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## Inorganic Polymers and Materials

### Final Report

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## TECHNICAL REPORT

Grant No. DE-FG02-87ER13732

Project Title

**"Inorganic Polymers and Materials"**

### Abstract

Our DOE sponsored project was focused on the design, synthesis, characterization and applications of new types of boron and silicon polymers with a goal of attaining processable precursors to advanced ceramic materials of technological importance. Our work demonstrated a viable design strategy for the systematic formation of polymeric precursors to ceramics based on the controlled functionalization of *preformed* polymers with pendant groups of suitable compositions and crosslinking properties. Both the new dipentylamine-polyborazylene and pinacolborane-hydridopolysilazane polymers, unlike the parent polyborazylene and other polyborosilazanes, are stable as melts and can be easily spun into polymer fibers. Subsequent pyrolyses of these polymer fibers then provide excellent routes to BN and SiNCB ceramic fibers. The ease of synthesis of both polymer systems suggests new hybrid polymers with a range of substituents appended to polyborazylene or polysilazane backbones, as well as other types of preceramic polymers, should now be readily achieved, thereby allowing even greater control over polymer and ceramic properties. This control should now enable the systematic tailoring of the polymers and derived ceramics for use in different technological applications. Other major recent achievements include: (1) the development of new types of metal-catalyzed methods needed for the polymerization and modification of inorganic monomers and polymers, and the modification studies of polyvinylsiloxane and related polymers with substituents that enable the formation of single source precursors to high strength, sintered SiC ceramics.

## Introduction

The development of efficient methods for the production of complex structural and electronic materials in usable forms is one of the most important problems of modern solid state chemistry and materials science. The polymeric precursor approach, in which a polymer is first formed into the desired shape and then decomposed to the final ceramic material with retention of this shape, has been shown to be an important new route for producing many ceramics in processed forms.<sup>1</sup> However, the design of new precursor polymers with the required composition and appropriate chemical and physical properties continues to be a formidable scientific challenge. *Our DOE sponsored project was aimed at the design, synthesis, characterization and applications of new types of inorganic polymers with a focus on the use of these polymers as processable precursors to technologically important nonoxide ceramic materials. A major emphasis of the research has been to develop general synthetic methodology, with a focus on new catalytic reactions, that allow the systematic syntheses and modification of both inorganic polymers and monomers.*

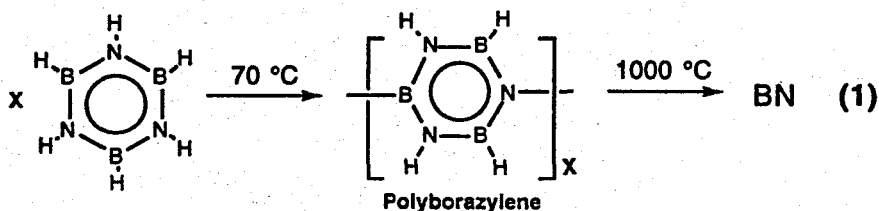
Major accomplishments include the development of a design strategy based on the controlled functionalization of *preformed* polymers with pendant groups of suitable compositions and crosslinking properties that was used to yield second-generation dipentylamine-polyborazylene (DPA) and pinacolborane-hydridopolysilazane (PIN-HPZ) polymers. These new polymers, unlike our previously developed parent polyborazylene (PB) and borazine-hydridopolysilazane (B-HPZ) polymers, are stable as melts and can be easily melt spun into polymer fibers. Subsequent pyrolyses of these polymer fibers then provide excellent routes to BN and SiNCB ceramic fibers with enhanced properties suitable for advanced structural applications. These and other major achievements of the DOE sponsored work are discussed in the following sections:

## Summary of Scientific Progress

### Second-Generation Polyborazylene Precursors to Boron Nitride

Boron nitride has a range of attractive properties, including high temperature stability and strength, a low dielectric constant, large thermal conductivity, hardness, and corrosion and oxidation resistance, leading to a number of applications as a structural or electronic material.<sup>2</sup> Boron nitride powders may be easily obtained,<sup>3</sup> but it has proven more difficult to prepare BN in more complex forms, especially fibers and coatings. Thus, there has been intense interest by many research groups on the development of polymeric precursors to BN.<sup>2a,b</sup>

