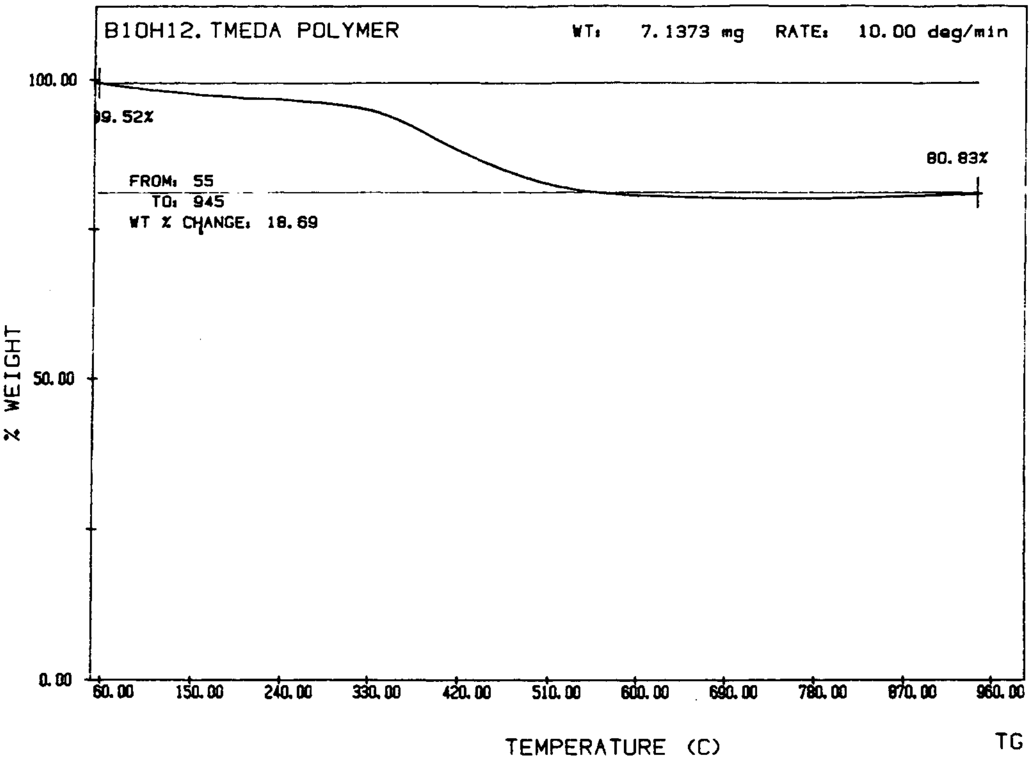

Figure 4. Thermogravimetric analysis plot of $[B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]_n$ between 50 and 950 °C at 10 °C/min; Ar atmosphere as percent weight retention.

$B_{10}H_{14}$ and the respective diamine in a 1:1 molar ratio in diethyl ether solution for several hours at room temperature. In most cases, the polymer yields were quantitative. Details of the polymer synthesis and characterization are given in the Experimental Section. All evidence indicates that polymers of type $[-B_{10}H_{12}\cdot R_2N\text{-org-}NR_2]-_n$ (Figure 3) were formed in these reactions.

Diethyl ether was found to be the most effective medium for these reactions, but other solvents such as tetrahydrofuran (THF), toluene, or hexane may be used. In general, products isolated from reactions carried out in diethyl ether contained small amounts of bound solvent that could be removed by prolonged heating at 140 °C and 10^{-4} mmHg. During the course of this research further experiments with these polymers generally were carried out using material containing ether of solvation, unless otherwise noted, since these products were more soluble than the ether-free materials. Reactions carried out in toluene or hexane using primary diamines such as $H_2NCH_2CH_2NH_2$ resulted in formation of 2:1 adducts of type $B_{10}H_{12}\cdot 2$ diamine rather than in $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ polymers, presumably as a result of the limited solubility of the initially formed $B_{10}H_{12}\cdot 2$ diamine adduct.[10] Secondary and tertiary diamines gave initial adducts on reaction with $B_{10}H_{14}$ in the reaction medium that are more soluble, so in those cases the polymerization reaction can proceed in less polar solvents.

In general, all of the $(B_{10}H_{12}\cdot\text{diamine})_n$ polymers are air and moisture stable, white-to-pale yellow solids that are soluble in polar organic solvents such as *N,N*-dimethylformamide (DMF), hexamethylphosphoric triamide (HMPA), and dimethyl sulfoxide (DMSO). They have limited solubility in acetone and acetonitrile as the Et_2O solvates; unsolvated, they are insoluble in these solvents. They decompose slowly in DMSO solution, a process that appears to be light-assisted. Reliable molecular weights of these polymers were difficult to obtain. Vapor pressure osmometry in acetone and DMF indicated a molecular weight in excess of 50 000 for $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ and $[-B_{10}H_{12}\cdot H_2NCH_2CH_2NH_2]-_n$. Gel permeation chromatography in DMF, in an experiment with the former, using polystyrene as a standard, suggested a molecular weight above 100 000. Dynamic laser scattering studies of this polymer in HMPA gave a molecular weight of 325 000 ± 10 000 D. Thus we appear to be dealing with linear polymers of high molecular weight.

The proton NMR spectra of all $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ polymers showed resonances that were in agreement with the organic portion of the diamine, along with broad signals attributable to protons present in terminal B–H bonds (+4 to –1 ppm) and bridging B–H–B bonds (–3.5 to –5 ppm). In all Et_2O-solvated samples, the presence of diethyl ether was confirmed by the observation of a triplet around 1.0–1.2 ppm and a quartet around 3.3–3.4 ppm. The $^{11}B\{^1H\}$ NMR spectra of these polymers showed broad resonances in a general pattern of 0 to –5, –15 to –20, and –35 to –40 ppm in 2:2:1 integrated intensity. Judged by comparison of the $^{11}B\{^1H\}$ NMR spectra of the polymers with those of authentic monomeric $B_{10}H_{12}\cdot 2L$ complexes,[6] the formulation of the polymers as $[-B_{10}H_{12}\cdot L—L]-_n$ is appropriate.

Pyrolysis of the $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ Polymers and Characterization of the Ceramic Materials Produced. (a) Pyrolysis in a Stream of Argon. The $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ polymers were converted to ceramic powders by pyrolysis to 1000 and 1500 °C (usually 10 °C/min heating rate) in a stream of argon using the procedure described previously in the report of our pyrolysis studies of the $[-B_{10}H_{12}\cdot Ph_2POPPh_2]-_n$ polymer.[9] The results of these experiments are summarized in Table I. Figure 4 shows the thermogravimetric analysis (TGA) trace of one such polymer, $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$. The major weight loss occurs around 400 °C. There is very little further weight loss above 550 °C. At 960 °C the ceramic residue yield was 81% by weight. The TGA traces of the

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[10] The $B_{10}H_{12}\cdot 2H_2NCH_2CH_2NH_2$ adduct is known: Green, J.; Groten, B. U.S. Patent 3,203,995, 1965; *Chem. Abstr.* **1965**, *63*, 13314g.

Table I. Data for Pyrolyses of $[-B_{10}H_{12}\bullet\text{diamine}]-_n$ Polymers under an Argon Atmosphere

			elem anal.,^{c} wt %			ceram composition					
						molar^d			weight %^{e}		
diamine	temp,^{a} °C	ceram yield^b	B	C	N	BN	B_4C	C	BN	B_4C	C
$H_2NCH_2CH_2NH_2$	1000		61.6	14.7	22.2	1.00	0.65	0.12	39.9	57.8	2.3
$H_2NCH_2CH_2NH_2$	1500	93^f	68.9	10.4	20.5	1.00	0.59	0.97, B	36.5	48.0	15.4, B
$Me_2NCH_2CH_2NMe_2$	1000	81	60.5	19.6	16.8	1.00	0.92	0.44	30.7	62.8	6.5
$Me_2NCH_2CH_2NMe_2$	1500	93^f	67.0	17.3	15.7	1.00	1.13	0.15	27.9	70.1	2.0
$H_2NCH_2CH_2NH_2/Me_2NCH_2CH_2NMe_2$ copolymer	1000	73	62.5	17.6	19.9	1.00	0.77	0.26	35.2	60.4	4.4
$H_2NCH_2CH_2NH_2$–$Me_2NCH_2CH_2NMe_2$ physical mixture	1000	94	49.7	15.2	16.9	1.00	0.70	0.35	36.7	57.1	6.2
85% $MeHNCH_2CH_2NHMe$/15% $MeHNCH_2CH_2NH_2$ mixture	1000	61	46.1	22.6	28.8	1.00	0.27	0.64	52.3	31.5	16.2
$H_2NCH_2CH_2CH_2NH_2$	1000	83	53.4	19.3	19.3	1.00	0.64	0.52	37.4	53.2	9.4
$H_2NCH_2CH_2CH_2NH_2$	1500		60.5	19.5	20.0	1.00	0.73	0.41	35.4	57.5	7.0
$HN(CH_2CH_2)_2NH$	1000	78	46.6	25.9	20.1	1.00	0.50	1.00	38.5	42.9	18.6
$HN(CH_2CH_2)_2NH$	1500		47.8	26.8	19.4	1.00	0.55	1.07	36.5	44.7	18.9
$N(CH_2CH_2)_3N$	1000	90	51.0	28.5	18.4	1.00	0.65	1.16	33.2	48.1	18.7
$HN(CH_2CH_2NH_2)_2$	1000	73	54.3	22.7	22.3	1.00	0.54	0.65	39.7	47.8	12.5

[a] Maximum temperature to which sample was heated. [b] Defined as 100(mass out/mass in), has no reflection on composition. [c] As found by elemental analysis. [d] Elemental analysis data converted to molar ratios for phases suspected of being present. [e] Weight percent composition of phases suspected of being present, calculated from elemental analysis data. [f] From 1000 to 1500 °C.

