

144.96, 144.51, 141.04, 140.52, 140.30, 140.23, 134.52, 133.47, 133.24, 132.62, 131.68, 131.50, 131.23, 131.03, 129.05, 128.93, 128.79, 128.61, 128.39, 128.15, 127.99, 127.87, 127.67, 127.52, 127.41, 127.33, 127.01, 126.92, 126.75, 126.60, 126.48, 126.40, 126.28, 126.15, 126.06, 123.35, 123.15 (Ar), 33.92, 33.59 ($C(CH_3)_3$), 32.60, 32.11, 31.83, 31.34, 31.05 ($ArCH_2Ar$), 31.47, 30.82 ($C(CH_3)_3$); FAB MS 1019 (M^+) (Calcd. M^+ 1019); Anal. Calcd. for $C_{68}H_{61}NO_8$: C, 80.05; H, 6.03. Found: C, 80.17; H, 6.09.

Acknowledgment. This study was supported financially from the Basic Science Research Institute Program, Ministry of Education, 1997, Project No. BSRI-97-3406 and the Organic Chemistry Research Center (OCRC).

References

- Gutsche, C. D. *Calixarenes*, Stoddart, J. F. Ed.; Royal Society of Chemistry; London, 1989.
- Calixarenes: A Versatile Class of Macrocyclic Compounds*, Vicens, J.; Böhmer, V. Eds.; Kluwer Academic Publishers: Dordrecht, 1991.
- Böhmer, V. *Angew. Chem. Int. Ed. Eng.* 1995, 34, 713.
- Muthukrishnan, R.; Gutsche, C. D. *J. Org. Chem.* 1979, 44, 3962.
- Arima, T.; Kawabata, H.; Matsuda, T.; Muramatsu, T.; Satoh, H.; Fujio, K.; Manabe, O.; Shinkai, S. *J. Org. Chem.* 1991, 56, 301.
- Ikeda, A.; Nagasaki, T.; Shinkai, S. *J. Phy. Org. Chem.* 1992, 5, 699.
- Böhmer, V.; Merkel, L.; Kunz, U. *J. Chem. Soc., Chem. Commun.* 1987, 896.
- Böhmer, V.; Mardhollek, F.; Zetta, L. *J. Org. Chem.* 1987, 52, 3200.
- Shinkai, S.; Arimura, T.; Kawabata, H.; Murakami, H.; Iwamoto, K. *J. Chem. Soc., Perkin Trans. 1* 1991, 2429.
- Reddy, P. A.; Gutsche, C. D. *J. Org. Chem.* 1993, 58, 3245.
- Verboom, W.; Bodewes, P. J.; van Essen, G.; Timmerman, P.; van Hammel, J.; Harkema, S.; Reinhoudt, D. N. *Tetrahedron* 1995, 51, 499.
- Iwamoto, K.; Yanagi, A.; Arimura, T.; Matsuda, T.; Shinkai, S. *Chem. Lett.* 1990, 44, 1901.
- Pappalardo, S.; Caccamese, S.; Guinta, L. *Tetrahedron Lett.* 1991, 32, 7747.
- Pappalardo, S.; Guinta, L.; Foti, M.; Ferguson, G.; Gallagher, J. F.; Kaitner, B. *J. Org. Chem.* 1992, 57, 2611.
- Ferguson, G.; Gallagher, J. F.; Guinta, L.; Neri, P.; Pappalardo, S.; Parisi, M. *J. Org. Chem.* 1994, 59, 42.
- Iwamoto, K.; Shimizu, H.; Araki, K.; Shinkai, S. *J. Am. Chem. Soc.* 1993, 115, 3997.
- No, K. H.; Kim, J. E. *Bull. Korean Chem. Soc.* 1995, 16, 1122.
- No, K. H.; Kim, J. E.; Kim, S. J. *Bull. Korean Chem. Soc.* 1996, 17, 869.
- No, K. H.; Kim, K. H.; Kim, T. E. *J. Korean Chem. Soc.* 1997, 41, 366.
- Nam, K. C.; Kim, J. M.; Park, Y. J. *Bull. Korean Chem. Soc.* 1998, 19, 770.
- Arnecke, R.; Böhmer, V.; Ferguson, G.; Pappalardo, S. *Tetrahedron Lett.* 1996, 37, 1497.
- No, K. H.; Kwon, K. M. *Synthesis* 1996, 1293.
- No, K. H.; Gutsche, C. D. *J. Org. Chem.* 1982, 47, 2713.
- No, K. H.; Hwang, K. L. *J. Korean Chem. Soc.* 1993, 37, 978.
- Böhmer, V.; Merkel, L.; Kunz, U. *J. Chem. Soc., Chem. Commun.* 1987, 896.
- Böhmer, V.; Mardhollek, F.; Zetta, L. *J. Org. Chem.* 1987, 52, 3200.
- Stewart, D. R.; Krawiec, M.; Kashyap, R. P.; Watson, W. H.; Gutsche, C. D. *J. Am. Chem. Soc.* 1995, 117, 586.
- Pappalardo, S.; Ferguson, G. *J. Org. Chem.* 1996, 61, 2407.