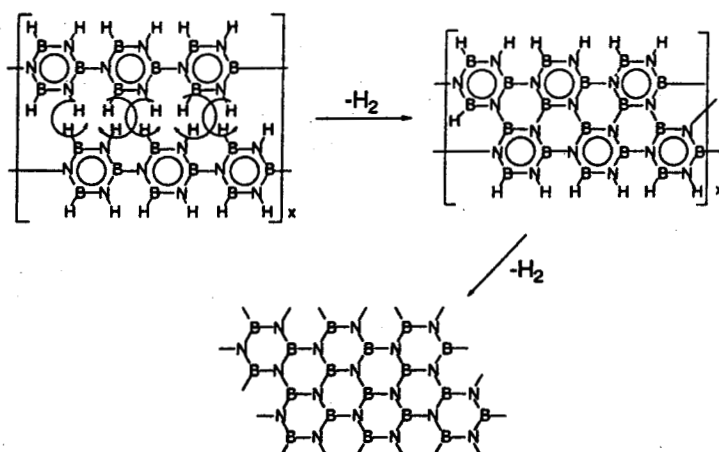
We have previously shown that borazine can be readily dehydropolymerized to give a soluble polymer, polyborazylene (PB), in excellent yields.<sup>4</sup>



The combined analytical, spectroscopic and molecular weight data indicate the borazine ring structure is retained in the polymer. The polymer has also been shown to have a complex

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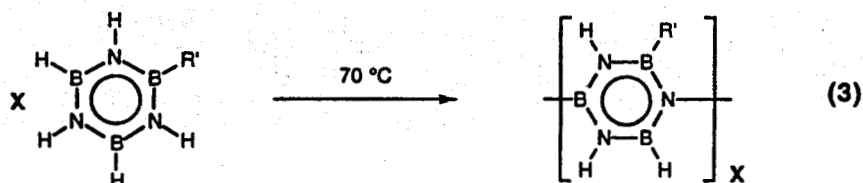
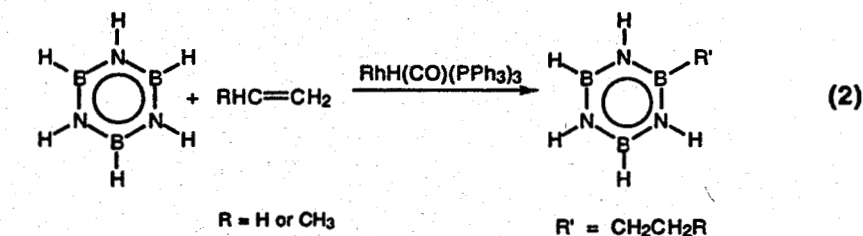
structure, related to those of the organic polyphenylenes, having linear, branched-chain and fused-cyclic segments with typical  $M_n = 500-900$  g/mol and  $M_w = 3000-8000$  g/mol. Furthermore, according to its powder X-ray diffraction spectra, the polymer appears to have a layered structure in the solid state. Pyrolysis studies show polyborazylene converts to boron nitride in excellent chemical, (89 to 99%) and ceramic yields (84 to 93%). Studies of the polymer to ceramic conversion-reaction suggest a process involving a two-dimensional cross-linking-reaction similar to that shown in the Figure.



While the parent polyborazylene proved to be an excellent precursor for the production of boron nitride coatings, films<sup>5</sup> and shaped materials, the crosslinking reaction depicted in the Figure occurs at low temperature and prevented the use of the polymer in applications requiring melt-processing. Thus, we felt that the key to the utilization of the polyborazylene polymer in other more demanding applications, such as the melt-spinning of fibers, was to control the dehydrocoupling reaction that leads to the formation of boron-nitrogen crosslinks between the polymer chains. One strategy by which we felt this could be accomplished was to reduce the number of reactive B-H or N-H sites by functionalizing the polymer with suitable substituents. This should improve the processability of polyborazylene by both increasing the thermal stability of the polymer and lowering its glass transition temperature ( $T_g$ ). Two new types of such "second generation" polyborazylens have now been produced: (1) polyorganoborazylens<sup>6,7</sup> and (2) amine-functionalized polyborazylens.<sup>7,8,9</sup>

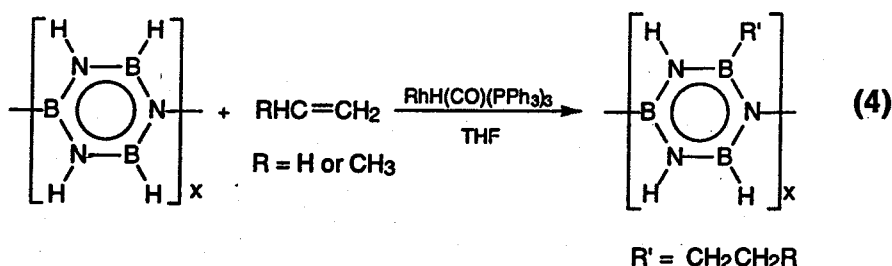
### Polyorganoborazylens<sup>6,7</sup>

B-alkyl-polyborazylens were synthesized by two different methods. First, B-alkylborazines, which we have shown can be readily obtained by the transition-metal catalyzed hydroboration of borazine with olefins (Eq. 2),<sup>6</sup> were thermally polymerized, as shown in Eq. 3.



