retained in the ceramic, the ceramic is nicely crystalline, and the formation of the crystalline phase occurs at a lower temperature than normally observed with other poly(borazinylamine) oligomers explored in our work. The crystallization behavior may result from the small LiCl impurity. Unfortunately, the organic solvent solubility of **8** is not well behaved; however, this material may find some special applications that utilize the lower processing temperature.

Oligomer **7**, with appropriate care, is converted to good quality h-BN with fair ceramic yield; however, the insoluble character of the oligomer limits its use for solution-based coating applications. Unfortunately, the one oligomer, **6**, with useful solubility properties is burdened by thermal chemistry that leaves carbon residues in the product. For applications that are not influenced by small amounts of carbon (5% or less), this material will be useful. Further chemical modifications of poly(borazinylamines) directed at achieving the design objectives for processible BN preceramics[3] are in progress.

Acknowledgment is made to Sandia National Laboratory (Contract 55-7566), the National Science Foundation (CHE-8503550), and the UNM/NSF Center for Microengineered Ceramics, which is supported by NSF (CDE-8803512), Los Alamos and Sandia National Laboratories, the New Mexico Research and Development Institute, and the ceramics industry for financial support of the chemical studies and to the U.S. Department of Energy (Grant DT-FGO5-86ER75294) for the purchase of the high-field NMR spectrometer. Transmission electron microscopy was performed at the Electron Microbeam Analysis facility in the UNM Department of Geology and Institute for Meteoritics.

Registry No. **2**, 127232-88-6; **3**, 21348-06-1; **4**, 127232-89-7; **5**, 15270-88-9; **6** (homopolymer), 127232-90-0; **7** (homopolymer), 127232-91-1; **8** (homopolymer), 127232-92-2; boron nitride, 10043-11-5.

Supplementary Material Available: Table S-1, listing additional crystallographic data, Table S-2, listing anisotropic thermal parameters, Table S-3, listing hydrogen atom positional parameters for compounds **2**–**5**, Table S-4, listing bond distances and angles, and Table S-6 listing infrared spectra for compounds **2**-**6** (24 pages); Table S-5, listing structure factor tables for compounds **2**–**5** (37 pages). Ordering information is given on any current masthead page.

Synthesis of Boron Nitride Ceramics from Oligomeric Precursors Derived from 2-(Dimethylamino)-4,6-dichloroborazine

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Received December 20, 1989

2-(Dimethylamino)-4,6-dichloroborazine has been combined with hexamethyldisilazane and heptamethyldisilazane, and the chemical and thermal processing of the resulting oligomers has been examined. Pyrolysis of the oligomers under selected conditions results in formation of turbostratic BN that has been characterized by powder X-ray diffraction and transmission electron microscopy techniques. The oxidation stability of the boron nitride prepared in this fashion has also been examined.

Introduction

Most ceramic materials, such as boron nitride, have been commercially prepared for years by using classical high-temperature reaction techniques and simple, inexpensive reagents. Unfortunately, this preparative approach is rather inflexible, and it is difficult to obtain nonpowder forms (e.g., films and fibers) or systematically alter compositions and properties of ceramic products obtained in this fashion. It has been suggested that preceramic polymer reagents could offer useful alternatives for advanced ceramic syntheses and processing,[1] and in the past five years attempts have been made to develop preceramic polymers and to explore their conversion to solid-state materials.[1,2] In particular, several useful preceramic polymer routes have been devised for boron nitride.[3-7] With several of these chemical systems, it is now possible to produce amorphous and crystalline powders, fibers, and films of pure BN. Expanding upon our previous reports on poly(borazinylamine) precursors,[4] we report here the

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formation of additional preceramic oligomers from oligomerization reactions of 2-(dimethylamino)-4,6-dichloroborazine[8] with hexamethyldisilazane and heptamethyldisilazane. The pyrolysis chemistry of the oligomers that provides boron nitride and carbon-contaminated boron nitride is also described.

Experimental Section

General Information. Standard inert-atmosphere techniques were used for the preparation and manipulation of all reagents. Solvents were carefully dried with appropriate drying agents[9] and distilled under dry nitrogen. Dimethylamine (Fischer) was dried over KOH, and $H_3B{\cdot}THF$ solution (Aldrich) was employed directly after checking purity by ^{11}B NMR spectroscopy. Trichloroborazine was prepared and purified as described in the literature.[10] Hexamethyldisilazane and heptamethyldisilazane (Aldrich) were distilled prior to use. Infrared spectra were recorded on a Nicolet 6000 FT-IR spectrometer, and NMR spectra were obtained from Varian FT-80A and JEOL GSX-400 NMR spectrometers. Spectral standards were $(CH_3)_4Si$ (^1H) and $F_3B{\cdot}O(C_2H_5)_2$ (^{11}B). Thermogravimetric analyses (TGA) were performed on Du Pont Model 1090 and Perkin-Elmer Delta Model TGA7 instruments. EDS analyses were performed by using a Tracor Northern Model 5500 system with a high take-off detector. The sample tilt was 0° during X-ray analysis. Transmission electron microscopy was accomplished on a JEOL JEM-2000 FX microscope operated at 200 kV. The point resolution was 0.3 nm. Powder X-ray diffraction analyses were performed with a Sintag PAD V diffractometer. Elemental analyses were obtained from Galbraith Laboratories and the UNM Microanalytical Services laboratory.

