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Synthesis of Novel Amorphous Boron Carbonitride Ceramics from the Borazine Derivative Copolymer via Hydroboration

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A preceramic polymer for boron carbonitride was synthesized for the first time by the hydroboration of borazine derivatives, B-triethynyl, N-trimethyl borazine and borazine, without a catalyst. A homogeneous, amorphous boron carbonitride ceramic was prepared by the thermolysis of a hydroborated copolymer in an argon atmosphere.

Preceramic polymers as non-oxide ceramic precursors have been used mainly for conventional applications such as fibers, composites, and coatings using liquid fabrication and subsequent pyrolysis.[1] Since Kosolapova et al. first reported an attempt to synthesize a BCN material using a solid−gas reaction, there has been increasing interest in novel ternary BCN compounds due to the expectation of its unique properties such as extreme hardness from diamond-like superhard materials (B_4C and c-BN), superconducting properties, which are intermediate between those of semimetallic graphite and insulating h-BN, and photoluminescence (PL) from the layered BCN materials.[2−8]

Recently, many studies into multinary ceramic systems via preceramic polymers have been examined due to the merit with which the coordination number and chemical composition can be tailored by controlling the starting substances. In particular, hydroboration, which is widely used for preparing alcohols or ketones in organic chemistry, plays an important role in preparing the intermediates of boron-containing preceramic polymers via a non-oxide sol−gel process.[9,10] However, the hydroboration of acetylenes as ceramic precursors has received little attention. The only example is a BCN ceramic material prepared by the pyrolysis of poly(B-vinylborazine) via a $RhH(CO)(PPh_3)_3$-catalyzed reaction of borazine with acetylene, as reported by Sneddon.[11] In addition, there have only been a few studies of BCN ceramics from carbon-containing borazine derivatives via the sol−gel route and thermolysis.[5,6]

This paper reports the synthesis and characterization of novel amorphous boron carbonitride from a hydrocarbon-bridged borazine copolymer via the hydroboration of an ethynyl group without a catalyst (Scheme 1).

The precursors, borazine and B-triethynyl, N-trimethyl borazine (TEB), were synthesized using previously reported methods.[12−14] Into precooled solution of 2 g (10.275 mmol) of B-triethynyl, N-trimethyl borazine dissolved in 50 mL of tetrahydrofuran (99.9%, Aldrich) was added dropwise 2.24 mL (1.815 g, 22.55 mmol) of borazine, which is a slight excess, within a range of temperatures around 0 °C. The temperature of the mixture was kept below 5 °C over 5 h and was gradually warmed to room temperature. After stirring for more than 30 h at room temperature, a wine-colored homogeneous liquid was obtained. By removing tetrahydrofuran under vacuum (0.023 Torr) at room temperature, 3.7 g of an irreversibly insoluble moisture sensitive orange solid was obtained in a synthetic yield of 97%. The resulting copolymeric product changed to a dark brown color