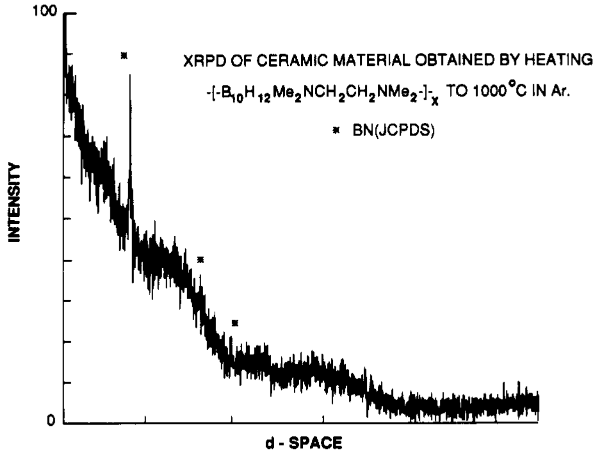

Figure 5. XRPD of ceramic material obtained by heating $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ to 1000 °C in Ar; JCPDS data file for BN coplotted.

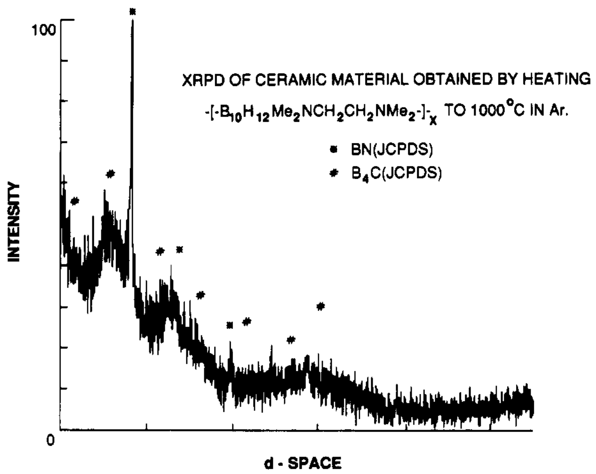

Figure 6. XRPD of ceramic material obtained by heating $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ to 1500 °C in Ar; JCPDS data file for B_4C coplotted.

other $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ polymers were qualitatively similar. In general, ceramic yields obtained by TGA were slightly higher than those obtained in the furnace pyrolysis of ca. 1-g samples of the same polymer. The ceramic products of the pyrolysis of the $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ polymers to 1000 °C were brown or black to silver/gray solids that were amorphous by X-ray powder diffraction (XRD; Figure 5). Diffuse reflectance infrared fourier transform (DRIFT) spectra of these pyrolysis products showed broad absorptions in the 3400–2480-cm^{-1} range that are attributable to the presence of residual N–H, C–H, and B–H bonds at this stage of processing. Further heating of these samples to 1500 °C under an argon atmosphere resulted in the disappearance of these bands in the DRIFT spectra of the products thus obtained and in appearance of crystalline hexagonal boron nitride (sometimes referred to as turbostratic[1]), as indicated by XRD (Figure 6). Also present in the XRD pattern were broad diffraction lines attributable to the presence of B_4C, but their width (>2°) and weak intensity (<5% relative to BN lines) suggest that only a relatively minor portion of the sample was composed of crystalline B_4C.

The ceramic "compositions" given in Table I require some discussion. As noted above, all ceramic samples pyrolyzed to 1000 °C in argon were amorphous. Therefore, a composition in terms of BN, B_4C, and C components is physically meaningless since separation of these as crystalline phases that can be distinguished by XRD has not occurred. Probably a covalent, three-dimensional lattice in which the boron atoms are more or less randomly bonded to carbon and nitrogen atoms is present, i.e., a "boron carbonitride". Thus the stated "ceramic composition" is merely a calculational exercise based on the elemental analysis which indicates what phases *might* be present if segregation and crystallization had occurred. After the 1500 °C treatment, XRD patterns attributable to the presence of partially crystalline boron carbide and crystalline, hexagonal boron nitride were observed, but this gives no information about what fraction of the sample has crystallized. Thus the "compositions" in terms of BN and B_4C given in Table I for "crystalline" products, like those of the amorphous products, are *nominal*. They were calculated by assuming that all nitrogen determined by microanalysis is present as BN, that the remainder of the boron is bound as B_4C, and that any carbon left over is present as the free element (except for a case in which boron was present in excess). An added complication is that carbon-poorer phases of boron carbide can exist and, indeed, one cannot differentiate between amorphous B_4C and an intimate 4:1 mixture of elemental boron and carbon by only XRD and elemental analysis. The DRIFT spectra of the ceramic samples, however, were suggestive of the presence of boron carbide in that absorption bands were observed in the 1090–1105 cm^{-1} region that could be at-

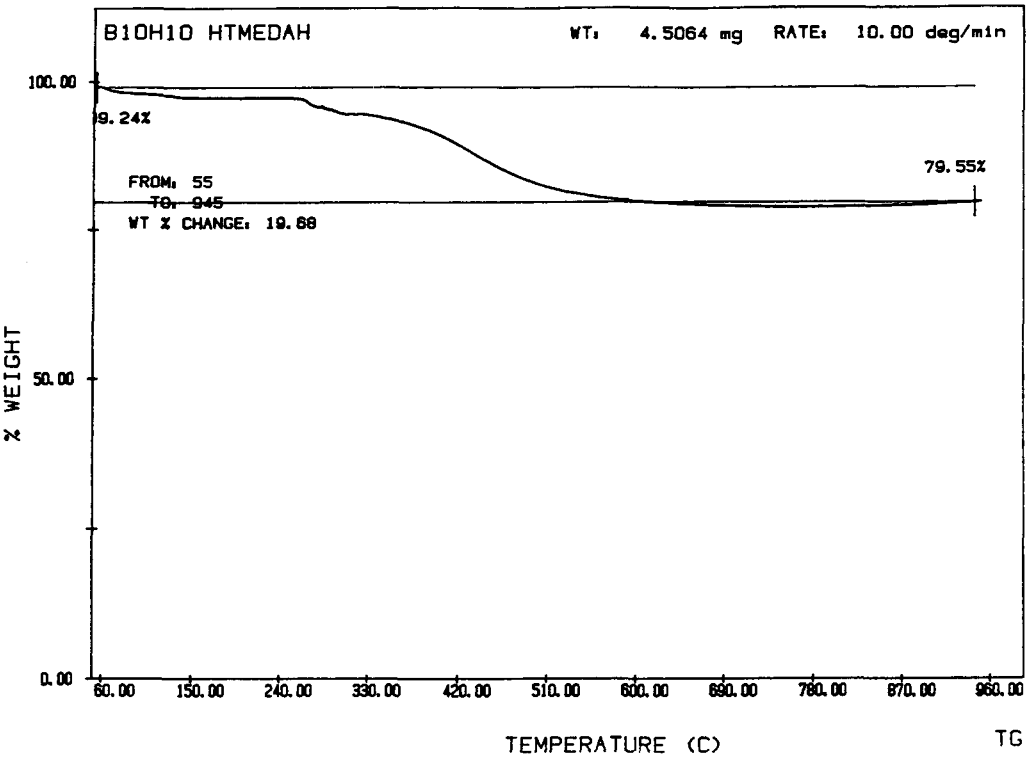

Figure 7. Thermogravimetric analysis plot of $[Me_2NHCH_2CH_2HNMe_2][B_{10}H_{10}]$ between 50 and 950 °C at 10 °C/min, Ar atmosphere, as percent weight retention.

tributed to the presence of B–C bonds. Thus we feel it is a reasonable supposition that we are dealing with BN/B_4C composites in samples heated at 1500 °C.

The mechanism of pyrolysis in a stream of argon of these $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ polymers is of special interest. As indicated, they appear to be linear polymers of high molecular weight. It is generally the case that linear polymers (in the absence of thermolabile functionality that would serve to cross-link them during the initial stages of the pyrolysis) will not give high ceramic yields when they are pyrolyzed. In most known cases (e.g., the poly(dimethylsiloxanes), poly(dimethylsilanes), and poly(dimethylsilenes)) thermal chain scission results in evolution of small, usually cyclic, molecules that are swept out of the hot zone by the carrier gas, leaving behind little or no ceramic residue.[2] In the case of the $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ polymers the acidic bridging B–H–B bonds of the $B_{10}H_{12}\cdot 2L$ cage unit possibly could be the required "thermolabile" functionality. In experiments directed toward investigating the question of pyrolysis mechanism, samples of the $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ polymer were heated in refluxing xylene suspension for 1 day and as the solid at 210 °C for 6 min. In the latter experiment, the residue was found by $^{11}B\{^1H\}$ NMR spectroscopy to be $[Me_2HNCH_2CH_2NHMe_2]^{2+}[B_{10}H_{10}]^{2-}$: δ_B (in DMF) 0.1 and −27.9 ppm, in 1:4 integrated ratio, vs δ_B (in H_2O) 1 and −28 ppm, for $[Et_3NH]_2[B_{10}H_{10}]$.[11] The $[B_{10}H_{10}]^{2-}$ salt thus obtained on pyrolysis to 1000 °C (10 °C/min, in argon) produced a ceramic material identical to that obtained in the pyrolysis (same conditions) of $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$. Figure 7 shows the TGA trace of the pyrolysis of $[Me_2HNCH_2CH_2NHMe_2]^{2+}[B_{10}H_{10}]^{2-}$ (under argon); it is almost identical to the TGA trace of $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ (Figure 4). In the experiment carried out in refluxing xylene the $^{11}B\{^1H\}$ NMR spectrum of the solid product indicated a greater than 80% conversion to the $[B_{10}H_{10}]^{2-}$ salt. Such proton transfer from the $B_{10}H_{12}$ cage of a $B_{10}H_{12}\cdot 2L$ complex to the ligand had been demonstrated in 1957 by Hawthorne and Pittochelli,[12] and the following mechanism, in the case of a basic amine ligand, was shown to be operative:

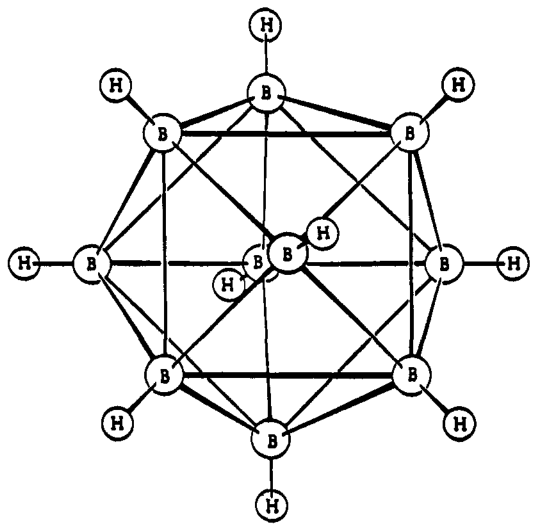

Figure 8. Stucture of the $B_{10}H_{10}^{2-}$ anion.

$$B_{10}H_{12}\cdot 2L \rightleftharpoons B_{10}H_{12}\cdot L + L \qquad (2)$$

$$B_{10}H_{12}\cdot L + \text{base} \rightarrow B_{10}H_{11}^- + [\text{base}\cdot H]^+ + L \qquad (3)$$

$$B_{10}H_{11}^- + \text{base} \xrightarrow{\text{fast}} B_{10}H_{10}^{2-} + [\text{base}\cdot H]^+ \qquad (4)$$

The high ceramic yields obtained in the pyrolysis of $[B_{10}H_{12}\cdot\text{diamine}]_n$ polymers thus now are understandable.

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[11] Lipscomb, W. N. *Boron Hydrides*; Benjamin: New York, 1963; p 152.

[12] Hawthorne, M. F.; Pittochelli, A. R. *J. Am. Chem. Soc.* **1962**, *84*, 1057.

Table II. Data for Pyrolysis of Polymers Based on Decaborane(14) under an Ammonia Atmosphere

						ceram composition			
		ceram	elem anal.,[c] wt %			weight %[d]		molar[e]	
polymer	temp,[a] °C	yield[b]	B	N	C	BN	C	BN	C
$[-B_{10}H_{12}\cdot H_2NCH_2CH_2NH_2]-_n$	1000	62	42.4	53.9	3.69	1.008	0.016	99.2	0.8
$[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$	1000	70	42.6	55.7	0.78	0.982	0.078	96.4	3.6
$[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2\cdot B_{10}H_{10}Et_2\cdot Me_2NCH_2CH_2NMe_2]-_n$	1500	56,[g] 95	39.0	45.9	0.42	0.909	0.010	99.5	0.5
$Et_2NH[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_8HNEt_2$	1500	60,[g] 89	41.9	48.4	0.37	0.892	0.008	99.6	0.4
$[-B_{10}H_{10}Et_2\cdot N(CH_2CH_2)_3N]-_n$	1500	70,[g] 98	39.9	46.8	0.18	0.905	0.004	99.8	0.2
$[-B_{10}H_{10}Et_2\cdot Me_2NCH_2CH_2NMe_2]-_n$	1500	61,[g] 95	42.1	51.4	<0.01	0.943	0.0002	99.99	0.01
$\{-B_{10}H_{12}\cdot[HN(CH_2CH_2NH_2)_2]_{2/3}\}-_n$	1000	88	41.2	57.8	0.53	1.081	0.012	99.4	0.6
Cerac BN			45.4	51.1	0.54	0.869	0.011	97.8	2.1
calc for BN			43.6	56.4		1.000		100.0	

[a] Maximum temperature to which sample was heated. [b] Defined as 100(mass out/mass in), has no reflection on composition. [c] As found by elemental analysis. [d] Elemental analysis data converted to molar ratios, normalized to $B_{1.00}$. [e] Weight percent composition of phases suspected of being present, calculated from elemental analysis data, assuming $(BN)_{1.000}(C)_x$. [f] Purchased BN commercially available. [g] Yield to 1000 °C is given first, yield from 1000 to 1500 °C is given second.

Intermediate heating to ca. 200 °C converts the initially covalent, linear polymers via proton-transfer reactions as indicated in eqs 2–4 to ionic salts containing the very thermally stable $[B_{10}H_{10}]^{2-}$ anion (Figure 8).[13] This salt is not volatile and stays in the hot zone as the temperature is increased to 1000 °C and is converted to the final boron carbonitride ceramic product. In fact, for some applications, for instance, as a binder for ceramic powders, and, possibility, for the preparation of coatings, preparation of a $[-B_{10}H_{12}\cdot L—L]-_n$ polymer really may not be necessary: the $[LH]^+{}_2[B_{10}H_{10}]^{2-}$ salts serve quite well as binders for ceramic powders.[14]

We have not studied the nature of the pyrolytic conversion of the $[H\cdot diamine\cdot H]^{2+}[B_{10}H_{10}]^{2-}$ salts to boron carbonitride. A patent by Drinkard[15] claims that such salts decompose to another covalent polymer, $[-B_{10}H_8\cdot diamine]-_n$, when heated in high vacuum for prolonged periods (3.5 days) at 165 °C at 0.1 Torr. It may be that such intermediates are involved when we heat these salts in a stream of argon relatively rapidly, and the observed minor weight loss of both the $[Me_2HNCH_2CH_2NHNMe_2]^{2+}[B_{10}H_{10}]^{2-}$ salt and the $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ polymer at around 200 °C may correspond to such a process. However, we have no experimental evidence for the intermediacy of a $[-B_{10}H_8\cdot Me_2NCH_2CH_2NMe_2]-_n$ polymer. In any case, at higher temperatures cation decomposition and formation of the amorphous boron carbonitride occur.

(b) Pyrolysis in a Stream of Ammonia. Pyrolysis of some $[-B_{10}H_{12}\cdot diamine]-_n$ samples in a stream of ammonia, rather than of argon, usually resulted in formation of a *white*, rather than a dark brown to black ceramic residue. Analysis of the ceramic residues from such pyrolyses in most cases showed a carbon content of less than 0.6% (Table II). The yields of ceramic residue obtained in these furnace pyrolyses carried out in a stream of ammonia to 1000 °C were quite high, e.g., 70% for the $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-n$ polymer and 84% for $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$. Such "carbon kick-out" processes are well-known in pyrolyses of organosilicon preceramic polymers that are carried out in a stream of ammonia. In those cases it usually is alkyl groups covalently bound to silicon that are displaced by nitrogen groups, usually in the temperature range 350–650 °C.[3,16] In the case of the $[-B_{10}H_{12}\cdot diamine]-_n$ polymers, it is the diamine ligand that is displaced. As in the case of the organosilicon polymers, here also the process appears to be a complicated one.

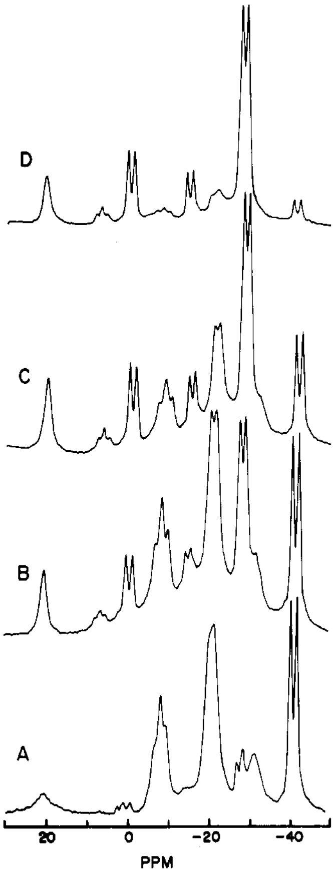

Figure 9. $^{11}B\{^1H\}$ NMR spectra (86.669 MHz, 10-Hz line broadening, 1.5-s relaxation delay, 15-μs 90° pulse width, 500 transients, 4K data points, DMF) of (A) $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_x$, (B) sample A heated for 1 h in refluxing xylene, (C) sample A heated for overnight in refluxing xylene, and (D) sample A heated for 1 day in refluxing xylene.

The "carbon kick-out" reaction occurs between 350 and 650 °C when $[-B_{10}H_{12}\cdot diamine]-_n$ polymers are pyrolyzed in a stream of ammonia. Thus when such pyrolyses of $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$ were interrupted at 250, 500, and 650 °C, the carbon contents of the solid residues formed at those temperatures were 10.6, 4.26, and 0.77%, respectively. In the 350 °C sample the B/N ratio was 0.48; in the 650 °C sample it was 0.93. In an argon stream the $[-B_{10}H_{12}\cdot diamine]-_n$ polymers undergo conversion to $[H\cdot diamine\cdot H]^{2+}[B_{10}H_{10}]^{2-}$ salts at temperatures above 200 °C, so it is likely that this process also occurs in pyrolyses carried out in a stream of ammonia prior to the "carbon kick-out" reaction. In this connection, we found that py-

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(13) For a review of the $[B_{10}H_{10}]^{2-}$ anion, see: Muetterties, E. L.; Knoth, W. A. *Polyhedral Boranes*; Dekker: New York, 1968.

(14) We have used some $[B_{10}H_{10}]^{2-}$ salts as binders for B_4C and BN powders: Rees, W. S.; Jr.; Seyferth, D. *J. Mater. Sci.* **1989**, *24*, 4220.