Synthesis and Ceramic Conversion Reactions of Decaborane-CERASET Polymers: New Processable Precursors to SiC/Si₃N₄/BN Ceramics

Won K. Seok* and Larry G. Sneddon†

Department of Chemistry, Dongguk University, Seoul 100-715, Korea

†Department of Chemistry and Laboratory for the Research on the Structure of Matter, University of Pennsylvania, Philadelphia 19104-6323, USA

Received August 27, 1998

There has been great recent interest in the development of new polymeric precursors to advanced silicon-based ceramic materials that enable their formation in technologically useful forms.¹ Polyborosilazanes polymers have been of particular interest since recent work has shown that they can serve as processable precursors to SiNCB ceramic materials that possess extraordinary properties.² Thus, these polyboro-

silazanes enable the homogeneous incorporation of boron into traditional silicon-based ceramics with the resulting amorphous SiNCB composites having greatly increased thermal and oxidative stabilities. The enhanced properties of these ceramics may now enable their use in many high temperature applications.

In this note, we report our preliminary studies of the

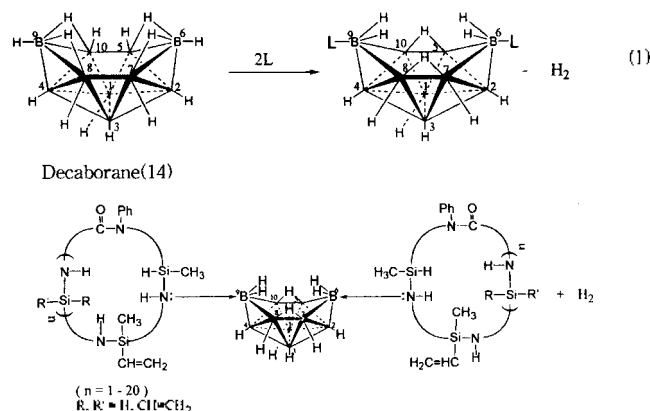
synthesis, characterizations, and ceramic conversion reactions of a new type of polyborosilazane that can be easily prepared via the reaction of the commercially available polysilazane, CERASET™ SN,³ with decaborane(14). Most significantly, we also report that, depending on the pyrolysis conditions, these new polymers can serve as excellent precursors to either SiC/BN or Si₃N₄/BN ceramic compositions.

Results and Discussion

CERASET™ SN (CER) is a liquid isocyanate-modified polysilazane that is synthesized by Lanxide Performance Materials, Inc., by the ammonolysis of a 4:1 mole ratio of dichloromethylsilane and dichloromethylvinylsilane, followed by reaction with phenylisocyanate under reflux.³ The polymer has a low molecular weight ($M_n = 564$; $M_w = 1,396$; $M_z = 5,215$) that is consistent with its proposed cyclic structure, shown schematically in Scheme 1. CERASET™ SN has been shown to be an excellent precursor to SiC ceramics when pyrolyzed under inert gases, and a precursor to Si₃N₄ ceramics when pyrolyzed under NH₃/N₂ atmospheres.³