Preparation of $H_3N_3B_3Cl_2(NMe_2)$. 2-(Dimethylamino)-4,6-dichloroborazine was prepared as described in the literature[11] with minor modifications. In a typical experiment (9.92 g, 54 mmol) 2,4,6-trichloroborazine was dissolved in diethyl ether (200 mL), and dimethylamine (4.86 g, 108 mmol) was slowly condensed into the reaction mixture with stirring at −78 °C. The contents were allowed to warm to 25 °C overnight, and the resulting mixture was filtered under nitrogen. The residue was washed with diethyl ether (2 × 100 mL), and the combined filtrate and extract solutions were evaporated to dryness with an oil pump vacuum. The remaining solid was sublimed, and the sublimate was dissolved in hexane (200 mL) and filtered to remove small amounts of dimethylammonium chloride that carried through the initial ether solution filtration and sublimation. The hexane filtrate was evaporated to dryness, and the resulting solid was sublimed again, yield 9.1 g, 87%. Anal. Calcd for $C_2H_9B_3N_4Cl_2$: C, 12.48; H, 4.71. Found: C, 12.64; H, 4.74. Mass spectrum m/e 196 (3) M^+, 190–196 (parent envelope, base peak 191); $^{11}B\{^1H\}$ NMR δ 30.0 (int 2), 24.3 (int 1).

Preparations of Preceramic Oligomers. (a) $[(CH_3)_3Si]_2NH$. 2-(Dimethylamino)-4,6-dichloroborazine (6.91 g, 35.7 mmol) was dissolved in chlorobenzene (50 mL), and hexamethyldisilazane (5.76 g, 355.7 mmol) was added in one portion to the stirred solution. After addition, stirring was stopped, and a white gel formed. The reaction mixture was refluxed for 5 h, and then the volatiles were removed at 25 °C under an oil pump vacuum. A white granular solid (**1**) was collected, yield 4.7 g. Anal. Calcd for $C_2H_{10}B_3N_5$: C, 17.6; H, 7.4; N, 51.3. Found: C, 24.9; H, 7.2; N, 41.9. Alternatively, the reaction may be accomplished in hexane without the intermediate formation of a gel. Instead, a white solid is obtained (**2**). Anal. Found: C, 18.2; H, 7.7; N, 49.5. IR (KBr, cm^{-1}) 3436 (m), 2957 (w), 2921 (w), 2872 (w), 2795 (w), 1513 (vs), 1464 (vs), 1415 (vs), 1386 (vs), 1105 (m), 1013 (w), 971 (w), 837 (w), 710 (s), 619 (s).

(b) $[(CH_3)_3Si]_2NCH_3$. 2-(Dimethylamino)-4,6-dichloroborazine (7.2 g, 44.8 mmol) was dissolved in chlorobenzene (100 mL), and heptamethyldisilazane (7.85 g, 44.8 mmol) was added in one portion to the stirred solution. The mixture was stirred at 25 °C overnight, and the volatiles were then removed by vacuum evaporation, leaving a white granular solid (**3**), yield 7.2 g. A gel forms from the original reaction mixture after prolonged stirring or during removal of the solvent. IR (KBr, cm^{-1}) 3471 (s), 3436 (s), 2971 (s), 2859 (s), 2788 (s), 1520 (vs), 1450 (vs), 1401 (s), 1083 (s), 957 (m), 893 (w), 703 (s), 604 (s), 576 (s), 534 (m). In a related fashion, 2-(dimethylamino)-4,6-dichloroborazine (10.76 g, 55.6 mmol) was combined in chlorobenzene with heptamethyldisilazane (9.75 g, 55.6 mmol), and the reaction mixture was heated to 60 °C. Gel formation was observed after warming. The mixture was refluxed for 5 h, and volatiles were then removed by vacuum evaporation, leaving a white granular solid (**4**), yield 8.6 g, 97%. Anal. Found C, 28.9; H, 8.0; N, 31.2.

In a third procedure, 2-(dimethylamino)-4,6-dichloroborazine and heptamethyldisilazane were combined in equimolar amounts (5.18 mmol) in hexane, and the mixture was refluxed for 5 h. The polymeric product (**5**) was collected by filtration and washed with fresh hexane, yield 0.55 g, 70%. Anal. Calcd for $C_3H_{12}N_5B_3$: C, 23.9; H, 8.0; N, 46.5. Found: C, 22.7; H, 7.87; N, 43.3. IR (KBr, cm^{-1}) 3450 (s), 2957 (s), 2929 (s), 2887 (s), 2802 (m), 1527 (vs), 1401 (vs), 1069 (vs), 964 (w), 929 (w), 703 (vs), 604 (s).

