Atoms in **3**), Table VII (Atomic Coordinates and Isotropic Thermal Parameters for Hydrogen Atoms in **3**), Table VIII (Bond Lengths and Bond Angles in **3**), and spectral/analytical data for compounds **1**, **2**, **4**, **5**, and **6** (23 pages); structure factor amplitude tables for **2** and **3** (18 pages). Ordering information is given on any current masthead page.

Synthesis of Boron Nitride Ceramics from Poly(borazinylamine) Precursors

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Several simple monomeric boron and nitrogen reagents have been utilized as starting materials in high-temperature pyrolyses or chemical vapor deposition schemes to prepare hexagonal boron nitride.[1,2] However, extensive applications and demands for new forms (films, gels, foams, fibers) have recently led to searches for improved syntheses and processing techniques for BN. Polymeric precursors might offer alternate low-energy syntheses of BN,[3] but, unfortunately, the oligomer and polymer chemistry of boron–nitrogen compounds is not well developed.[4] Several substituted borazenes have been examined as BN precursors;[4-6] however, recent thorough studies indicate that carbon-contaminated, boron-rich materials are typically obtained from pyrolyses of these reagents.[7,8] Nevertheless, the proposed mechanism for borazene thermal condensation[4h,8] and chemistry for organoborazinylamines reported by Meller and co-workers[9] suggest that amino cross-linked borazenes, without organic substituent groups, might lead to oligomeric gel precursors for pure boron nitride. Furthermore, such a synthesis should lend itself to modern nonaqueous sol-gel processing techniques.[10]

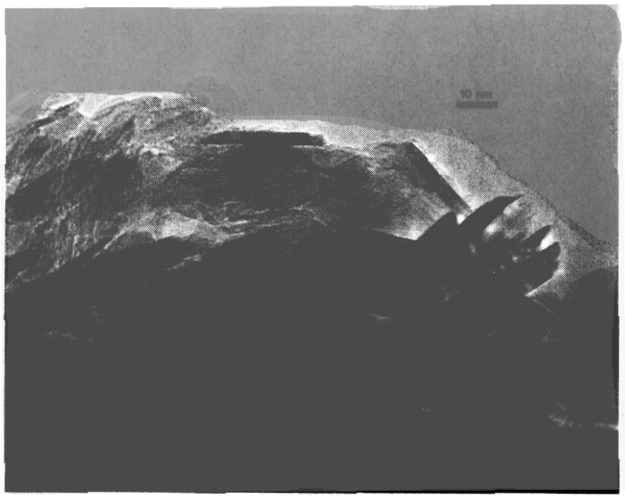
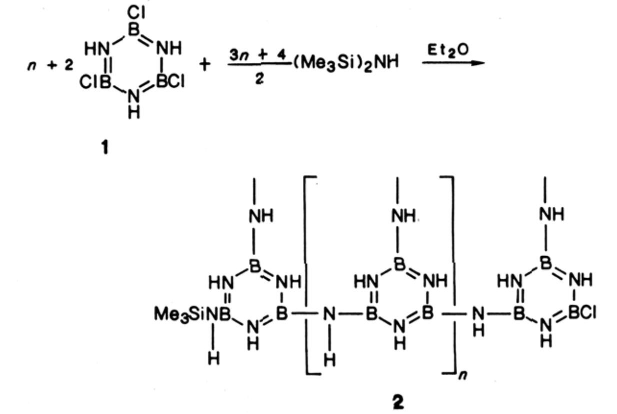
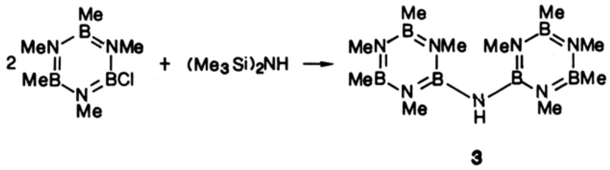


Figure 1. Transmission electron micrograph of sample **5**.

In a typical experiment, trichloroborazene **1** (10.4 g, 56.5 mmol) in dry diethyl ether (100 mL) is cooled to −78 °C, and hexamethyldisilazane (17.7 g, 84.9 mmol) is added. The mixture is agitated and allowed to warm slowly to 25 °C (2 h). A white gel is isolated by vacuum evaporation of the solvent and Me_3SiCl. The reaction is outlined in eq 1. This cross-linking proposal is supported by model reactions with substituted borazenes (eq 2), in which bis(pentamethylborazinyl)amine (**3**) is isolated.[11] The gel **2** would be expected to have a N/B ratio of 1.5 with small amounts of C, Si, and Cl present in oligomer-capping groups. Indeed, elemental analyses[12] indicate a partial formula $BN_{1.49}Cl_{0.06}Si_{0.09}$.