Syntheses of CER-DECA Polymers. The liquid CERASET™ SN polymer (CER) was found to readily react with decaborane(14) (DECA-H, B₁₀H₁₄) at 65 °C with evolution of hydrogen gas to afford solid CER-DECA polymers that are soluble in acetonitrile and acetone. As can be seen in Table 1, the amount of decaborane(14) in the polymers can be controlled by simply increasing the amounts of decaborane(14) in the reaction mixture and/or going to more extended reaction times. For example, the empirical formulas determined by total elemental analyses of CER-DECA-1 and CER-DECA-4 changed from (B₁₀H₁₂)_{0.004}(Si_{1.00}N_{0.71}C_{1.47}H_{4.37}) to (B₁₀H₁₂)_{0.129}(Si_{1.00}N_{0.16}C_{1.29}H_{4.93}) when the DECA-H/CER ratio and reaction time were increased. The modified polymers are stable for short periods in air, but discolor upon longer exposures.

Since decaborane(14) is well known⁴ to react with a wide variety of Lewis bases (L) to form L₂B₁₀H₁₂ adducts (Eq. 1), the modified CER-DECA polymers are proposed to have similar types of structures in which the B₁₀H₁₂-fragments are



Scheme 1

coordinated to basic nitrogen atoms on the polymer backbone (Scheme 1). The spectroscopic data for the polymers strongly support this conclusion.

In all known L₂B₁₀H₁₂ adducts, the Lewis bases are coordinated to the boron atoms in the equivalent 6,9-skeletal positions, as shown in the structure in Eq. 1.⁴ As a result, these compounds show very characteristic features in their ¹¹B NMR spectra. For example, the ¹¹B NMR spectrum of 6,9-(MeCN)₂B₁₀H₁₂ shows one singlet and three doublet resonances in 2:4:2:2 ratios at -5.7, -20.4, -31.2, and -42.8 ppm, with the singlet resonance at -31.2 ppm corresponding to the 6,9-borons that are substituted by the MeCN bases.⁵ The shifts of the remaining resonances, which appear as doublets owing to the coupling of these borons with one terminal hydrogen, are likewise highly characteristic of boron atoms in the 2,4 (-5.7 ppm), 5,7,8,10 (-20.4 ppm) and 1,3 (-42.8 ppm) skeletal positions. Like the L₂B₁₀H₁₂ adducts, the ¹¹B NMR spectra of the CER-DECA polymers show one singlet and three doublet resonances in 2:4:2:2 ratios at -7.2, -20.1, -26.4, and -42.8 ppm, with the singlet resonance at -26.4 ppm corresponding to the 6,9-borons that are substituted by the polymer.

Both the ¹H NMR spectra and the FT-IR studies of the CER-DECA polymers are likewise consistent with the

Table 1. The characterization of modified-CER-DECA polymers prepared at 65 °C and their pyrolysis products (A) under Ar to 1600 °C for 1h (B) under NH₃ to 800 °C for 8 h, then under N₂ to 1600 °C for 1 h

Entry	CER-DECA Polymers			SiNCB Ceramics ^A			SiNCB Ceramics ^B		
	CER:DECA (g)	reaction time(h)	elemental composition	char yield(%)	elemental composition	density g/cm ³	char yield(%)	elemental composition	density g/cm ³
CER-DECA-1	6.59 : 0.11	133	Si _{1.00} B _{0.04} N _{0.71} C _{1.47} H _{4.42}	67.7	(SiC) _{1.00} C _{0.56} (Si ₃ N ₄) _{0.18} (BN) _{0.09}	2.63	80.0	(Si ₃ N ₄) _{1.00} (BN) _{0.40} C _{1.00} (SiO ₂) _{0.40} *	2.42
CER-DECA-2	6.20 : 0.20	109	Si _{1.00} B _{0.14} N _{0.77} C _{1.43} H _{5.39}	70.7	(SiC) _{1.00} C _{0.40} (Si ₃ N ₄) _{0.11} (BN) _{0.22}	2.48	62.1	(Si ₃ N ₄) _{1.00} (BN) _{0.70} (SiC) _{0.20} (SiO ₂) _{0.20} *	2.29
CER-DECA-3	5.53 : 0.72	78	Si _{1.00} B _{0.06} N _{0.69} C _{1.10} H _{6.62}	83.7	(SiC) _{1.00} C _{0.20} (Si ₃ N ₄) _{0.07} (BN) _{0.80} (SiO ₂) _{0.06} *	2.28	90.5	(Si ₃ N ₄) _{1.00} (BN) _{3.33} (SiC) _{0.22} (SiO ₂) _{1.78} *	2.15
CER-DECA-4	5.80 : 1.50	203	Si _{1.00} B _{1.29} N _{0.73} C _{1.29} H _{6.49}	81.1	(SiC) _{1.00} C _{0.30} (BN) _{1.10} (SiO ₂) _{0.07} *	2.30	93.7	(Si ₃ N ₄) _{1.00} (BN) _{4.60} (SiC) _{0.10} (SiO ₂) _{0.50} *	1.92
CER			Si _{1.00} N _{0.89} C _{1.46} H _{5.41}	51.1	(SiC) _{1.00} (SiO ₂) _{0.16} *	3.21	46.0	(Si ₃ N ₄) _{1.00} (SiC) _{0.22} (SiO ₂) _{0.22} *	2.76