(15) Drinkard, W. C., Jr. US Patent 3,344,108, 1967.

(16) Okamura, K.; Sato, M.; Hasegawa, Y. *Ceram. Int.* **1987**, *13*, 55.

rolysis of $[Me_2HNCH_2CH_2NHMe_2]^{2+}[B_{10}H_{10}]^{2-}$ to 1000 °C in a stream of ammonia gave a white solid residue whose elemental analysis was almost identical with the analysis of the solid residue obtained in the ammonia pyrolysis to 1000 °C of the $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ polymer. It is known that gaseous ammonia will react with solid trialkylammonium salts to give the respective ammonium salt and the trialkylamine,[17] so one possibility is that NH_3 displaces the diamine from the $[H\cdot \mathrm{diamine}\cdot H]^{2+}[B_{10}H_{10}]^{2-}$ salt to give $[NH_4]_2{}^+[B_{10}H_{10}]^{2-}$, whose high-temperature decomposition in the ammonia stream then results in formation of boron nitride. However, we were unable to recover the diamine from such pyrolyses of $[-B_{10}H_{12}\cdot \mathrm{diamine}]-_n$ polymers in more than very low yields. Furthermore, the "carbon kick-out" reaction starts at temperatures at which the polymer already is decomposing. Also, gaseous ammonia begins to decompose at 450–500 °C and traces of organic matter lower its dissociation temperature.[18] Thus the "carbon kick-out" reaction may not be a process involving the intact NH_3 molecule. In an experiment performed to shed some light on this question, we carried out the pyrolysis of a sample of the $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$ polymer to 1000 °C in a stream of forming gas (95/5 N_2/H_2). The ceramic product obtained was brown-black and contained 7.54% C (1.00/0.68 B-to-N ratio). In contrast, when the same polymer was pyrolyzed to 1000 °C in a stream of NH_3, a white ceramic residue resulted that contained only 0.78% C (1.00/1.01 B-to-N ratio). In view of this result, we are led to the tentative suggestion that it is $^\bullet NH_2$ and :NH radicals, present in decomposing ammonia in small quantities at higher temperatures, that may be responsible for the "carbon kick-out" in a complicated free radical process.

Experiments with Polymers Other Than $[-B_{10}H_{12}\cdot \mathrm{diamine}]-_n$. Polymers other than the $[-B_{10}H_{12}\cdot \mathrm{diamine}]-_n$ were prepared and examined. In one experiment, $B_{10}H_{14}$ was treated with a 1:1 (molar) mixture of $H_2NCH_2CH_2NH_2$ and $Me_2NCH_2CH_2NMe_2$ to produce a copolymer, $[-B_{10}H_{12}\cdot \mathrm{diamine}]-_n$, containing both diamines. The signal-rich ^1H NMR spectrum of the product suggested a random distribution of the diamines. In an attempt to limit the molecular weight of the $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ polymer, a preparation was carried out in which a 7:2 molar mixture of $Me_2NCH_2CH_2NMe_2$ and Et_2NH was allowed to react with 8 mol equiv of $B_{10}H_{14}$ in diethyl ether. The white solid product, whose ^1H NMR spectrum showed that Et_2NH had been incorporated, however, had solubility properties similar to those of the $[-B_{10}H_{12}\cdot \mathrm{diamine}]-_n$ polymers and size exclusion chromatography indicated the presence of a mixture of products of various molecular weights.

Some polymers also were prepared using a mixture of ethyl-substituted decaboranes that had been prepared by Friedel–Crafts ethylation of $B_{10}H_{14}$[19] and found by gas chromatographic analysis to consist of 6.9% $EtB_{10}H_{12}$, 81.4% $Et_2B_{10}H_{12}$, 10.4% $Et_3B_{10}H_{11}$, and 1.3% $Et_4B_{10}H_{10}$. This mixture was used to prepare various polymers, including $[-Et_nB_{10}H_{12-n}\cdot N(CH_2CH_2)_3N]-_n$, $[-Et_nB_{10}H_{12-n}\cdot Me_2NCH_2CH_2NMe_2]-_n$, and $-\{[B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]_{1.8}[Et_nB_{10}H_{12-n}\cdot Me_2NCH_2CH_2NMe_2]_{1.0}\}-$.

Applications of the $[-B_{10}H_{12}\cdot \mathrm{diamine}]-_n$ Polymers. As noted in the Introduction, preceramic polymers can be useful binders for ceramic powders. The qualitative results of our experiments in which various $[-B_{10}H_{12}\cdot \mathrm{diamine}]-_n$ were used at a loading of 16.7 wt % as binders for B_4C or BN powders are listed in Table III. In most cases, shape retention of the fired composite bar (compared to the green composite bar) was excellent. Also, a bar of the $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$ polymer alone was pyrolyzed. The resulting ceramic bar retained its shape, but with 48% volume shrinkage. The ceramic bar could not be broken manually; its apparent density was 1.68 g/cm³. Characteristic of polymer/ceramic powder green test bars, the unfired ceramic composites were broken easily. Preparation and evaluation procedures previously have been described in detail.[9a] Cross-sectional examination with SEM indicated that no definite grain structure developed to 1000 °C in the pyrolyzed pure polymer bar.

Table III. Summary of Experiments Utilizing 16.7 wt % $[-B_{10}H_{12}\bullet \mathrm{diamine}]-_n$ Polymers as Binders for Ceramic Powders

diamine	ceram powder	pyrolysis atm	shape retention[a]	color
$H_2NCH_2CH_2NH_2$	none[b]	Ar	S	brown
$H_2NCH_2CH_2NH_2$	B_4C	Ar	E	gray
$H_2NCH_2CH_2NH_2$	BN	NH_3	E	white
$Me_2NCH_2CH_2NMe_2$	none	Ar	S	black
$Me_2NCH_2CH_2NMe_2$	B_4C	Ar	E	gray
$Me_2NCH_2CH_2NMe_2$	BN	NH_3	S	white
$N(CH_2CH_2)_3N$	none	Ar	E	black
$N(CH_2CH_2)_3N$	B_4C	Ar	E	black
$N(CH_2CH_2)_3N$	BN	NH_3	E	white

[a] Based on the fired composite ceramic bar as compared to the unfired, composite polymer bar. Qualitative order: E = excellent > S = satisfactory. [b] None refers to a polymer bar fired to a ceramic monolith without added ceramic powder.

In view of the interest in ceramic fibers, we investigated the potential utility of the $[-B_{10}H_{12}\cdot \mathrm{diamine}]-_n$ polymers as precursors for boron nitride or boron carbonitride fibers. Short (~5 cm) fibers could be hand-drawn from a syrup of these polymers in DMF. Such fibers could be pyrolyzed either in an argon or an ammonia stream to yield boron carbonitride or boron nitride fibers, respectively. SEM photomicrographs (Figure 10) showed these fibers to be solid, spherical, 1–3 μm in diameter and smooth-surfaced. They contained flaws of less than 0.01 μm. Melt-spinning of the $[-B_{10}H_{12}\cdot \mathrm{diamine}]-_n$ polymers is not possible because of their high melting (decomposition) points.

In conclusion, the polymers reported here, especially $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ and $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$, have potential as precursors for boron-containing ceramics. They are easily prepared and handled. They are soluble, at least in polar organic solvents. Their pyrolysis, in a stream either of argon or of ammonia, gives a ceramic residue, boron carbonitride and boron nitride, respectively, in high yield. The *chemistry* is quite satisfactory, but the ceramics issues remain to be addressed. In principle, since they are linear polymers of high molecular weight, one might have expected them to be suitable for fiber production. A $[-B_{10}H_{12}\cdot \mathrm{diamine}]-_n$ polymer that can be melt-spun should be achievable if polymers of lower melting point can be prepared. We will report on our further investigations aimed at the preparation of a melt-spinnable $[-B_{10}H_{12}\cdot \mathrm{diamine}]-_n$ fiber in a future paper. In two patents,[20] of which we became aware only after this work was completed, Johnson has described very similar chemistry.

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[17] Jolly, W. L. *The Inorganic Chemistry of Nitrogen*; Benjamin: New York, 1964; pp 13–15.

[18] Mellor, J. W. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*; Longmans Green: London, 1940; Vol. VIII, p 153.

[19] (a) Blay, N. J.; Dunstan, L.; Williams, R. L. *J. Chem. Soc.* **1960**, 430. (b) Blay, N. J.; Williams, J.; Williams, R. L. *J. Chem. Soc.* **1960**, 424.

[20] (a) Johnson, R. A. US Patent 4,810,436, Mar 7, 1989; *Chem. Abstr.* **1990**, *111*, 44257d. (b) Johnson, R. A. US Patent 4,832,895, May 23, 1989; *Chem. Abstr.* **1990**, *111*, 218405t.