(1)



(2)

The infrared spectrum of **2** is similar to a spectrum of **1**[13] except that ν_{BCl}, 741 cm^{-1}, present for **1**, is absent in **2**. Thermogravi-

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(1) Balmain, J. *J. Prakt. Chem.* **1982**, *27*, 422.

(2) Meller, A. *Gmelin Handbuch der Anorganische Chemie, Boron Compounds* **1974**, *13*, 1; first supplement **1980**, *2*, 1; second supplement **1983**, *1*, 304.

(3) Wynne, K. J.; Rice, R. W. *Ann. Rev. Mater. Sci.* **1984**, *14*, 297 and references therein.

(4) The majority of this chemistry is summarized in the following: (a) Gaines, D. F.; Borlin, J. In *Boron Hydride Chemistry*; Muetterties, E. L., Ed.; Academic Press: New York, 1975. (b) Steinberg, H.; Brotherton, R. J. *Organoboron Chemistry*; Wiley: New York, 1966; Vol. 2. (c) Lappert, M. F. Developments *in Inorganic Polymer Chemistry*; Lappert, M. F., Leigh, G. J., Eds.; Elsevier: New York, 1962; p 20. (d) Lappert, M. F. *Proc. Chem. Soc.* **1959**, 59. (e) Aubrey, D. W. *J. Chem. Soc.* **1959**, 2927. (f) Laubengayer, A. W.; Moews, P. C.; Porter, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 1337. (g) Wagner, R. I.; Bradford, J. L. *Inorg. Chem.* **1962**, *1*, 99. (h) Toeniskoetter, R. H.; Hall, F. R. *Inorg. Chem.* **1963**, *2*, 29.

(5) Taniguchi, I.; Harada, K.; Maeda, T. *Jpn. Kokai* 7653000, 1976; *Chem. Abstr.* **1976**, *85*, 96582v.

(6) Constant, G.; Feurer, R. *J. Less-Common Met.* **1981**, *82*, 113.

(7) Bender, B. A.; Rice, R. W.; Spann, J. R. *Ceram. Eng. Sci. Proc.* **1985**, *6*, 1171.

(8) Paciorek, K. J. L.; Kratzer, R. H.; Harris, D. H.; Smythe, M. E.; Kimble, P. F. U.S. Patent 4581468, **1986**. Paciorek, K. J. L.; Harris, D. H.; Kratzer, R. H. *J. Polym. Sci.* **1986**, *24*, 173.

(9) (a) Gutmann, V.; Meller, A.; Schlegel, R. *Monatsch. Chem.* **1963**, *94*, 1071. Gutmann, V.; Meller, A.; Schlegel, R. *Monatsch. Chem.* **1964**, *95*, 314. Meller, A.; Füllgrabe, H.-J. *Angew. Chem., Intl. Ed. Engl.* **1975**, *14*, 359. Meller, A. Füllgrabe, H.-J. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 156. Meller, A.; Füllgrabe, H.-J.; Habben, C. D. *Chem. Ber.* **1979**, *112*, 1252.

(10) The term sol-gel processing refers to the method of preparing glasses or ceramics from the chemical conversion (usually solvolysis) of an appropriate precursor. For example, the alcohol conversion of silicon tetraalkoxides produces a sol, then a gel, and finally a glass at temperatures usually well below the temperatures normally employed to make a glass or ceramic product. Brinker, C. J.; Drotning, W. D.; Sherer, G. W. *Mat. Res. Soc. Symp. Proc.* **1984**, *32*, 25. Hench, L. L.: Ulrich, D. R. *Ultrastructure Processing of Ceramics, Glasses and Composites*; Wiley: New York, 1984.

(11) Narula, C. K.; Paine, R. T.; Schaeffer, R., Manuscript in preparation.

(12) Elemental Anal. Found: C, 11.07; H, 5.91; B, 24.00; N, 46.53; Cl, 4.92; Si, 5.83.

(13) Meller, A. *Organomet. Chem. Rev.* **1967**, *2*, 1. Although B–Cl bonds are present in end-capping groups, their number are estimated to be few: B/Cl ~20:1 to 40:1.