*SiO₂ content is calculated based on the assumption that if the total pyrolyses for Si, N, C, B, and H were less than 100%, the difference was due to oxygen. Thus, the SiO₂ contents may be substantially less.

structure proposed in Scheme 1. For example, the ^1H NMR spectra of the polymers show that the singlet resonance for the 6,9-BH protons at 4.0 ppm in decaborane has disappeared, consistent with polymer substitution at this cage position. The FT-IR spectra of CER-DECA-1 showed the absorptions characteristic of the N-H, C-H, Si-H, and Si-C functional groups of the CERASET polymer, as well as absorptions arising from the B-H-B and B-H stretches in the decaborane fragment. The relative intensities of the two sets of absorptions varied in the spectra of the other polymers, according to the relative amounts of incorporated decaborane. The ^1H NMR spectra also show the characteristic resonance near 6.0 ppm for the vinyl-protons, and the IR spectra exhibit the vinyl stretching band near 1590 cm^{-1} . Thus, both the ^1H NMR and FT-IR studies demonstrate that the vinyl group in the original polymer has not been hydroborated by the decaborane fragment. These important functional groups are needed to crosslink the polymer after processing.

CER-DECA Ceramic Conversion Reactions. The elemental compositions and crystallinity of the ceramic materials derived from the CER polymer have previously been shown to be highly dependent on the pyrolysis atmospheres and temperatures.³ As shown in Table 1, when the unmodified CER polymer is pyrolyzed under Ar to $1600\text{ }^\circ\text{C}$, amorphous ceramic materials that contain predominantly SiC are produced. The formation of crystalline β -SiC is observed by XRD in these ceramics above $1600\text{ }^\circ\text{C}$. However, when the unmodified CER polymer is pyrolyzed under ammonia to $800\text{ }^\circ\text{C}$, then under nitrogen to $1600\text{ }^\circ\text{C}$, a mixture of crystalline α - and β - Si_3N_4 is the major ceramic product. Consistent with these results, we have now found that the CER-DECA polymers can serve as excellent precursors to ceramics containing predominantly SiC/BN or Si_3N_4 /BN compositions by controlling the pyrolysis atmospheres.

Black, carbon-rich ceramics composed mainly of SiC and BN were obtained from the CER-DECA polymers when the ceramic conversion reactions were performed under an argon atmosphere. Pyrolyses were carried out with a ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ until the furnace reached $1600\text{ }^\circ\text{C}$. The furnace was held at this temperature for 1 h and then allowed to cool slowly to room temperature. While pyrolysis of the unmodified CER polymer under these conditions yielded SiC ceramics with no retention of nitrogen, the CER-DECA polymers yielded materials that, although still predominantly SiC, also contain significant amounts of both boron and nitrogen. The compositions indicated in Table 1 are consistent with the elemental analyses given in the experimental section. The XRD spectra (Figure 1a) of the $1600\text{ }^\circ\text{C}$ CER-DECA ceramics confirmed the presence of β -SiC, but showed no other crystalline species.^{1,2,3} Their DRIFT spectra, however, showed the broad absorptions centered at 1450 and 890 cm^{-1} , characteristic of boron nitride.⁶