Reaction of Oligomer 1 with $H_3B{\cdot}THF$. Poly(2-(dimethylamino)borazin-4,6-diylimino) (**1**, 2.25 g, 16 mmol) was suspended in diethyl ether (150 mL), and $H_3B{\cdot}THF$ (33 mL, 1 M solution) was added via a gas-tight syringe. After 24 h, no $H_3B{\cdot}THF$ could be detected in an aliquot of the solution by ^{11}B NMR analysis; however, signals for μ-$Me_2NB_2H_5$ (major component) and $Me_2N(H)BH_3$ (minor component) could be observed in the ^{11}B NMR spectrum. Volatiles were removed by vacuum evaporation, leaving 1.7 g of a white residue (**6**). Anal. Found: B, 31.07; N, 55.62; H, 8.15; C, 3.90.

Pyrolysis of Oligomers. (a) 2-(Dimethylamino)-4,6-dichloroborazine. A sample (1.5 g) of the borazine monomer was slowly heated, in a closed quartz tube, to 200 °C under nitrogen for 4 h. The tube was further heated to 600 °C (rate = 100 °C/h) and then to 1200 °C over 2 h under a stream of nitrogen. After 12 h at 1200 °C, a black solid (0.55 g) was collected. An infrared spectrum and powder X-ray diffraction pattern showed the presence of turbostratic BN. Anal. Found: B, 33.1; C, 18.7; N, 43.4; H, 1.1.

(b) Pyrolysis of 1 and 2. Typically, a sample of **1** (4.5 g) was pyrolyzed at 900 °C in a quartz tube for 12 h with continuous removal of the volatiles. The residual solid was then heated at 1200 °C for 2 h, and 2.4 g of a grey solid was isolated: IR (KBr, cm^{-1}) 3415 (w, br), 1430 (vs, br), 795 (s); XRD d = 3.44, 2.13. Alternatively, a sample of **1** (3.5 g) was pyrolyzed in vacuo for 6 h at 900 °C and then under ammonia at 1200 °C for 12 h, and a faintly grey or white powder (1.8 g) was isolated: XRD d = 3.46, 2.13. Identical results were obtained from pyrolysis of **2**. Anal. Calcd for BN: B, 43.56; N, 56.44. Found: B, 42.87; N, 56.21; C, 0.71.

(c) Pyrolysis of 3. A sample of **3** was pyrolyzed at 900 °C for 12 h in a quartz tube under a nitrogen atmosphere, and 2.85 g of a black solid was isolated. This sample was heated in air at 1100 °C for 12 h with formation of ~3.1 g of a grey solid. The gain in weight results from air oxidation. A portion of this sample (1.0 g) was washed with 40% HF, and 0.2 g of h-BN was recovered and identified by its XRD pattern. In a second procedure, 4.81 g of **3** was pyrolyzed at 900 °C for 12 h under N_2, and 2.18 g of a black residue was collected. This was further heated to 1200 °C under NH_3 for 12 h, leaving 1.92 g of a faintly yellow powder. A 1.0-g sample was then briefly heated in air at 700 °C with negligible weight loss, and h-BN was isolated: IR (KBr, cm^{-1}) 3422 (w, br), 1379 (vs, br), 773 (vs); XRD d = 3.40, 2.15. In a thrid procedure, 3.87 g of **3** was heated in vacuo at 900 °C for 6 h and then in NH_3 at 1200 °C for 12 h, and 1.65 g of a faintly yellow

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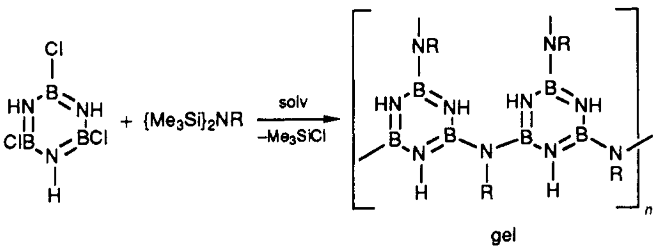
Scheme I



powder was isolated. A sample (0.80 g) of this powder was briefly heated in air at 700 °C, leaving a crystalline sample of h-BN (0.73 g): IR (KBr, cm^{-1}) 3429 (w), 1394 (vs, br), 795 (vs); XRD d = 3.42, 2.14. Pyrolysis of 5 gave similar results. Anal. Calcd for BN: B, 43.56; N, 56.44. Found: B, 41.07; N, 53.79; C, 2.01; H, 0.92.