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metric analysis of **2** in argon shows a gradual weight loss (ca. 35%) in the region 25–700 °C and a slight weight loss in the region 700–1000 °C.[14]

Pyrolysis of a sample (7.5 g) of **2** at 900 °C in vacuo (24 h) and then at 1200 °C in air (2 h) results in the formation of a white crystalline solid **4** (4.4 g) and Et_2O, NH_3, and NH_4Cl as identified by mass spectrometry and infrared spectroscopy. Elemental analysis[15] of **4** yields B/N = 1.15. An infrared spectrum is very similar to a spectrum obtained from commercial h-BN.[16] An X-ray powder pattern of **4** is consistent with the powder pattern for turbostratic modified h-BN.[17] TEM analysis[18,19] of **4** shows regions of well-developed crystallinity interspersed with amorphous material. The crystalline BN grains are approximately 5–10 nm on a side and 30–40 nm long, and the BN (002) lattice fringes are clearly visible. EDS[18,19] analysis shows a Si peak in all regions of the sample. The BN aggregates are porous with pores ~2 nm in diameter. There is no evidence for microporosity, and the BET[18] surface area is 34 $m^2 g^{-1}$. Additional characterization details are provided in the Supplementary Material.

A sample of **4** was treated with 40% aqueous HF solution for 15 min at 25 °C to remove any boron oxides and silica formed.[20] The remaining white powder **5** was washed with distilled water and air dried. Infrared spectra show no changes in the region 1600–400 cm^{-1} compared to the spectrum of **4**, and the X-ray powder pattern of **5** shows no noticeable changes. The microstructure of **5**, as revealed by TEM analyses (Figure 1), appears less porous with sharper lattice fringes, as if removal of the intervening amorphous material allows the grains to collapse together. EDS analyses show a complete absence of Si in most regions. Carbon arc emission spectroscopy shows silicon present at a level of 0.03–0.05%.[21]

These preliminary studies indicate that an oligomeric borazinylamine gel can be prepared in high yield, and this gel provides a useful precursor for the formation of hexagonal boron nitride. It is also very important to note that this chemistry provides a system which is adaptable to sol-gel processing.[22] Although several features require additional study, it is apparent that the amine cross-linking of borazene fragments offers a beneficial and important advance in the use of borazenes as sources for BN. It is interesting to note that some investigators have suggested that the presence of silica in boron nitride improves its processing characteristics as well as prevents hydrolysis of boron nitride.[23] Therefore, the presence of organosilicon in our synthesis may prove beneficial. Additional studies of chemically modified borazenes and other cross-linking reagents are in progress.

Acknowledgment is made to Sandia National Laboratory (contract 56-6882) for financial support of this work. We also thank Dr. Rod Quinn, Dr. D. Doughty, and Dr. J. Ritter for helpful discussions. Transmission electron microscopy was performed at the Electron Microbeam Analysis facility in the UNM Department of Geology and Institute for Meteoritics.

Supplementary Material Available: Figures showing infrared spectra, TGA and DTA traces, infrared spectra, X-ray powder patterns, TEM photographs, and EDS patterns (12 pages). Ordering information is given on any current masthead page.

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[14] TGA traces obtained in air are similar to those obtained in UHP argon, except above 1000 °C a slight weight gain is observed. This suggests a degree of oxidation of boron and residual silicon.

[15] Elemental Anal. Found: B, 36.7; N, 41.2. Analyses for Si and Cl were not obtained. Accurate elemental analyses are difficult to obtain due to incomplete dissolution of the samples.

[16] Brame, E. G.; Margrave, J. L.; Meloche, V. W. *J. Inorg. Nucl. Chem.* **1957**, *5*, 48. Rand, M. J.; Roberts, J. F. *J. Elect. Chem. Soc.* **1968**, *115*, 423. Takahoshi, T.; Itoh, H.; Takeuchi, A. *J. Cryst. Growth* **1979**, *47*, 245.

[17] Pease, R. S. *Acta Crystallogr.* **1952**, *5*, 356. Biscoe, J.; Warren, B. E. *J. Appl. Phys.* **1942**, *13*, 364. Thomas, J.; Weston, N. E.; O'Connor, T. E. *J. Am. Chem. Soc.* **1963**, *84*, 4619. Economy, J.; Anderson, R. *Inorg. Chem.* **1966**, *5*, 989. Matsuda, T.; Uno, N.; Nakae, H.; Hirai, T. *J. Mat. Sci.* **1986**, *21*, 649.