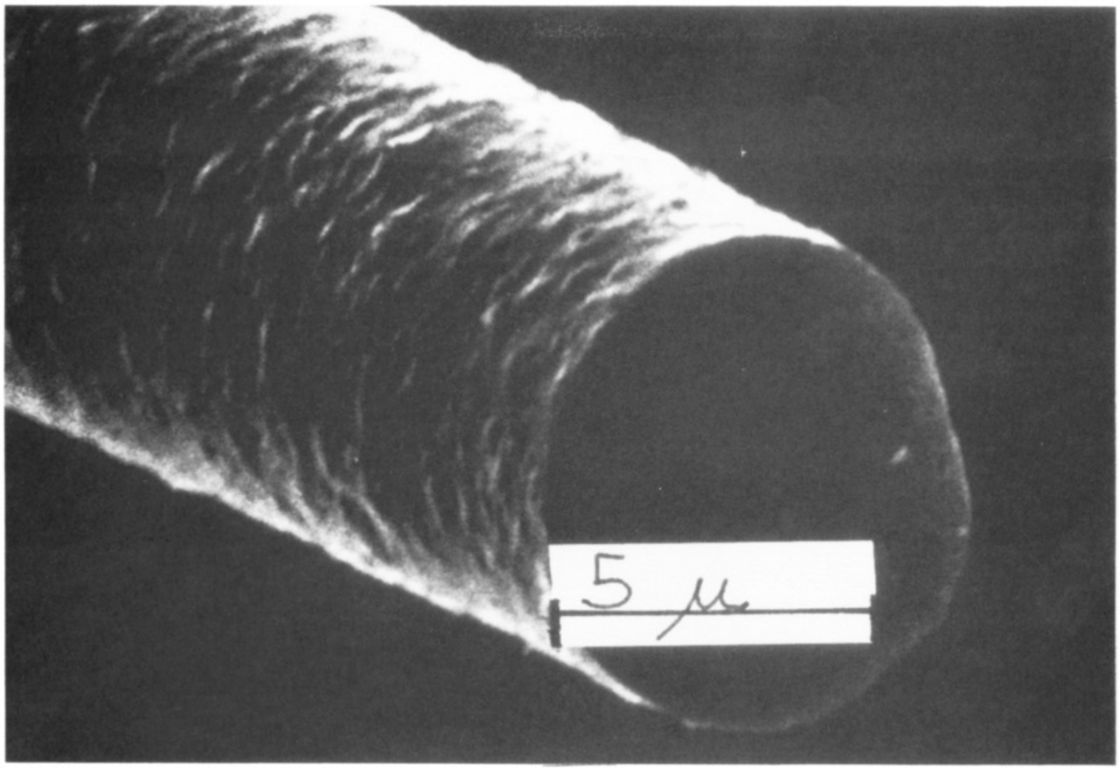

Figure 10. SEM of a boron carbonitride fiber obtained by pyrolysis of $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ fibers in a stream of argon.

Experimental Section

General Comments. The "general comments" of our paper on the material derived from the pyrolysis of the $[-B_{10}H_{12}\cdot Ph_2POPPh_2]-_n$ polymer system apply to this work.[9a] All TGA data are reported as percent of initial charge remaining after heating to 950 °C at 10 °C/min in an argon atmosphere. Unless otherwise given, all polymers had no onset of softening detected by TMA below 300 °C. All work was carried out according to standard practice for synthetic inorganic chemistry.[21] The preparation of composite ceramic bars using polymers as binders for ceramic powders has been described in detail.[9a] Likewise, the general procdure employed for preparing ceramic monoliths by polymer pyrolysis has been described.[9a] Boron nitride and boron carbide powders (99.5% pure, <5-μm average particle size) were purchased from Cerac, Inc., Milwaukee, WI. All ceramic powders and substrates were washed with hexane and dried at 150 °C, 10^{-4} mmHg for 18 h prior to use. Forming gas was purchased from Colony Welding Supply, Cambridge, MA, and used as received.

GLC analysis was carried out on a HP 5890A instrument equipped with a HP 3390A auto integrator, using a $^1/_4$-in. by 6 ft SE 30 column. A Branson laboratory ultrasonicator was employed for all experiments utilizing sonication. Size exclusion chromatography (SEC) was carried out on a Waters Millipore GPC II liquid chromatograph equipped with 10^3, 10^4, and 10^5 Å Ultrastyragel columns and a refractive index detector at a flow rate of 1 mL/min and ambient temperature. Polystyrene standards (admittedly not the most comparable in size to the preceramic polymers under consideration) were used for a calibration curve (2350, 17500, 50800, 110000, 470000, 1295000). Although samples from this work appear to be "monodisperse" upon first inspection, this may be a consequence of (1) polymer decomposition on the separation column and (2) all injected material possibly not eluting. Therefore, these SEC results should be relied upon with caution, both for MW and polydispersity values. Vapor pressure osmometry and polymer and ceramic analyses were carried out by Galbraith Laboratories, Knoxville, TN.

Molecular weight measurements by dynamic laser light scattering were carried out on $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ using methods previously described.[22]

Preparation of $[-B_{10}H_{12}\cdot$diamine$]-_n$ Polymers. The preparation of $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ is described as an example of the procedure used for all such preparations. In most cases, these reactions were carried out using 0.041 mol of $B_{10}H_{14}$ (purchased from Callery Chemical Co.). The progress of the reactions was monitored by $^{11}B\{^1H\}$ NMR spectroscopy. Workup was begun when the amount of $B_{10}H_{14}$ remaining in solution was negligible. All such polymers are soluble in DMF and HMPA, sparingly soluble in acetone and acetonitrile, and insoluble in aliphatic and aromatic hydrocarbons. They decompose on standing in DMSO. The polymers usually contained small amounts of diethyl ether of solvation as isolated. Complete removal of Et_2O could be effected by heating the $[-B_{10}H_{12}\cdot$diamine$(Et_2O)_n]-_n$ polymers >100 °C at 10^{-4} mmHg, but the ether-free materials were insoluble in acetone and acetonitrile. The solvated polymers were, in general, used in further studies.

Preparation of $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$. A 250-mL Schlenk flask equipped with a magnetic stirring bar, a nitrogen inlet, and a rubber septum ("standard reaction setup") was charged with 5.00 g (0.041 mol) of $B_{10}H_{14}$ and 100 mL of Et_2O under a vigorous inert gas purge. At ambient temperature, over a period of ca. 0.5 h, 4.76 g (0.041 mol) of $Me_2NCH_2CH_2NMe_2$, dissolved in 50 mL of Et_2O, was added dropwise, with stirring. Immediate gas evolution was observed, and a white precipitate began forming.

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(21) Shriver, D. F.; Drezdzon, M. A. *Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(22) (a) Dynamic laser light scattering spectroscopy is a well-known methodology which measures the intensity correlation from the time-dependent fluctuations in the intensity of light scattered by particles in solution. From such measurements performed at a scattering angle of 90° using an argon$^+$ laser (wavelength = 5145 Å) at room temperature (296 K), the average translational diffusion coefficient (D) for $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2-]_n$ polymer in HMPA was determined to be $(1.99 \pm 0.38) \times 10^{-8}$ cm^2/s. Further, the hydrodynamic radius of the polymer ($R_h \sim 3.82 \times 10^{-6}$ cm) was obtained from D based on the Stokes–Einstein relation: $D = kT/6\pi\eta R_h$, where k is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity. Assuming that the polymer in HMPA has a Gaussian random coil configuration, the radius of gyration (R_g) is given by[21d] $R_g = 0.665R_h$. The molecular weight of the $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2-]_n$ polymer then was determined to be 325 ± 10 kD by making use of the scaling relation[21e] $R_g \sim aN^{1/2}$, where N is the number of monomers each of a unit length a. (b) Nishio, I.; Sun, S.-T.; Swislow, G.; Tanaka, T. *Nature* **1979**, *281*, 208. (c) Tanaka, T.; Hocher, L. O.; Benedek, G. B. *J. Chem. Phys.* **1973**, *59*, 5151. (d) Tanford, C. *Physical Chemistry of Macromolecules*; Wiley: New York, 1961; pp 344–346. (e) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979.

After stirring at ambient temperature overnight, the precipitate was collected at ambient temperature by vacuum filtration, washed with two 50-mL portions of diethyl ether, and dried at 60 °C and 0.01 mmHg, for 18 h ("standard isolation"). The white powder (9.60 g, 96% based on 0.1 Et_2O/unit) isolated after this treatment was found by ^1H NMR to contain Et_2O of solvation (3.3–3.4 ppm, q; 1.0–1.2 ppm, t). Ceramic yield (TGA): 81%, TMA: onset of softening, complete melt 232–240 °C, mp 246–250 °C. Anal. Calcd for $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2(Et_2O)_{0.10}]-_n$: C, 31.52; H, 12.01; N, 11.49. Found: C, 31.84; H, 12.03; N, 11.38.

This material is soluble in HMPA and DMF. It decomposes upon standing in DMSO. It is sparingly soluble in acetone and MeCN. It is insoluble in aliphatic and aromatic hydrocarbon solvents. ^1H NMR δ 3.61–3.52, 3.25–3.16 (NCH_2, area 1.0); 2.81, 2.64, 2.55 (NCH_3, area 3.2) (d_6-DMSO). $^{11}B\{^1H\}$ NMR δ −3.7, −5.1, −16.9, −37.1 (1:1:2:1, d_6-DMSO).

The Et_2O of solvation may be removed by drying at 10^{-4} mmHg, 125 °C, for 3 h, leaving 9.31 g (100%, based on solvated polymer) of a white powder which is prone to heavy static electricity buildup in an inert-atmosphere box. This desolvated material is insoluble in MeCN and acetone. It is not known whether it is the removal of the solvent which alters the solubility or whether it is the employment of conditions necessary to effect solvent removal which alters the solubility. Anal. Calcd for $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$: C, 30.47; H, 11.96; N, 11.85. Found: C, 29.76; H, 12.52; N, 11.60.

This method has been scaled up and used to prepare large quantities of polymer which could be isolated in high purity and nearly quantitative yield. For example, in a manner as described above, 35.0 g (0.287 mol) of $B_{10}H_{14}$ and 33.3 g (0.287 mol) of $Me_2NCH_2CH_2NMe_2$ were used in a total solvent volume of 1.0 L of Et_2O to prepare 67.1 g (99%) of solvent-free $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$. Anal. Calcd: C, 30.47; H, 11.96; N, 11.85. Found: C, 29.8; H, 12.5; N, 11.6.