(d) Pyrolysis of 4. A portion of 4 (7.5 g) was first heated for 40 h at 900 °C with continuous removal of the volatile byproducts with an oil pump vacuum, and a black residue (3.1 g) was collected. A sample (3.0 g) of this solid was pyrolyzed in air for 12 h at 1100 °C, leaving a white solid (3.47 g). Extraction of a 1.0-g sample of this solid with 40% HF left 0.18 g of h-BN identified by its XRD pattern. Alternatively, a sample of the black solid (4.61 g) was heated under NH_3 for 12 hours at 1200 °C, and a yellow powder (3.97 g) was recovered. A sample of this powder (2.0 g) was subsequently pyrolyzed in air at 700 °C for 12 h, and 1.87 g of white solid with low crystallinity was obtained. In a third procedure, a sample of 4 (3.89 g) was pyrolyzed in vacuo at 900 °C and then in NH_3 at 1200 °C for 12 h, and a faintly yellow solid (1.65 g) was obtained. A portion of this (0.8 g) was heated at 700 °C in air, and a white solid (0.7 g) was obtained and identified as boron nitride. IR (KBr, cm^{-1}) 3429 (vw), 1393 (vs, br), 795 (vs). XRD d = 3.42, 2.13. Anal. Calcd for BN: B, 43.56; N, 56.44. Found: B, 42.07; N, 54.15; C, 1.62; H, 0.85.

(e) Pyrolysis of 6. A sample (1.7 g) was heated at 900 °C for 12 h with continuous removal of the volatiles. The residual material was heated under N_2 or NH_3 for 12 h, and the remaining white solid (1.0 g) was identified as boron nitride: IR (KBr, cm^{-1}) 1390 (vs, br), 809 (vs); XRD d = 3.46, 2.12. Anal. Calcd for BN: B, 43.56; N, 56.44. Found: B, 43.34; N, 56.38; C, 0.12.

Oxidation Studies. The oxidation studies were performed by TGA analyses in air.

Results and Discussion

Synthesis. We have previously reported[4] that combinations of trichloroborazines, $(ClBNH)_3$ or $(ClBNCH_3)_3$, with hexamethyldisilazane, $[(CH_3)_3Si]_2NH$, and heptamethyldisilazane, $[(CH_3)_3Si]NCH_3$, in several organic solvents, produce oligomeric poly(borazinylamine) gels. Although the detailed structures of the gels have not been fully elucidated, it has been concluded that the majority of borazine rings are cross-linked at all three boron atoms of each ring, forming a "three-point" oligomer[12] through NH or NCH_3 bridge bonds as depicted in Scheme I. Model chemistry generally supports this concept.[13] Pyrolysis of a "carbon-free" gel, $[(N(H)BNH)_3]_n$, under inert gases (N_2, Ar) or a reducing atmosphere (NH_3) produces high-quality hexagonal BN powder. On the other hand, oligomers that contain methyl groups, upon pyrolysis under inert atmospheres, typically retain carbon in the ceramic powder product. This impurity is reduced but usually not completely eliminated by pyrolysis of the oligomer in an NH_3 atmosphere. Similar observations of carbon inclusions in BN ceramics have been made by Paciorek and co-workers[5] during their studies of the pyrolysis of several organic-fragment-substituted borazine monomers and oligomers. The "carbon-free" oligomer and its solutions in liquid NH_3 have proven to be useful for coating and fiber-forming applications; however, the very low solubility of the oligomer in organic solutions has limited its use for several potential applications.

Building upon our previous results, it was conceptually important to inquire if potentially more soluble "two-point"[12] or "linear" poly(borazinylamine) oligomers could be prepared from borazine monomers containing a boron site that would not participate in the initial ring condensation chemistry. Many functional groups may be considered for blocking oligomerization at one boron site in a borazine. However, from a processing standpoint, it is necessary to recognize that some blocking or protecting groups may not be practical. For example, strongly bonded organic groups (e.g., alkoxy, alkyl, and aryl fragments) may be difficult to remove from ring boron atoms under gentle processing conditions following monomer oligomerization. Therefore, subsequent pyrolysis products may contain contaminate atoms (e.g., oxygen and/or carbon). Alternatively, weakly bonded blocking groups or inherently reducing substituents (e.g., sulfido, amino, or H) should function in an acceptable fashion.

Surprisingly, there are relatively few well-documented singly B-substituted borazine compounds,[14,15] $(X)(Y)_2B_3N_3H_3$, and even fewer that might be useful in oligomerization chemistry. One potentially useful monomer is $(Me_2N)(Cl)_2B_3N_3H_3$. This compound should permit two-point oligomerization without competitive attack at the amino boron site, and the amino group should be subject to cleavage chemistry in a later stage of processing. In fact, Beachley and Durkin[11] have prepared the monomer in good yield from the combination of $(ClBNH)_3$ and dimethylamine in diethyl ether. Furthermore, they observed that the Me_2N group is replaced with hydride by addition of B_2H_6,[16] although the yield of $(H)(Cl)_2B_3N_3H_3$ was reported to be only 58%. These observations suggested a general reaction scheme (eq 1 and 2) for the production of a useful two-point borazine oligomer.