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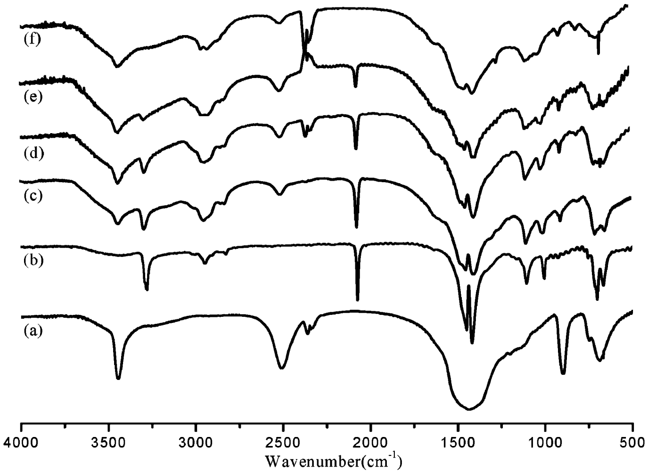
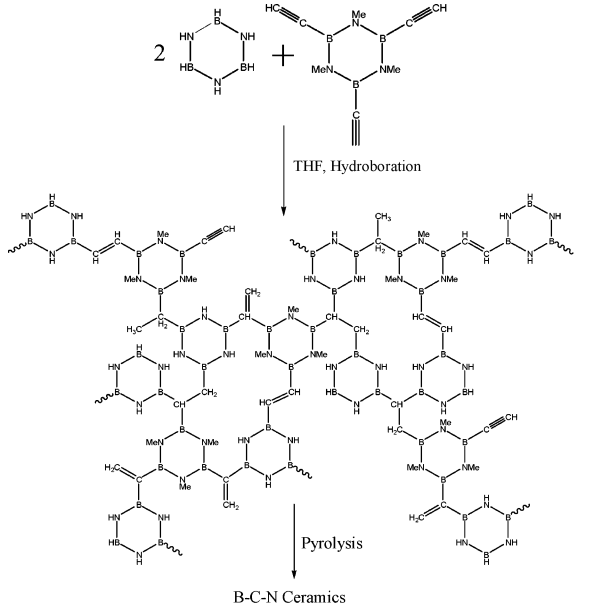


Figure 1. IR spectra of monomers and the various hydroborated copolymers: (a) borazine, (b) TEB, (c) as-synthesized, and cured at (d) 120 °C, (e) 200 °C, and (f) 300 °C.

Scheme 1. Suggested Polymer Structure via Hydroboration of Two Borazine Derivatives and Its Synthetic Route to BCN Ceramics



due to cross-linking at higher temperatures. The samples were then pyrolyzed by annealing at temperatures up to 1400 °C for 3 h in an argon atmosphere at a heating rate of 5 °C min^{-1} (2 °C min^{-1} in the temperature range 200−600 °C due to the characteristic weight loss). A blackish hard but rather porous material was finally obtained.

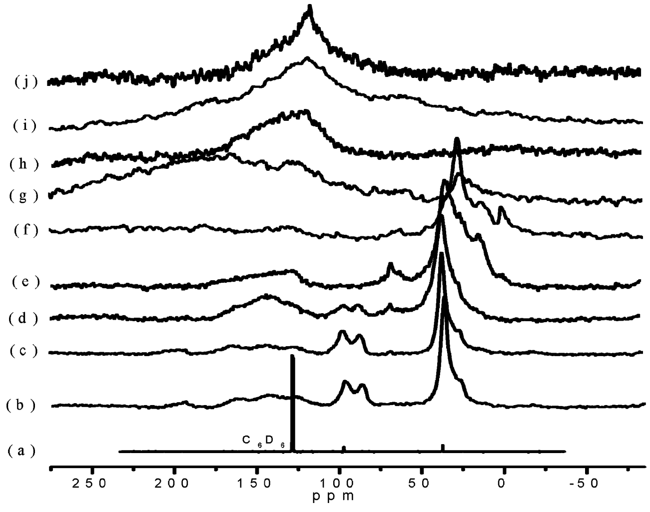


Figure 2. ^{13}C NMR and ^{13}C MAS NMR spectra of starting substance and hydroborated copolymers cross-linked at different temperatures: (a) TEB, (b) as-synthesized, (c) 120 °C, (d) 200 °C, (e) 300 °C, (f) 400 °C, (g) 600 °C, (h) 900 °C, (i) 1100 °C, and (j) 1400 °C.