Solvate-free material may also be prepared using hexane as the reaction solvent. Utilizing the standard reaction setup described above, 5.00 g (0.041 mol) of $B_{10}H_{14}$ in 150 mL of hexane was allowed to react with 4.76 g (0.041 mol) of $Me_2NCH_2CH_2NMe_2$ in 50 mL of hexane at ambient temperature overnight. Gas evolution was observed, and a white precipitate began forming. Isolation as described above yielded 9.60 g (99%) of a white powder. Anal. Calcd: C, 30.47; H, 11.96; N, 11.85. Found: C, 30.27; H, 12.52; N, 11.60. ^1H NMR δ 3.71–3.58, 3.33–3.24 (NCH_2, area 1.0), 2.89, 2.71, 2.64 (NCH_3, area 3.15) (d_6-DMSO). $^{11}B\{^1H\}$ NMR δ −3.7, −5.1, −16.9, −37.1 (1:1:2:1, d_6-DMSO).

Also prepared in this manner using 0.041 mol of $B_{10}H_{14}$ were the following polymers:

$[-B_{10}H_{12}\cdot H_2NCH_2CH_2NH_2]-_n$, a white powder, 7.55 g, which proton NMR showed to contain Et_2O of solvation. Mp >275 °C. Ceramic yield (TGA) 84%. Anal. Calcd for $[-B_{10}H_{12}\cdot H_2NCH_2CH_2NH_2\cdot(Et_2O)_{0.06}]-_n$: C, 16.41; H, 11.35. Found: C, 16.35; H, 11.88. ^1H NMR δ 3.30, 3.28, 3.06, 3.09, 3.11 (d_7-DMF). $^{11}B\{^1H\}$ NMR δ −74, −9.1, −22.6, −42.6 (1:1:2:1, d_7-DMF).

The Et_2O of solvation may be removed by drying at 10^{-4} mmHg, 125 °C, for 3 h, leaving 7.38 g (99%, based on solvated material) of a white powder. Ceramic yield (TGA) 90%. Anal. Calcd for $[-B_{10}H_{12}\cdot H_2NCH_2CH_2NH_2]-_n$: C, 13.32; H, 11.20. Found: C, 13.98; H, 11.28.

A similar reaction (same scale) carried out in THF (150 mL total) gave the same polymer as a white powder that was a THF solvate (by ^1H NMR). Mp >300 °C. Anal. Calcd for $[-B_{10}H_{12}\cdot H_2NCH_2CH_2NH_2(THF)_{0.25}]-_n$: C, 26.19; H, 11.80; N, 11.66. Found: C, 26.31; H, 11.63; N, 10.89.

$[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$, a white powder, 7.85 g, that contained Et_2O of solvation (by ^1H NMR), mp >275 °C. Ceramic yield (TGA) 80%. Anal. Calcd for $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N\cdot(Et_2O)_{0.08}]-_n$: C, 34.28; H, 10.14; N, 11.29. Found: C, 33.70; H, 10.69; N, 11.09. ^1H NMR δ 3.03, 3.14, 3.15 (d_6-DMSO). $^{11}B\{^1H\}$ NMR δ −7.5, −9.5, −21.5, −40.2 (1:1:2:1, d_6-DMSO).

$[-B_{10}H_{12}\cdot HN(CH_2CH_2)_2NH]-_n$, a white powder, that contained Et_2O of solvation (by ^1H NMR), mp >275 °C. Ceramic yield (TGA): 89%. Anal. Calcd for $[-B_{10}H_{12}\cdot HN(CH_2CH_2)_2NH(Et_2O)_{0.05}]-_n$: C, 27.43; H, 11.05. Found: C, 27.48; H, 10.89.

$[-B_{10}H_{12}\cdot H_2N(CH_2)_3NH_2]-_n$, a white powder, mp >275 °C, that ^1H NMR showed to be an ether solvate. Ceramic yield (TGA) 88%. Anal. Calcd for $[-B_{10}H_{12}\cdot H_2N(CH_2)_2NH_2(Et_2O)_{0.06}]-_n$: C, 21.32; H, 11.56. Found: C, 21.01; H, 12.06. ^1H NMR δ 6.3–4.7 (NH, br, maxima at 6.05, 5.54, 5.42), 2.74 (q), 2.60 (br), 2.49 (br), 1.76 (t) (d_6-DMSO). $^{11}B\{^1H\}$ NMR δ −9.0, −21.2, −22.6, −42.8 (d_7-DMF).

Preparation of $[-B_{10}H_{12}\cdot NH_2CH_2CH_2NH_2\cdot B_{10}H_{12}\cdot NMe_2CH_2CH_2NMe_2]-_n$. A standard reaction setup was charged with 5.00 g (0.041 mol) of $B_{10}H_{14}$ and 100 mL of Et_2O under a vigorous inert gas purge. At 0 °C, over a period of ca. 0.5 h, a solution containing a mixture of 1.20 g of $H_2NCH_2CH_2NH_2$ (0.02 mol) and 2.35 g of $Me_2NCH_2CH_2NMe_2$ (0.02 mol) in 50 mL of Et_2O was added. Immediate gas evolution was observed and a white precipitate began forming. After stirring for 12 h at 0 °C, the precipitate was collected by standard isolation. The white powder, mp >275 °C, (8.28 g, 96%, based on 0.05 Et_2O/unit) isolated after this treatment was found by ^1H NMR to contain Et_2O of solvation. Ceramic yield (TGA) 82%. Anal. Calcd for $[-B_{10}H_{12}\cdot NH_2CH_2CH_2NH_2\cdot B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2(Et_2O)_{0.05}]-_n$: C, 23.42; H, 11.65; N, 13.33. Found: C, 24.17; H, 11.95; N, 13.28. ^1H NMR δ 6.40–6.60, 5.45–5.72, 3.51, 3.22, 2.98, 2.84, 2.81, 2.70, 2.58, 2.54, 2.51, 2.48 (d_6-DMSO). $^{11}B\{^1H\}$ NMR δ −3.1, −14.9, −35.8 (2:2:1, d_6-DMSO).

Preparation of $[-(B_{10}H_{12}\cdot MeHNCH_2CH_2NMeH)_{0.85}(B_{10}H_{12}\cdot MeHNCH_2CH_2NH_2)_{0.15}]-_n$. A standard reaction setup was charged with 5.00 g (0.041 mol) of $B_{10}H_{14}$ and 100 mL of Et_2O under a vigorous inert gas purge. At ambient temperature, over a period of ca. 0.5 h, 3.46 g of a solution containing a mixture (Aldrich Chemical Co.) of 85% $MeHNCH_2CH_2NHMe$ (3.09 g, 0.035 mol) and 15% of $MeHNCH_2CH_2NH_2$ (0.037 g, 0.005 mol) in 50 mL of Et_2O was added. Immediate gas evolution was observed, and a white precipitate began forming. After stirring for 12 h at 0 °C, the precipitate was collected by standard isolation. The white powder (8.35 g, 93%, based on 0.17 Et_2O/unit) isolated after this treatment was found by ^1H NMR to contain Et_2O of solvation. Ceramic yield (TGA) 44%, mp 222–225 °C dec with gas evolution, TMA 144–189 °C, onset of softening. Anal. Calcd for $[-(B_{10}H_{12}\cdot MeHNCH_2CH_2NMeH)_{0.85}(B_{10}H_{12}\cdot NHMeCH_2CH_2NH_2)_{0.15}(Et_2O)_{0.17}]-_n$: C, 30.05; H, 12.34; N, 11.84. Found: C, 29.61; H, 11.94; N, 11.27. ^1H NMR δ 3.19, 2.85, 2.56, 2.47, 2.45 (d_6-DMSO). $^{11}B\{^1H\}$ NMR δ −8.4, −9.0, −22.8, −42.5 (1:1:2:1, d_6-DMSO).

Preparation of $B_{10}H_{14-n}Et_n$ (n = 0–4). Following a published procedure,[19a] 25.0 g (0.20 mol) of $B_{10}H_{14}$ wsa dissolved in 1 L of carbon disulfide in a nitrogen-flushed 2-L, three-necked, round-bottomed flask equipped with a nitrogen inlet, reflux condenser, and a magnetic stirring bar. To the flask was added 70.0 g (0.52 mol) of $AlCl_3$ under a nitrogen purge, followed by 15.4 g (0.375 mol) of EtI. The flask was attached to a mineral oil bubbler, and the reaction mixture was stirred at ambient temperature for 15 min and then heated at reflux, with constant stirring under a nitrogen atmosphere, for 5 days. After cooling, the reaction mixture was filtered under nitrogen, and the solvent was evaporated at ambient temperature and ca. 0.01 mmHg pressure. The red residue was extracted three times with 250-mL portions of diethyl ether, the combined extracts were filtered, and the solution was evaporated at ambient temperature and ca. 0.01 mmHg pressure. A reddish liquid remained, with some small colorless crystals deposited on the upper walls of the flask. Sublimation at ca. 0.001 mmHg from flask kept at ca. 60 °C to a dry ice cooled coldfinger afforded 1.2 g of unreacted $B_{10}H_{14}$ (4.8%, based on initial charge). Consistent with reports by previous workers,[19b] the sample was found by GLC analysis to be composed of a mixture of isomeric products. If the decaborane was not first removed by sublimation (as described above), its presence was confirmed by a leading GLC peak (identification is based on co-injection of an authentic sample of $B_{10}H_{14}$). However, if the sublimation was carried out, the peak attributed to $B_{10}H_{14}$ was not observed in the GLC trace. The interpretation of the GLC data follows the earlier reference,[19a] and no attempt was made to differentiate among positional isomers, only among products of differing ethyl content, based on retention time. Thus, a composition of 6.9% $EtB_{10}H_{13}$ (mixture of 1 and 2 isomers), 81.4% $Et_2B_{10}H_{12}$ (mixture of 1,2, 1,3, and 2,4 isomers), 10.4% $Et_3B_{10}H_{11}$ (mixture of 1,2,3 and 1,2,4), and 1.3% $Et_4B_{10}H_{10}$ was isolated and used without separation into pure components. This mixture is referred to in this work as $B_{10}H_{14-n}Et_n$. ^1H NMR δ 5.1 to −0.01

(br, terminal BH), 1.15, 1.05 (CH_3), 0.78, 0.65 (CH_2), −1.8 to −3.4 (br BHB) (C_6D_6). $^{11}B\{^1H\}$ NMR δ 26.2, 14.8, 13.3, 11.2, 10.1, 8.0, 2.4, 1.1, −23.6, −33.9, −35.0.