The initial monoamination reaction of trichloroborazine proceeds smoothly to give high yields of crystalline $(Me_2N)(Cl)_2B_3N_3H_3$. Combination of the monomer with hexamethyldisilazane in chlorobenzene produces a white gel that following solvent reflux for 5 h and subsequent evaporation of the solvent gives a white granular solid, 1. The reaction also is accomplished in hexane without intermediate gel formation, and a granular white solid, 2, is obtained after vacuum evaporation of the solvent. In a similar fashion, mixtures of the monomer and heptamethyldisilazane produce oligomers. In chlorobenzene at 25 °C, a gel is formed at a much slower rate than observed with $(Me_3Si)_2NH$, and a white granular solid, 3, is deposited following solvent evaporation. The rate of for-

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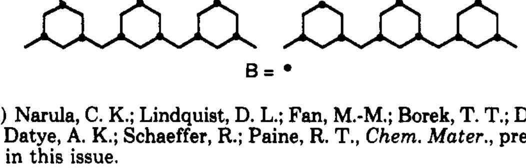
[12] The term three-point oligomer is used to indicate oligomerization through all three boron atoms of the borazine ring. Two-point oligomers are those that have ring attachment through only two boron atoms:



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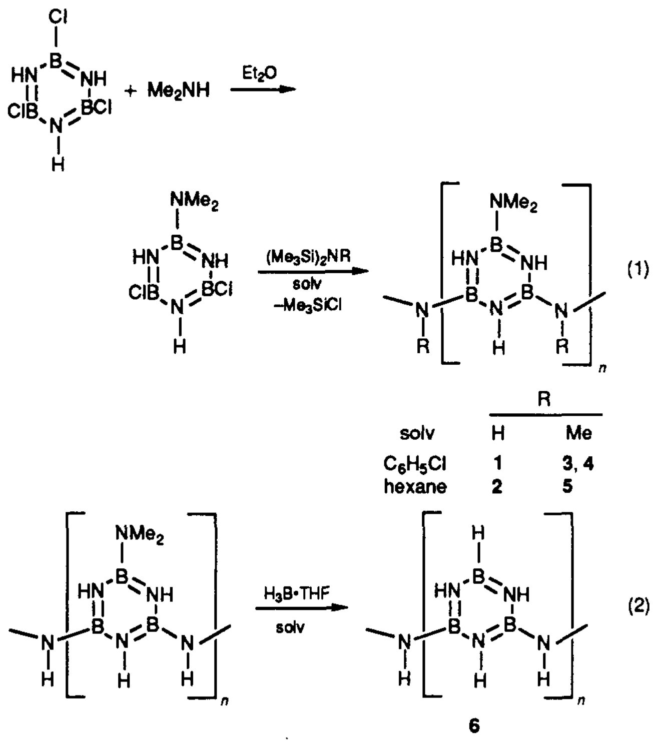

solv	R: H	R: Me
C_6H_5Cl	**1**	**3, 4**
hexane	**2**	**5**

6

mation of the gel is accelerated by gentle heating at 60 °C, followed by reflux of the solvent for 5 h. A white solid, **4**, is isolated by evaporation of the solvent. In hexane, an insoluble oligomer, **5**, is formed from the refluxed reaction mixture, and this is isolated by filtration.

The reaction of **1** with $H_3B·THF$ in diethyl ether was initially followed by ^{11}B NMR spectroscopy. During a 24-h period, the resonance due to $H_3B·THF$ (^{11}B δ −0.7) completely disappears and a major peak due to formation of μ-$Me_2NB_2H_5$ (^{11}B δ −17.9)[17,18] and a minor peak ascribed to $Me_2NH·BH_3$ (^{11}B δ −13.5)[17,18] appear in an area ratio ~7:1. The formation of μ-$Me_2NB_2H_5$ is consistent with observations made by Beachley[11,19] on the reaction of $(Me_2N)(Cl)_2B_3N_3H_3$ with B_2H_6 in diethyl ether. The appearance of the small amount of (dimethylamino)borane may result from residual dimethylamine or from a competing side reaction involving BH_4^- present as a stabilizer in the $H_3B·THF$ reagent. On a synthetic scale, the reaction of the oligomer with $H_3B·THF$ proceeds smoothly, and vacuum evaporation of the volatiles leads to isolation of a granular white solid, **6**. Elemental analyses for this material indicate that a small quantity of carbon is retained (<4%), and this suggests that the cleavage of the NMe_2 groups is not complete, the removal of $Me_2NH·BH_3$ and μ-$Me_2NB_2H_5$ is not entirely accomplished, or some solvent remains in micropores of the gel.