The IR spectra of the two monomers and the copolymers heated at 120, 200, and 300 °C for 3 h in argon atmosphere are shown in Figure 1. The TEB monomer exhibits relatively sharp characteristic acetylenic C—H (3275 cm^{-1}), aliphatic C—H (2948, 2825 cm^{-1}), C≡C (2074 cm^{-1}), and B—N (1500−1430, 1430−1400 cm^{-1}, 760−800 cm^{-1}) absorption peaks,[1−4] while borazine shows quite broad NH (3420 cm^{-1}), BH (2500 cm^{-1}), and BN (1500−1385^{-1}, 760−800 cm^{-1}) absorption bands.[12−15] As polymerized, the IR absorption spectra became broader with significantly weakened BH absorption and a new additional band assigned to a vinyl group at 1645 cm^{-1}. As the copolymeric product was cured, the intensity of the major monomeric peaks such as B—H, acetylenic C—H, and C≡C bands were gradually reduced whereas the vinyl band increased. These peaks had completely disappeared at 300 °C, but the aliphatic band was observed with an increasing intensity.[12−15]

The ^{13}C NMR spectra of the TEB monomer and solid-state ^{13}C MAS NMR spectra of the copolymers heat-treated at various temperatures are shown in Figure 2. The TEB monomer showed only three sharp peaks, 97.0, and 87.0 ppm, which were assigned to the two carbons of the ethynyl group on boron, and 37.0 ppm for the methyl group on nitrogen.[15] The as-synthesized copolymer exhibited very broad ethynyl and methyl peaks, and the additional new broad resonances observed at 125−132 and 135−140 ppm were assigned to the vinyl group, and a weak shoulder at 16−27 ppm was assigned to an ethyl group.[16,17] As the cross-linking reaction proceeded, the characteristic vinyl and aliphatic hydrocarbon peak intensities increased gradually whereas the ethynyl group peaks became weaker. In addition, a peak at 69 ppm possibly due to tertiary or quaterary carbon atoms with more than two boron atoms attached by a 2-fold hydroboration reaction began to appear. The copolymer cured at 300 °C no longer showed the ethynyl peaks with a slightly reduced intensity of the vinyl group, while there were significantly stronger aliphatic hydrocarbon peaks at 0−50 and 65−70 ppm. When the sample was then cured at 400 °C, the vinyl peak disappeared totally due to the complete transfer to aliphatic broad resonance.[16,17]

In the spectra for the specimens annealed at 400 °C, only the aliphatic broad resonance remained, but it was slightly shifted downfield due to the decomposed methyl group on the N atom observed at 37 ppm. This indicates the beginning

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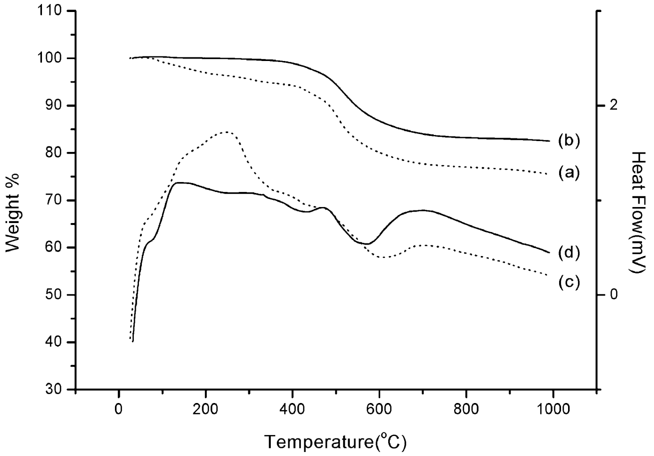

Figure 3. TGA and DTA curves of the polymer-to-ceramic transformation of hydroborated copolymers: TGA thermograms of (a) as-synthesized, and (b) cured at 120 °C; DTA thermograms of (c) as-synthesized, and (d) cured at120 °C.

of the ceramization of the copolymer by the thermal decomposition of the organic moieties. As shown in Figure 2g, an obvious change in the molecular structure was observed in the specimens annealed at 600 °C as a result of the appearance of a new broad resonance at 120−130 ppm with a drastically decreased aliphatic resonance. When the samples were pyrolyzed at above 900 °C, the resonance shifted to the center at approximately 130 ppm, which was assigned to graphite-like carbon. This might be significant evidence that the ethyl bridge on the boron atom was converted to an amorphous carbon and BCN ceramic product.[7]