Preparation of $[-B_{10}H_{12-n}Et_n\cdot Me_2NCH_2CH_2NMe_2]-_n$. The same general procedure was followed as that given above for the preparation of $\{-B_{10}H_{12}\cdot$diamine$]-_n$ for a reaction in 100 mL of Et_2O on a scale of 2.00 g of ethyldecaborane mixture and 1.21 g (0.011 mol) of $Me_2NCH_2CH_2NMe_2$. After stirring at ambient temperature for 1 day, the dark yellow-orange gummy solid product was isolated by filtration and dried at 0.01 mmHg and 60 °C for 2 days to give a light yellow powder (3.14 g, 86%), mp 258–266 °C. Ceramic yield (TGA) 67%. Anal. Found: C, 38.24; H, 11.14; N, 8.51. ^1H NMR δ 3.56, 3.18, 2.78, 2.62, 2.59, 0.90 to −0.1 (br, maxima at 0.53). $^{11}B\{^1H\}$ NMR δ 7.0, 4.4, −0.1, −1.1, −5.1, −8.1, −9.1, −20.0, −26.0, −28.0, −38.1, −39.5, −41.2, −42.6 (d_7-DMF).

Preparation of $[-B_{10}H_{12-n}Et_n\cdot N(CH_2CH_2)_3N]-_n$. The same procedure (2.00 g of the ethylated decaborane mixture) gave 2.36 g of a yellowish solid, mp >250 °C. Ceramic yield (TGA) 65%. Anal. Found: C, 35.69; H, 9.69; N, 9.75. ^1H NMR δ 3.80 to 2.95 (br, maxima at 3.27, NCH_2CH_2N), 0.5 to 1.2 (br, BCH_2CH_3, no clear maxima). $^{11}B\{^1H\}$ NMR δ 4.8, 0.9, −2.8, −7.0, −9.5, −15.0, −18.5, −38.3, −40.2 (CD_3COCD_3).

Preparation of $[-(B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2)_{1.0}$-$(B_{10}H_{12-n}Et_n\cdot Me_2NCH_2CH_2NMe_2)_{1.0}]-_n$. Following the same general procedure described above for the preparation of $[-B_{10}H_{12}\cdot$diamine$]-_n$ polymers, a solution of 1.86 g of $Me_2NCH_2CH_2NMe_2$ (0.016 mol) in 50 mL of Et_2O was added to a solution containing a mixture of 1.0 g of $B_{10}H_{14}$ (0.008 mol) and 1.46 g of ethyldecaborane mixture dissolved in 100 mL of Et_2O at ambient temperature. After stirring for 8 h, the product was collected by filtration at ambient temperature and dried as described above to yield 3.03 g (71%) of an off-yellow solid, mp 190–210 °C (dec). Anal. Found: C, 29.84; H, 10.67; N, 10.01.

The resonances attributed to the $B_{10}H_{12}$ unit were considerably stronger in the $^{11}B\{^1H\}$ NMR spectrum of the product polymer than those believed due to the $B_{10}H_{12-n}Et_n$ units. $^{11}B\{^1H\}$ NMR δ 7.2, 2.3, 0.1, −7.2, −9.0, −20.8, −25.5, −28.0, −31.2, −41.2 (d_7-DMF).

Preparation of $Et_2NH[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]_7-B_{10}H_{12}\cdot HNEt_2$. Following the general procedure described above for the preparation of $[-B_{10}H_{12}\cdot$diamine$]-_n$ polymers, a solution containing a mixture of 0.80 g of Et_2NH (0.01 mol) and 4.07 g (0.035 mol) of $Me_2NCH_2CH_2NMe_2$ in 50 mL of benzene was added to a solution containing 5.0 g of $B_{10}H_{14}$ (0.041 mol) in 150 mL of benzene at ambient temperature. After stirring for 15 h, the product was collected by filtration at ambient temperature and dried as described above to yield 9.70 g of a white solid, mp >250 °C. Ceramic yield (TGA) 78%. Anal. Calcd for Et_2NH-$[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_8B_{10}H_{12}\cdot HNEt_2$: C, 29.74; H, 11.93; N, 12.01. Found: C, 29.23; H, 12.13; N, 10.66. ^1H NMR δ 3.90–3.80, 2.50–3.40 (NCH_2 from TMEDA, area 1.00), 3.21 (NCH_2CH_3, area 0.53), 3.08, 2.77, 2.69 (NCH_3 from TMEDA, area 3.64), 1.30 (NCH_2CH_3, area 0.71) (d_7-DMF). $^{11}B\{^1H\}$ NMR δ +7.4, +0.2, −3.8, −6.4, −7.1, −20.1, −27.6, −31.2, −34.3, −40.2 (d_7-DMF).

Preparation of $([-B_{10}H_{12}\cdot H_2NCH_2CH_2NH_2]-_n)_{1.0}/([-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n)_{1.0}$ Physical Mixture. In an inert-atmosphere box, a mixture of 1.0 g each of $[-B_{10}H_{12}\cdot H_2NCH_2CH_2NH_2]-_n$ and $[-B_{10}H_{12}\cdot Me_2N$-$CH_2CH_2NMe_2]-_n$ was ground in an alumina mortar and pestle for 15 min. The resulting mixture had a ceramic yield (TGA) of 84% and a mp of >250 °C. ^1H NMR δ 6.50, 3.51, 3.22, 2.97, 2.90, 2.81, 2.75, 2.62, 2.58, 2.55, 2.52, 2.49 (d_6-DMSO). $^{11}B\{^1H\}$ NMR δ −1.6, −3.8, −15.0, −22.3, −35.8 (1:1:2:1:1, d_6-DMSO).

Preparation of $B_{10}H_{12}\cdot(H_2NCH_2CH_2NH_2)_2$. Utilizing a standard reaction setup, 5.00 g (0.041 mol) of $B_{10}H_{14}$ in 150 mL of toluene was allowed to react with 2.46 g (0.041 mol) of $H_2NCH_2CH_2NH_2$ in 50 mL of toluene. Gas evolution was observed, and a white precipitate formed. Isolation as described above gave 4.56 g of a white, lumpy material (93%, based on $H_2NCH_2CH_2NH_2$ employed; unreacted $B_{10}H_{14}$ was recovered from solution), mp 130–144 °C (dec with gas evolution). Anal. Calcd for $B_{10}H_{12}\cdot(H_2NCH_2CH_2NH_2)_2$: C, 19.98; H, 11.76; N, 23.70. Found: C, 20.59; H, 12.19; N, 23.41. This material has been reported previously.[10] ^1H NMR δ 3.37, 2.60 (d_6-DMSO). $^{11}B\{^1H\}$ NMR δ +4.8, −1.4, −4.3, −6.0, −7.6, −12.9, −21.0, −34.8, −35.7, −41.2 (d_6-DMSO).

A similar reaction was carried out in 150 mL of hexane (same scale). The product, 4.51 g of a snow white powder, was obtained (92%), mp 128–136 °C (dec with gas evolution). Anal. Found: C, 20.39; H, 11.71. ^1H NMR δ 3.21, 2.59 (d_6-DMSO). $^{11}B\{^1H\}$ NMR of +4.9, −1.5, −4.4, −6.0, −7.5, −12.9, −21.8, −35.4, −33.9, −35.4, −41.1 (d_6-DMSO).

Conversion of $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ to $[Me_2HNCH_2CH_2NHMe_2]^{2+}[B_{10}H_{10}]^{2-}$. A 3.00-g sample of $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ was heated as a suspension in 150 mL of xylene held at the reflux temperature for 1 day. The precipitate of $[Me_2NHCH_2CH_2NHMe_2][B_{10}H_{10}]$ was collected at ambient temperature by vacuum filtration and dried at 60 °C, 10^{-2} mmHg, for 2 h. The yield of white powder was quantitative. By $^{11}B\{^1H\}$ NMR spectroscopy (−0.5, −28.4 ppm, 1:4 integrated ratio, in DMF), the predominant (>80%) species present in the residue after removal of the xylene was $[B_{10}H_{10}]^{2-}$. Figure 10 shows $^{11}B\{^1H\}$ NMR spectra of (a) the starting polymer, (b) a sample removed after the polymer had been heated for 1 h in refluxing xylene, (c) a sample after refluxing overnight, and (d) a sample after refluxing for 1 day. The slight borate peak at ~20 ppm probably is due to minor hydrolysis caused by traces of moisture present in the xylene.

In another experiment a 1.00-g sample of the solid $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ polymer was heated at 210 °C for 6 min under an argon atmosphere. The solid residue was found by $^{11}B\{^1H\}$ NMR spectroscopy (0.1, −27.9, 1:4, in DMF solvent) to consist purely of a $[B_{10}H_{10}]^{2-}$ salt.

Anal. Calcd for $[Me_2HNCH_2CH_2NHMe_2]^{2+}[B_{10}H_{10}]^{2-}$: C, 30.5; H, 11.0; N, 11.8. Found: C, 30.2; H, 11.1; N, 12.1.