The CER-DECA polymers also had significantly higher ceramic yields (68-84%) than that found for the unmodified CER (51%). The compositions, densities and ceramic yields of the CER-DECA ceramics could be controlled by altering the amounts of decaborane contained in the CER-DECA polymer. Thus, those ceramics derived from the polymers containing the highest boron contents (CER-DECA-3 and CER-DECA-4) exhibited the highest BN/SiC ratios, the

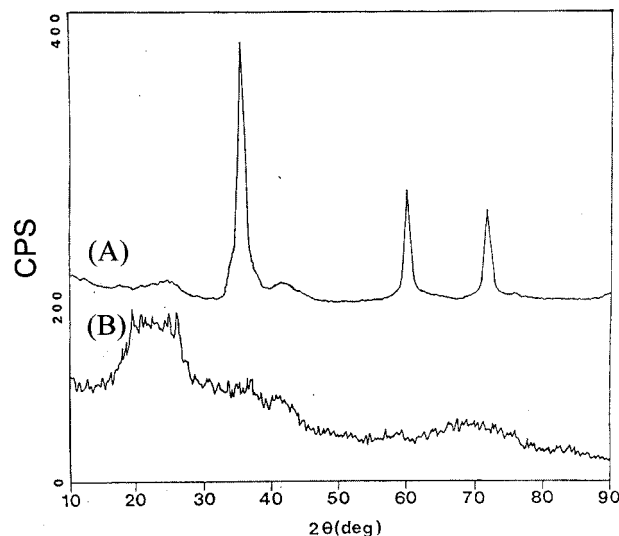


Figure 1. XRD spectra of ceramics derived from modified CER-DECA-4 polymer: (A) under argon at $1600\text{ }^\circ\text{C}$ (B) under NH_3 at $800\text{ }^\circ\text{C}$ at the rate of $5\text{ }^\circ\text{C}/\text{min}$ for 8 h followed by pyrolysis under N_2 at $1600\text{ }^\circ\text{C}$.

lowest densities, and the highest ceramic yields. The decrease in density is consistent with the trend in BN/SiC ratios, as the ceramics change from a predominantly SiC ceramic (density of pure SiC $\approx 3.2\text{ g}/\text{cm}^3$)¹ to that containing larger amounts of BN (turbostratic BN density $\approx 1.7\text{--}2.0\text{ g}/\text{cm}^3$).⁶ The increased char yields of the CER-DECA polymers over that observed for the unmodified CER (51%) is a result of both the addition of boron to the ceramic and to a more efficient crosslinking of the CER-DECA polymers during their ceramic conversions. The crosslinking reactions of the CER-DECA polymers probably involve dehydrocoupling reactions of the B-H groups of the decaborane cages and retard the loss of polymer fragments. Indeed, TGA studies under argon (Figure 2) showed that while the unmodified CER polymer has an initial low temperature major weight loss of $\sim 45\%$ in the range of $100\text{--}300\text{ }^\circ\text{C}$, the CER-DECA-2 polymer showed essentially no weight change in this region. Instead, the CER-DECA-2 polymer showed only a one-step weight loss in the $300\text{--}800\text{ }^\circ\text{C}$ range to give a final 89.7% ceramic yield, compared to the final 47% ceramic yield of the unmodified CER polymer. TGA/MS studies of CER-DECA-2 showed no elimination of boron-containing species during the ceramic conversion reaction, with only hydrogen, methane and ammonia being directly observed.

Nitrogen-rich, carbon-poor ceramics composed mainly of Si_3N_4 and BN were obtained in 68-93% ceramic yields from the CER-DECA polymers when the polymers were pyrolyzed using the procedure described in the experimental section under ammonia at $800\text{ }^\circ\text{C}$ for 8h, followed by further pyrolysis to $1600\text{ }^\circ\text{C}$ under nitrogen. Elemental analyses of the ceramic products confirmed that boron was contained in all ceramics and that the amount of boron in the ceramic increased according to the amount in the CER-DECA polymers. The compositions presented in Table 1 are consistent with the elemental analyses given in the experimental section and show that the higher boron content ceramics have the highest BN/ Si_3N_4 ratios and, as a result,