The thermal behavior of the hydroborated copolymers was measured using thermogravimetric analysis and differential thermal analysis (TGA/DTA), as shown in Figure 3. The as-synthesized polymer exhibited two major weight loss regions in the temperature intervals at 25−400 and 400−700 °C, obtaining a ceramic yield of 75% at 1000 °C. However, those cross-linked at 120 °C for 3 h showed no weight loss in the former region due to the formation of a thermally stable dense network, and only 17% of the total weight was lost at 1000 °C. In addition, the exothermic part in the temperature range 100−300 °C was attributed to cross-linking hydroboration, which correlates with the smaller exothermic peak of the cured material at 120 °C. The significant weight loss at the range 400−700 °C suggests that the hydroborated copolymer was decomposed or rearranged to form a BCN ceramic phase, which is consistent with the ^{13}C MAS NMR results.

By XRD investigation of the specimens annealed at 900, 1100, and 1400 °C, all three patterns presented the typical amorphous phase of a ceramic, which was unusually retained even at 1400 °C with broad bands centered at approximately 24.5° and 43° as 2θ. The diffraction pattern is similar to that of layered graphite with the (002){$2\theta = 26.5°$} and (101){ $2\theta = 44.6°$} diffraction peaks, or the h-BN phase with the (002){$2\theta = 26.7°$} and (100){$2\theta = 41.6°$} planes. In addition, selected area electron diffraction of a transmission electron microscope (TEM) showed only broad, diffuse rings that are characteristic of an amorphous phase with a mixed ring pattern of graphite and BN.

Table 1. Charge Corrected Peak Energies from the Deconvoluted Narrow-Scan XPS Spectra on the Specimens Annealed at 1400 °C and Comparison with Literature Values

	binding energy/eV	literature comparison/eV	ref
B1s	188.4	B−C bonding (189.5)	
B1s	190.2	B−N bonding (190.1)	
B1s	192.2	B−(N−C)$_3$ bonding (192.1)	
C1s	282−290	C−N (>284.9), C−B (<284.9)	8, 18
C1s	284.9	graphite (284.9)	
N1s	398.1	B−N bonding (398.1)	
N1s	399.6	C−N bonding (399.3)	

The chemical bonding of the BCN ceramic specimens annealed at 900, 1100, and 1400 °C was investigated by X-ray photoelectron spectroscopy (XPS, VG-Scientific ESCALAB 250 spectrometer). Table 1 shows XPS spectra of the specimens annealed at 1400 °C. The B1s spectrum suggests the existence of 3 types of B atoms in the BCN network. A major chemical shift at 190.2 eV is assigned to h-BN as a dominant species. The higher binding energy at 192.2 eV indicates the presence of B atoms surrounded by three N atoms connected to C atoms, while Kawaguchi assigned the lower binding energy at 188.4 eV to the other B atoms connected with the electropositive C atoms.[8,18] Moreover, in the C1s spectrum, a major peak at 284.9 eV was assigned to graphite, which is consistent with the ^{13}C MAS NMR result. The lower binding energy at 284.4 eV showed the presence of C partly connected to N atoms. The N1s spectrum reasonably confirmed the existence of h-BN at 398.1 eV and N atoms partly bonded to C atoms at 399.6 eV.[8,18] When compared to the spectra of the samples heated at 900 and 1100 °C, the spectra were generally distributed over a wider range with a similar shape of convoluted curves. This suggests that the chemical environments of the atoms are more diverse with the same major peaks. Finally, it was found that the amorphous layered BCN ceramics obtained at 1400 °C were made of the unit structures of BN, graphite-like carbon, and BC_xN_y. It is worth noting that the microstructure is similar to graphite-like layered BCN and BC_3N materials.

It is believed that this is the first example of hydroborated polymerization between the borazine derivatives without the use of a catalyst, as a novel precursor for BCN ceramics. The fabrication of spin-coated BCN thin films, macroporous BCN ceramics, and BCN nanotubes is being investigated to determine the properties and possible applications.

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