As is the case with many preceramic reagents, characterization of the oligomers **1**–**6** remains incomplete due to the relatively low solubility of the initial oligomers prior to solvent evaporation and complete insolubility in common organic solvents after vacuum drying. Attempts to obtain reproducible molecular weight measurements on soluble fractions prior to full gelation have also been unsuccessful. The compositions of the vacuum-dried gels, **1**, **2**, **4**, and **5**, have been examined by C, H, N elemental analyses, and these data are presented in the Experimental Section. The data are useful but not unambiguous since the gels, even after extensive vacuum drying, retain small amounts of solvent. This observation is substantiated by the appearance of solvent in low-temperature pyrolysis off-gases. Further, the theoretical composition is unclear since the identity and number of end-capping groups (assumed to be Cl and/or $N(H)SiMe_3$) have not been determined. Nonetheless, relatively good agreement between theoretical (with no end-capping groups) and observed C, H, N compositions are obtained for oligomers in **2** and **5** prepared in hexane solutions where solvent retention is considered to be low.

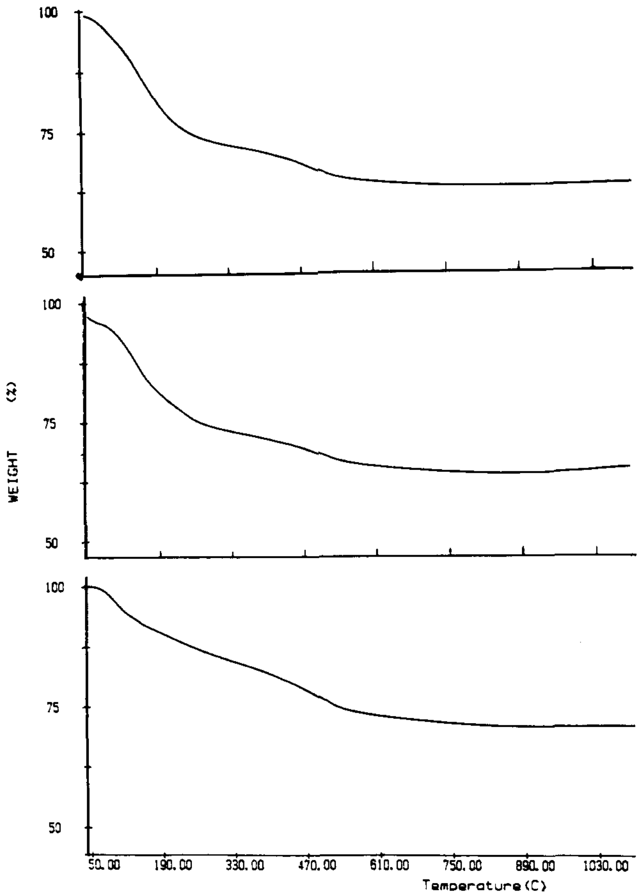

Figure 1. Thermogravimetric analyses for samples of **2**, **3**, and **6**. Pyrolysis atmosphere: Ar, 25 cm³, min⁻¹. Heating rate: 10.0 °C min⁻¹. Sample weights: 10–15 mg.

Infrared spectra for gels **2**, **3**, **5**, and **6** also provide data supportive of the general synthetic scheme summarized in eqs 1 and 2. Each spectrum shows an absorption in the region 3475–3430 cm^{-1} that is typical of $\nu_{N(bridge)-H}$ and $\nu_{N(ring)-H}$ stretching frequencies in substituted borazines.[19-22] Further, **2**, **3**, and **5** show three or four bands in the region 2975–2785 cm^{-1} that may be attributed to CH_3 stretching modes for NCH_3 and $N(CH_3)_2$ groups. The spectral pattern is similar to the features found for trisaminoborazines.[22] Only very weak bands are found in the range 2975–2785 cm^{-1} for **6**, and this is consistent with removal of the majority of the terminal $N(CH_3)_2$ groups in **1** by addition of $H_3B·THF$. The frequency range 1550–1440 cm^{-1} is complex in each sample, and this region is typically

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associated with B–N ring stretching modes and terminal B–NMe_2 stretching frequencies in aminoborazines.[19–22] Last, a weak absorption at 2535 cm^{-1} in **6** may be tentatively assigned to a B–H stretching mode.

Despite the deficiency of detailed characterization data for the oligomeric gels, it is likely that "two-point" structures such as shown in eq 1 are present, and this conclusion is supported by model chemistry studied in our laboratory[4,13] and by work reported by Meller.[23]

Oligomer Pyrolyses. As a base-line study, a sample of the monomer $(Me_2N)(Cl)_2B_3N_3H_3$ was heated at 200 °C under N_2 for 4 h, then at 600 °C briefly, and finally at 1200 °C. The sample was maintained at 1200 °C under nitrogen for 12 h, and a black solid was isolated. An X-ray powder pattern showed the presence of turbostratic boron nitride, although the yield was relatively small. Elemental analyses also showed the presence of carbon in the ceramic product. This pyrolysis behavior resembles reports given by Paciorek and co-workers[5] for the pyrolysis of other monomeric substituted borazine compounds.