Pyrolysis of $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ in a Stream of Ammonia. A 0.500-g sample of the polymer was heated to 1000 °C in a stream of NH_3. The gas was dried by passage through a 2 in. × 3 ft column of KOH. The ceramic residue obtained on cooling to ambient temperature, 0.417 g (84%), was a white solid. The heating rate (2 °C/min) and the gas flow rate (5 mL/s) used were found to be of crucial importance. A lower gas flow rate or a more rapid thermal rise rate gave a material exhibiting brown to black color. The experiment was conducted in a Lindberg tube furnace equipped with a Eurotherm programmable controller. Samples were placed in alumina boats in a quartz tube. The boats had been prefired in O_2 for 24 h at 1000 °C. The tube was flushed with NH_3 at ambient temperature for 30 min prior to introduction of the sample and boat. The flow was continued for an additional 30 min at ambient temperature, prior to the initiation of the thermal cycle. A 1-h pause was introduced at 200 °C. The final hold was 10 h at 1000 °C. The cooling cycle was uncontrolled (~6 h) in a flowing NH_3 atmosphere. Anal. Calcd for BN: B, 43.57; N, 56.47. Found: B, 40.39; N, 54.20; C, <0.5%.

Pyrolysis of $[Me_2HNCH_2CH_2NHMe_2]^{2+}[B_{10}H_{10}]^{2-}$. A 0.200-g sample of the salt was heated to 1000 °C in a stream of NH_3. The ceramic residue obtained on cooling to ambient temperature, 0.150 g (75%) was a white, free-flowing powder. All experimental parameters were identical to those employed in the pyrolysis of $[B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]_n$. Anal. Found: B, 41.15; N, 57.43; C, <0.5%.

Characterization of Intermediate Products and Volatile Species Evolved during the Pyrolysis of $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$ in a Stream of Ammonia. A 1.00-g sample of $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$ was subjected to a standard pyrolysis experiment in a stream of ammonia. The volatile species formed during the pyrolysis were trapped from the exit gas at −5 °C. To 350 °C no visible compounds were caught in the trap. The light brown residue, partially soluble in DMF ($^{11}B\{^1H\}$ NMR δ +2, −29 ppm, indicative of $[B_{10}H_{10}]^{2-}$) remaining in the hot zone of the furnace (0.77 g, 77%) contained (elemental analysis) 10.59% carbon. A 0.370-g sample pyrolyzed to 500 °C left 0.342 g (92%) of a light tan powdery solid that contained 4.26% C. A similar experiment with a 0.200-g sample that was heated to 650 °C left a residue of 0.160 g (80%) of an insoluble, creamy tan residue that contained 0.77% C.

Pyrolysis of $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$ in Forming Gas. A sample of 0.400 g of $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$ was pyrolyzed in a stream of 95/5 nitrogen/hydrogen, "forming gas", to 1000 °C at a rate of 10 °C/min. All furnace conditions, except pyrolysis atmosphere, were identical to those already described. Anal. Found: C, 7.54; H, 0.93; B, 31.77; N, 27.94.

Pyrolysis of $[NH_4]_2[B_{10}H_{10}]$ in a Stream of Ammonia. A 0.500-g sample of the salt was heated to 1000 °C in a stream of dry NH_3. The ceramic residue obtained on cooling to ambient temperature, 0.450 g (90 wt %, based on initial charge) was a light brown solid. The heating rate (2 °C/min) and the gas flow rate (5 mL/s) each were found independently to contribute to the visible appearance of the ceramic material. The visual consequence of either a lower gas flow rate or a more rapid thermal increase was a material exhibiting darker brown to reddish-black color. The experiment was conducted in a Lindberg tube furnace equipped with a Eurotherm programmable controller. Samples were placed in alumina boats in a quartz tube. The boats had been prefired in O_2 for 24 h at 1000 °C. The tube was flushed with NH_3 at ambient temperature for 0.5 h prior to introduction of the sample and boat. The flow was continued for an additional 0.5 h at ambient temperature, prior to the initiation of the thermal cycle. A 1-h pause was introduced at 200 °C. The final hold was 10 h at 1000 °C. The cooling cycle was uncontrolled (~6 h) in a flowing NH_3 atmosphere. Anal. Found: B, 64.45; N, 31.90.

Since BN requires 43.55% B and 56.45% N, obviously the ceramic residue in this experiment contains an excess of free elemental boron.

Preparation of a Ceramic Monolith by Pyrolysis of a Polymer Monolith from $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$. Following a procedure described in detail,[9] 1.80 g of polymer was formed into a monolith and compacted to 25.0 × 12.5 × 6.4 mm (2.0 cm^3), giving an apparent "green" density of 0.90 g/cm^3. After a standard pyrolysis to 1000 °C in an argon atmosphere, the mass was 1.64 g and the dimensions were 22.3 × 9.4 × 4.6 mm (0.97 cm^3), giving an apparent "fired" density of 1.68 g/cm^3. This corresponds to a weight retention of 91%, a volume change of 48% and an increase in density of 187% during the polymer to ceramic conversion process. Using the composition of the ceramic powder obtained by similar pyrolytic treatment of a powdered sample of polymer, the *nominal* formula of this material may be expressed as 48.1% B_4C, 33.2% BN, and 18.7% C (weight %). Employing known densities (BN 2.27, B_4C 2.52, C 1.8, all in g/cm^3), the above described ceramic monolith has an apparent density 74% of its theoretical value.

Preparation of Ceramic Fibers from $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ Polymers: General Procedure. The procedure used with $[-B_{10}H_{12}\cdot H_2NCH_2CH_2NH_2]-_n$ is described as an example. A 0.05-g sample of the polymer was dissolved in a minimum amount (ca. 0.1 mL) of DMF in an inert-atmosphere box and worked with a spatula on a watch glass until a thick, viscous syrup resulted. More polymer and/or solvent were added as required to maintain a consistency of tacky honey. Fibers up to about 5 cm in length could be drawn from this solution, placed in fused silica pyrolysis boats and quickly transferred to a quartz tube that had been flushed previously with the desired pyrolysis gas (Ar or NH_3) for 15 min. The end of the quartz tube was immediately attached to an oil bubbler, and after ~15 min the gas flow was reduced from ~100 to ~25 mL/min and the quartz tube was placed in a Lindberg furnace. The sample was heated from ambient temperature to 200 °C at a rate of 7 °C/min, held at 200 °C for 12 min, heated to 1000 °C at 5 °C/min, held at 1000 °C for 2.5 hr, and allowed to cool to ambient temperature overnight, and the ceramic fibers were removed from the furnace and subjected to evaluation by SEM.

Similar experiments were performed using $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$, $[-B_{10}H_{12}\cdot H_2NCH_2CH_2CH_2NH_2]-_n$, $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$, $[-B_{10}H_{12}\cdot H_2NCH_2CH_2NMe_2]-_n$, $Et_2NH[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_8HNEt_2$, $[-B_{10}H_{12}\cdot H_2NCH_2CH_2NH_2]-_n/[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$, $[-(B_{10}H_{12}\cdot H_2NCH_2CH_2NH_2)_{1.0}—[-(B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2)_{1.0}]-_n$, $[-B_{10}H_{12-n}Et_n\cdot N(CH_2CH_2)_3N]-_n$, $[-B_{10}H_{12-n}Et_n\cdot Me_2NCH_2CH_2NMe_2]-_n$, and $[-(B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2)_{1.0}—[-(B_{10}H_{12-n}Et_n\cdot Me_2NCH_2CH_2NMe_2)_{1.0}]-_n$ polymers as fiber precursors. All polymers, copolymers, end-capped oligomers, and mixtures examined served equally well in the formation of "green" polymer fibers. The polymer fibers derived from $[-B_{10}H_{12}\cdot Me_2NCH_2CH_2NMe_2]-_n$ and $[-B_{10}H_{12}\cdot N(CH_2CH_2)_3N]-_n$ served best in the production of either B_4C/BN or BN ceramic fibers after the appropriate pyrolysis of the polymer fibers.

Preparation of Ceramic Powder Composites. Weighed quantities of $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ (0.5 g) and B_4C or BN powder (2.5 g) were mixed and ground for 15 min in an alumina mortar and pestle in an inert-atmosphere box. The samples thus prepared were placed in a 0.5 in. × 1.5 in. rectangular die and formed into bars in a Carver laboratory press at 5000 pounds (6667 psi uniaxially), removed to an ambient temperature isostatic press, and further compacted to 50 000 psi after being wrapped in cellophane and placed in an evacuated, sealed rubber bag. The uniaxial pressing time duration was ~5 min, and the isostatic pressing time duration was ~15 min. The resulting bar was pyrolyzed in a stream of argon to 1000 °C (10 °C/min heating rate, hold at 1000 °C for 30 min) and allowed to cool to ambient temperature over a period of ~3.5 h. The pyrolyzed sample was handled in an inert-atmosphere box.

For the purposes of this initial screening, a ceramic bar was considered to be "excellent" if it was a uniform, black rectangular monolithic body that had retained its shape (vs the polymer bar before pyrolysis) in all three dimensions without undergoing any discernible shrinkage or bloating above the detectable level of 3–5% and if its strength was such that it could not be broken manually without employing the aid of mechanical means (e.g., a vise and pliers). The results of experiments evaluating such composite bars prepared by using the $[-B_{10}H_{12}\cdot\text{diamine}]-_n$ polymers as binders for B_4C or BN powder are summarized in Table III.

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Registry No. BN, 10043-11-5; $B_{10}H_{14}\cdot H_2NCH_2CH_2NH_2$ (copolymer), 121202-56-0; $B_{10}H_{14}\cdot Me_2NCH_2CH_2NMe_2$ (copolymer), 121202-57-1; $B_{10}H_{14}\cdot NH(CH_2CH_2)_2NH\cdot Me_2NCH_2CH_2NMe_2$ (copolymer), 136538-83-5; $B_{10}H_{14}\cdot N(CH_2CH_2)_3N$ (copolymer), 121436-68-8.