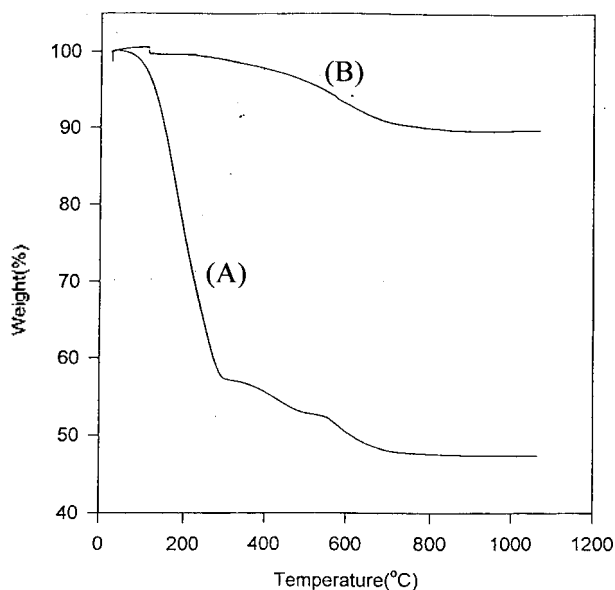


Figure 2. TGA analyses of (A) CER polymer and (B) CER-DECA-2 polymer at heating rate of 10 °C/min under flowing argon.

the lowest densities. As shown in Figure 1b, the XRD spectra of the 1600 °C ceramic chars showed these materials to be amorphous, but their DRIFT spectra clearly showed absorption bands centered at 1450 and 890 cm^{-1} that are characteristic of boron nitride.⁶ Upon heating these samples to 1800 °C, the XRD spectra showed the crystallization of both α - and β - Si_3N_4 and boron nitride.

In conclusion, the work described in this note has clearly demonstrated that the CER-DECA polymers are important new precursors to SiNCB ceramic materials. They are easily synthesized and can be used to make a variety of SiNCB compositions by simply altering the polymer composition and/or the conditions of their ceramic-conversion. This versatility should now allow the formation of ceramic materials that have properties tailored for many technological applications.

Experimental Section

All synthetic manipulations were carried out using standard high vacuum or inert atmosphere techniques as described by Shriver.⁷

Materials. CERASET™ SN (CER) is a liquid isocyanate-modified polysilazane,³ that was obtained from Drs. James Jensen and Alex Lucas at Lanxide Performance Materials, Inc. Decaborane(14) (DECA-H) was obtained as gifts from either Callery Chemical Company (Dr. Joe Barendt) or Dr. Thomas Baker and vacuum sublimed before use. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories and used without further purification.

Physical Measurements and Instrumentation. The ^{11}B NMR spectra were obtained at 64.2 MHz and ^1H NMR spectra were obtained at 200.1 MHz on a Bruker AF-200 spectrometer equipped with the appropriate decoupling accessories. All ^{11}B chemical shifts are referenced to $\text{BF}_3\cdot\text{O}(\text{C}_2\text{H}_5)_2$ (0.0 ppm) in C_6D_6 with a negative sign indicating an

upfield shift. All ^1H chemical shifts were measured relative to internal residual protons from the deuterated solvents and are relative to tetramethylsilane (0.0 ppm). Diffuse-Reflectance Infrared Fourier Transform Spectrometry (DRIFTS) of the polymers and ceramics were recorded on a Perkin-Elmer 2000 Fourier transform spectrophotometer equipped with a diffuse-reflectance attachment. Elemental analyses of the polymers and ceramics were performed at the Nesmeyanov Institute of Organoelement Compounds (INEOS), Moscow, Russia.

Thermogravimetric analysis (TGA) was performed on the polymers to 1100 °C at a heating rate of 10 °C/min under flowing argon using a Du Pont 951 Thermogravimetric Analyzer interfaced to an IBM computer. X-ray powder diffraction spectra of the ceramic chars were obtained on a Rigaku Geigerflex X-ray powder diffractometer using $\text{Cu-K}\alpha$ radiation with a graphite monochromator.