[18] Abbreviations used in the text are defined as follows: TEM = transmission electron microscopy; EDS = energy dispersive X-ray spectroscopy; BET = Brunauer, Emmett, and Teller method for surface area measurement; TGA = thermal gravimetric analysis; DTA = differential thermal analysis.

[19] EDS analyses were performed by using a Tracor Northern 5500 system with a high take-off detector. The sample tilt was 0° during X-ray analysis. The microscope used was a JEOL JEM-2000 FX operated at 200 kV. The point resolution is ~0.3 nm.

[20] HF solutions (40%) are unreactive toward h-BN. Kubo, T.; Inoc, H.; Ochiai, T. Jpn. Kokai. Tokkyo Koho 79 1457 25, **1979**; *Chem. Abstr.* **1980**, *92m*, 134 047d.

[21] Trace analyses obtained from Spectra Co., San Diego, CA.

[22] Transparent plugs of the gel **2** have been formed in several organic solvents, and these have been found to withstand critical point drying in liquid carbon dioxide.

[23] Tsapuk, A. K.; Popobeda, L. G.; Kovalevskii, N. N. *Poroshkovaya Met.* **1978**, *18*, 51; *Chem. Abstr.* **1978**, *88*, 196 260.

The Order of Proton Affinities of the 20 Common L-α-Amino Acids

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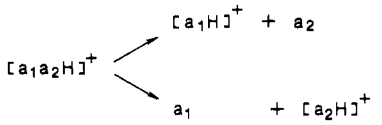
On the basis of the unimolecular decomposition of cluster ions the order of proton affinity (PA) of the 20 common L-α-amino acids is suggested. The results are shown in Table I, where the PA decreases from arginine to glycine. The order obtained agrees with the PA's that have been measured for six of the amino acids.[1]

A protonated dimer of two different amino acids a_1 and a_2 can be observed in the FAB spectrum of a mixture of the two amino acids.[2] It decomposes unimolecularly according to



$$[a_1a_2H]^+ \rightarrow \begin{cases} [a_1H]^+ + a_2 \\ a_1 + [a_2H]^+ \end{cases} \quad (1)$$

The relative rates of the competing reactions in eq 1 can be determined from the relative abundances of $[a_1H]^+$ and $[a_2H]^+$ in the mass-analyzed ion kinetic energy (MIKE)[3] spectrum of the protonated dimer.[4] The order of the rates of the two reactions in eq 1 is the same as the order of the PA's of a_1 and a_2 when the reverse activation energies and the entropy effects of the two reactions can be ignored.

The reverse activation energies can be ignored if they are either close to zero or very similar in magnitude. Assuming that the proton is bridging the two amino acids in the protonated dimer, this will indeed be the case.[5]

Although the structures of the protonated monomers can be guessed with some assurance, this is not the case for the structures of the protonated dimers. Hence the entropy effect is more difficult to assess. For the amino acids where equilibrium measurements on proton exchange reactions have been carried out no appreciable entropy effect has been noticed.[1a]

When the α-NH_2 group is the site of protonation, charge-induced dipole interaction with the side chain leads to stabilization

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[1] (a) Meot-Ner (Mautner), M.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1979**, *101*, 686. (b) Locke, M. J.; McIver, R. T. *J. Am. Chem. Soc.* **1983**, *105*, 4226.

[2] Bojesen, G. *J. Chem. Soc., Chem. Commun.* **1986**, 244.

[3] (a) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1977. (b) Beynon, J. H.; Cooks, R. G.; Amy, J. W.; Baitinger, W. E.; Ridley, T. Y. *Anal. Chem.* **1973**, *45*, 1023A.

[4] (a) The protonated dimers were generated by fast atom bombardment (Xe, ~9 keV) of a mixture of two L-α-amino acids (Sigma) in 1 M trichloroacetic acid in glycerol (87%). The mass spectrometer employed was a Varian 311A (BE geometry). The intensities of the peaks in the MIKE spectrum (average of 3–5 scans) were corrected for the energy dependent yield of secondary electrons at the multiplier. For analyses of daughter ions with mass differences of 1 or 2 the decomposition was studied in the third field free region of a ZAB-3F (BEB geometry).

[5] Cooks, R. G.; Kruger, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 1279.