To guide the examinations of the pyrolysis chemistry of bulk samples of oligomers, thermogravimetric analyses under argon were obtained. Typical thermograms are shown in Figure 1 for samples of **2**, **3**, and **6**. The curves for **2** and **3** are similar, with the major weight loss occurring between 50 and 200 °C and negligible weight loss above 600 °C. For oligomer **6**, the thermal chemistry is more gradual, and weight loss is also nearly complete at 600 °C. The TGA data suggest ceramic yields of 60–70%. The off-gases from pyrolysis of bulk samples of the oligomers were collected and identified as solvent, ammonia, methylamine (**3**, **4**, and **5**), and dimethylamine. No attempt was made to carefully quantify the yields of the individual off-gases. Since the TGA traces gave no clue of any abrupt or unusual thermal chemistry, bulk pyrolyses were studied by ramping the pyrolysis temperature of each sample at a rate of ~100 °C/h. Specific results from the pyrolyses are outlined.

Pyrolyses of **1** and **2** proceed in an identical fashion. Samples were placed in a quartz tube and heated at 900 °C for 12 h under vacuum to remove the majority of volatile pyrolysis products. The remaining solid was pyrolyzed under vacuum or under flowing NH_3 at 1200 °C. The resulting ceramic powders are faintly grey. Infrared spectra of the solids show two absorptions typical of boron nitride[24–27] centered at ~1430 and 795 cm^{-1} plus a weak absorption at ~3400 cm^{-1} that suggests the presence of residual N–H groups in the solid. Powder X-ray diffraction patterns show relatively broad lines with *d* values ~3.4 (002) and ~2.1 (100, 101). These compare well with literature data for turbostratic BN.[28] Transmission electron microscopic (TEM) analyses of a sample obtained from **1** shows well-defined lattice fringes on the BN particles. Energy-dispersive X-ray analyses showed no evidence for heavy-atom impurities. The samples retain very small amounts of carbon impurities estimated by elemental analysis (<1%) with cleaner samples obtained from pyrolysis at 1200 °C in an ammonia atmosphere.

The thermal chemistry of the oligomers **3** and **5**, which contain methyl groups on bridging nitrogen atoms, was examined under several conditions. Pyrolysis of **3** or **5** at 900 °C for 12 h under a nitrogen atmosphere produces brown solids that contain 5–15% carbon. Subsequent pyrolysis in air at 1100 °C produces grey solids with a weight *gain* with respect to the weight of the brown solids that suggests oxidation of boron nitride. Indeed, the majority of the mass of these products (80–95%) is soluble in 40% HF, and the remaining residues are identified as turbostratic BN by X-ray powder patterns. Alternatively, when the second-stage pyrolyses are accomplished at 1200 °C under NH_3, faintly yellow solids are obtained. Characterization of these samples by elemental analyses, infrared spectroscopy, X-ray powder diffraction, and TEM gave results comparable with those obtained from the ceramic products from **1** and **2**. In each case, the overall ceramic yields are 45–60%,[29] and the turbostratic BN contains 1–5% carbon impurity.

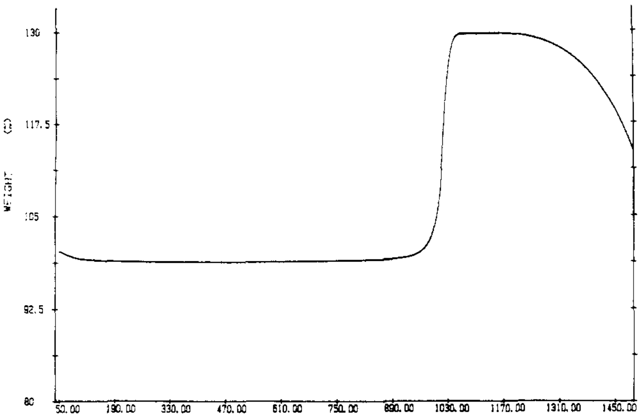

Figure 2. Thermogravimetric analysis of ceramic product obtained from **6**. Pyrolysis atmosphere: air, 25 cm^3 min^{-1}. Heating rate: 10 °C min^{-1}. Sample weight: 18 mg.

A sample of **4** heated for 40 h at 900 °C in a vacuum gave a black residue (~40% yield). A sample of this solid heated at 1100 °C in air for 12 h shows a gain in weight, and the majority of the residue is a boron oxide soluble in 40% HF solution. Alternatively, a sample of the black residue pyrolyzed under NH_3 at 1200 °C for 12 h produces a faintly yellow solid. Infrared and X-ray diffraction analyses show that the material is boron nitride, although the degree of crystallinity is relatively low. Last, a sample of **4** pyrolyzed only under NH_3 for 12 h at 1200 °C gave a faintly yellow solid also identified as BN by XRD. These samples also typically retain 1–5% carbon impurities.

Pyrolysis of gel **6** obtained from treatment of **1** with $H_3B{\cdot}THF$ to remove the blocking groups, Me_2N, was examined in two stages. The gel was first heated at 900 °C for 12 h under a vacuum, and the resulting solid was then heated at 1200 °C under N_2 for 12 h. The remaining white product is identified as turbostratic boron nitride by infrared spectroscopy, X-ray powder diffraction, and TEM analyses. Elemental analyses shows traces of carbon impurities (<0.5%), and the X-ray analyses indicate that these samples have the highest degree of crystallinity.