Bulk polymer pyrolyses were carried out in borosilicate or mullite pyrolysis tubes using a Lindberg 54000 series tube furnace with an Eurotherm 818 temperature control unit. Argon (99.999% pure) and nitrogen (99.999% pure) were purchased from Airco and passed through a Lab Clear (No. DGP-250-R1) oxygen scavenger. Ammonia (electronic grade) was obtained from Matheson and used as purging gas. All furnace firings to 1800 °C were done in a Lindberg furnace equipped with Eurotherm temperature controllers. Temperatures were monitored by a type K thermocouple below 900 °C and an Ircan Modeline Plus optical pyrometer for temperatures above 900 °C. The system was controlled with a CAMILE control system. The densities of the ceramics were determined by floatation in a mixture of halogenated hydrocarbons.

Reactions of CER with Decaborane (DECA-H).

In a typical reaction, a CER sample in a 100 mL reaction flask equipped with a stirring bar and high vacuum stopcock was purged under a nitrogen atmosphere for 3-4 h. The DECA-H was added to the flask, which was then sealed and brought in the glove box. The reaction mixture gradually dissolved to form a yellow to colorless solution depending on the amount of DECA-H used. The mixture was heated in an oil bath at 65 °C, as summarized in Table 1. After removal from the oil bath, the flask was attached to the vacuum line and frozen at -196 °C. Evolved hydrogen gas was measured by expansion into a known volume. The process was repeated until negligible amounts of hydrogen was observed. After the reaction, the modified polymers were isolated as solids following vacuum sublimation of excess DECA-H from the reaction vessel and were obtained quantitatively based on the measured amounts of evolved hydrogen gas. Anal. Found for CER: C, 27.35%; H, 8.51%; N, 19.50%; Si, 43.86%. CER-DECA-1: C, 27.89%; B, 0.74%; N, 15.61%; Si, 44.36%; H, 7.03%. CER-DECA-2: C, 27.16%; B, 2.41%; N, 16.66%; Si, 43.33%; H, 8.20%. CER-DECA-3: C, 18.31%; B, 12.78%; N, 13.30%; Si, 38.79%; H, 9.21%. CER-DECA-4: C 19.37%; B, 17.49%; N, 12.90%; Si, 35.24%; H, 8.21%. NMR data for CER-DECA-1, ^{11}B NMR (δ , acetone- d_6), -7.2 (d, B2,4), -20.1 (d, B5,7,8,10), -26.4 (s, B6,9) -42.8 (d, B1,3). ^1H NMR (δ , acetone- d_6), 5.9 (br, Si-CH=CH₂), 5.0 (br, Si-H), 4.5 (br, N-H), 3.0 (s, HB5,7,8,10), 1.0 (br, BH1,3), 0.2 (br, Si-CH₃), -0.9 (br, bridged H). IR data (cm^{-1} , KBr) for CER-DECA-1: 3255 (s,

br) (N-H), 2950 (s) (C-H), 2500 (s) (B-H), 2140 (w), (Si-H), 1910 (w) (bridged B-H), 1700 (m), 1590 (m) (CH=CH₂), 1400 (vs, br) (B-N), 1255 (m), 900 (vs, br) (Si-C). Similar NMR and IR spectra were observed for each polymer, but with the relative intensities of the spectral features varying according to the amounts of decaborane incorporated into the polymer.

Ceramic Conversion Reactions

Pyrolysis under Argon. Al₂O₃ pyrolysis tubes were dried by heating at 1600 °C and then cooled under argon. An aliquot of polymer was weighed into a graphite boat in a Vacuum Atmospheres drybox and quickly transferred into a Lindberg tube furnace. After purging the system with argon for 1 h, the samples were heated to 1600 °C at 10 °C/min and held for 1 h before cooling to room temperature. After pyrolysis, all manipulations of ceramics were carried out in air. Anal. Found for CER: C, 23.57%; N, trace; Si, 63.86%; H, no.; CER-DECA-1: C, 24.94%; H, 0.36%; B, 1.19%; N, 15.03%; Si, 58.40%; CER-DECA-2: C, 25.35%; H, 0.70%; B, 3.87%; N, 13.95%; Si, 56.12%; CER-DECA-3: C, 18.45%; H, 1.28%; B, 11.35%; N, 20.45%; Si, 45.91%; CER-DECA-4: C, 19.20%; H, no; B, 19.65%; N, 17.75%; Si, 39.82%.

Pyrolysis under Ammonia and Nitrogen. Al₂O₃ pyrolysis tubes were dried by heating at 1600 °C and then cooled under nitrogen. An aliquot of polymer was weighed into an alumina crucible in a Vacuum Atmospheres drybox and quickly transferred into a Lindberg tube furnace. After purging the system with ammonia for 1 h, the samples were heated under ammonia to 800 °C at 5 °C/min and held for 8 h before being cooled to room temp. Subsequent pyrolysis at 1600 °C under nitrogen was performed at the rate of 10 °C/min. After pyrolysis, all manipulations of the ceramics were carried out in air. Anal. Found for CER, C; 1.08%; H, no; N, 36.96%; Si, 52.65%; CER-DECA-1: C, 6.12%; H, 1.50%; B, 0.89%; N, 35.15%; Si, 49.85%; CER-DECA-2: C, 1.03%; H, 0.29%; B, 3.81%; N, 37.05%; Si, 52.66%; CER-DECA-3: C, 0.79%; H, 0.24%; B, 10.38%; N, 32.13%; Si, 39.97%; CER-DECA-4: C, 0.67%; H, 0.22%; B, 17.26%; N, 41.93%; Si, 34.27%.

Acknowledgment. We thank the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic

Energy Sciences, and Office of Energy Research for support of this research. Won K. Seok is very grateful to the Korea Research Foundation for its support of his stay at the University of Pennsylvania, and to the Korea Science and Engineering Foundation.

References

1. For recent reviews of polymeric precursors to silicon-based ceramics, see (a) Laine, R. M.; Babonneau, F. *Chem. Mater.* **1993**, *5*, 260. (b) Birot, M.; Pillot, J.-P.; Duno-gues, J. *Chem. Rev.* **1995**, *95*, 1443 and references therein.
2. See, for example: (a) Riedel, R.; Kienzle, A.; Dressler, W.; Rowisch, L.; Bill, J.; Aldinger, F. *Nature* **1996**, *382*, 796-798. (b) Baldus, H. P.; Jansen, M. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 328 and references therein. (c) Bill, J.; Aldinger, F. *Metallkd.* **1996**, *11*, 827 and references therein. (d) Funayama, O.; Aoki, T.; Isoda, T. *J. Ceram. Soc. Jpn.* **1996**, *104*, 355 and references therein. (e) Wide-man, T.; Cortez, E.; Remsen, E. E.; Zank, G. A.; Carroll, P. J.; Sneddon, L. G. *Chem. Mater.* **1997**, *9*, 2218 and references therein.
3. (a) Matsumoto, R. L. K. *Mat. Res. Soc. Symp. Proc.* **1990**, *180*, 797. (b) Schwark, J. M.; Sullivan, M. J. *Mat. Res. Soc. Symp. Proc.* **1992**, *271*, 807. (c) Matsumoto, R. L. K.; Schwark, J. M. U.S. Patent No. 5,206,327, 1993. (d) Matsumoto, R. L. K.; Schwark, J. M. U.S. Patent No. 5, 386,006, 1995. (e) Miller, D. V.; Pommell, D. L.; Schiroky, G. H. *Ceramic Engineering and Science Proc.* **1997**, *18*, 409.
4. Shore, S. G. in *Boron Hydride Chemistry*; Muetterties, E. L. ed. Academic Press: 1975; pp 79-114.
5. Hyatt, D. E.; Scholer, F. R.; Todd, L. J. *Inorg. Chem.* **1967**, *6*, 630.
6. (a) Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73 and references therein. (b) Fazen, P. J.; Remsen, E. E.; Beck, J. S.; Carroll, P. J.; McGhie, A. R.; Sneddon, L. G. *Chem. Mater.* **1995**, *7*, 1942.
7. Shriver, D. F.; Drezdson, M. A. *The Manipulation of Air Sensitive Compounds*, 2nd Ed.; Wiley: New York, 1986.