Oxidation Studies. During the course of the pyrolysis studies, it was noted that significant weight gain, followed by weight loss, occurred when samples of the ceramic products were heated in air at 1100 °C and above. It has been previously noted many times that boron nitride is sensitive to oxidation; however, systematic studies of this

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(29) One explanation for the low ceramic yields obtained in bulk pyrolysis studies, compared with those deduced from TGA analysis, is that the samples for TGA analyses were ground to fine powders and highly evacuated prior to analysis. This sample preparation would remove a greater percentage of any retained solvent.

chemistry are few in number.[27] In the present study, oxidation of turbostratic BN samples obtained from 2 and 6 (vacuum pyrolysis at 900 °C, pyrolysis at 1200 °C under N_2) was studied by TGA in air. A typical curve for 6 is shown in Figure 2. The samples show no weight gain or loss from 50 to ~900 °C. Above 900 °C, an abrupt weight gain corresponding to oxidation of the BN occurs. Above ~1050 °C, a weight loss occurs that corresponds to volatilization of the boron oxide species formed in the oxidation process. More detailed examinations of the oxidation behavior of other turbostratic and highly ordered h-BN samples are in progress that address the effects of crystallinity, surface area, and other features on oxidation characteristics.[30]

Conclusion

This study shows that a series of two-point poly(borazinylamine)s, protected from three-point polymerization by a NMe_2 group on each borazine monomer unit, can be prepared and used as oligomeric precursors to form turbostratic boron nitride powder that contains small (1–5%) carbon impurity. The ceramic products obtained under several pyrolysis conditions are sensitive to air oxidation above ~900 °C. Further, it is found that the majority of dimethylamino protecting groups may be readily removed from the two-point oligomer 1 at room temperature by treatment of the gel with $H_3B{\cdot}THF$. The resulting oligomer is converted to turbostratic BN in good yield (55–60%) with or without the use of NH_3 in the pyrolysis atmosphere, and carbon impurities are negligible. Although these reagents have been found to be useful only for the preparation of BN powders, the results suggest additional chemical modifications that should provide fusible or soluble polymeric precursors.

Acknowledgment. Financial assistance for this study was provided by Sandia National Laboratory (Contract 55-7566) and the National Science Foundation (Grant CHE-8503550). A DOE contract (DE-FG05-86ER75294) provided support for the purchase of the high-field NMR spectrometer used to characterize the soluble borazine compounds.

Registry No. BN, 10043-11-5; ([$(CH_3)_3Si]_2NCH_3$)(2-(dimethylamino)-4,6-dichloroborazine (copolymer), 127491-80-9; ([$(CH_3)_3Si]_2$)(2-(dimethylamino)-4,6-dichloroborazine (copolymer), 127516-89-6.

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Oxygen-17 Nuclear Magnetic Resonance Studies of Lanthanum Strontium Copper Oxide

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Received January 3, 1990

We have obtained oxygen-17 nuclear magnetic resonance spectra of $La_{1.85}Sr_{0.15}CuO_4$ at temperatures ranging from 12 to 295 K. We observe three resonances and assign them to planar oxygen sites, axial oxygen sites, and a satellite peak of the lanthanum-139 resonance. Temperature-dependent studies of the resonance frequency associated with the axial site show that this resonance moves to higher frequency just above the critical temperature and then rapidly shifts to lower frequency upon formation of the superconducting state. It is suggested that the spin susceptibility of this oxygen site is affected by the onset of superconductivity. Spin–lattice relaxation of this resonance appears to be dominated by quadrupolar mechanisms at temperatures above the critical temperature; the relaxation rate is nearly constant below the critical temperature.

Introduction

The discovery of superconductivity above 30 K in alkaline-earth-metal-substituted lanthanum copper oxides in 1986[1] has led to numerous research efforts aimed at characterizing and understanding the mechanism of high-temperature superconductivity in these materials. Because oxygen plays a key role in the superconducting mechanism as well as in the processing of these oxides, we decided to probe the microstructure around the oxygen nuclei using oxygen-17 nuclear magnetic resonance (NMR) experiments. Of the many high-temperature superconducting oxides discovered in the last few years, the lanthanum copper oxide systems lend themselves particularly well to oxygen-17 NMR studies because of their relatively simple crystal structures and high symmetry around the two distinct oxygen sites. Furthermore, we hoped that an increased understanding of the role of oxygen in these systems would assist the efforts at understanding superconductivity in more complex systems that superconduct at higher temperatures.

NMR measurements of the spin–lattice relaxation rates ($1/T_1$) and the Knight shift (K) can provide local, microscopic information on the spin dynamics in these materials. In particular, we surmised that determination of the spin–lattice relaxation rates above and below the critical temperature would give a localized measure of the density of states at the Fermi level and of the superconducting bandgap.[2] In metallic compounds where relaxation pro-

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