Molecular weight studies of the polymerized B-alkylborazines indicate these polymers have  $M_n$  similar to the parent polymer ( $M_n = 540$  for polyethylborazylene and  $M_n = 468$  for polypropylborazylene). However,  $M_w$  is considerably less than the parent polymer, ( $M_w = 926$  for polyethylborazylene and  $M_w = 824$  for polypropylborazylene). This is consistent with a decrease in crosslinking and chain branching, as would be expected given that one of the borazinyl B-H groups has been removed.

Alternatively, B-alkylpolyborazylene polymers were directly produced in excellent yields by the  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  catalyzed modification of the performed polyborazylene backbone as shown in Eq. 4.



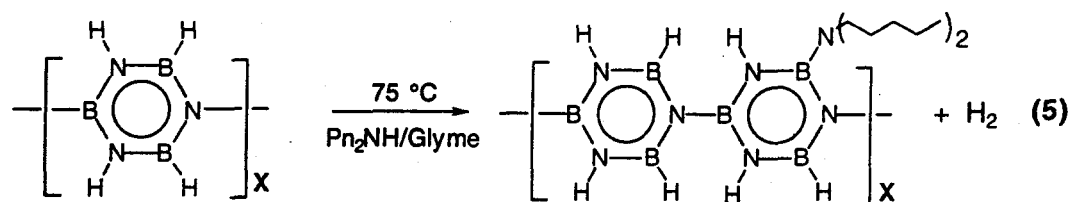
The degree of alkylation can be controlled from an average of less than one alkyl group per every two rings for the propyl-substituted polymer,  $\text{B}_3\text{N}_3\text{H}_3(\text{C}_3\text{H}_7)_{0.4}$ , to almost one alkyl group for every borazine ring in the ethyl-substituted polymer,  $\text{B}_3\text{N}_3.2\text{H}_2.4(\text{C}_2\text{H}_5)_{0.9}$ . Molecular weight studies showed increased molecular weights,  $M_n = 1349$ , compared to the crude starting polymer ( $M_n = 506$ ) with incorporation of ethyl groups into the polymer.

Studies of the ceramic conversion reactions of both types of B-alkylated polyborazylenes demonstrated that the thermally-induced crosslinking reactions are reduced compared to the polyborazylene polymer. TGA studies showed the onset of their initial weight losses are at higher temperatures than the parent polymer suggesting the alkyl groups do, in fact, inhibit interchain dehydrocoupling.

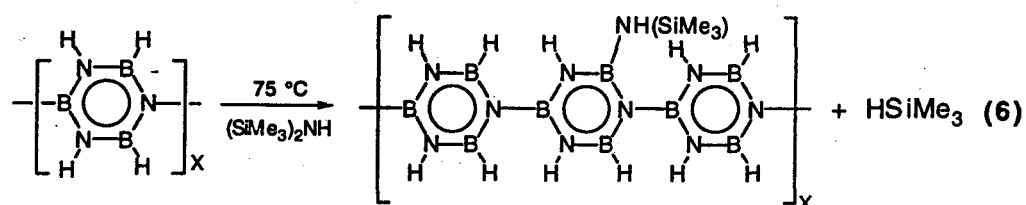
#### Amine Modified Polyborazylenes<sup>7,8,9</sup>

While the polyorganoborazylenes described above showed a decrease in the degree of low-temperature crosslinking reactions, the  $T_g$  of the polymers could not be reduced below the onset of crosslinking. Thus, these polymers are not meltable. Furthermore, due to inefficient elimination of the alkyl groups during pyrolysis, high carbon contents (2.0-6.5%) were found in the ceramics derived from both types of organopolyborazylenes. Therefore, a second approach for the formation of hybrid polyborazylenes was initiated.

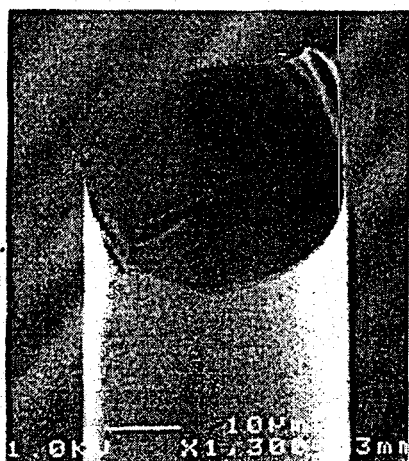
Previous work by Kimura<sup>10</sup> had shown that processable BN polymer precursors can be obtained from the reaction of B-trimethylaminoborazine with lauryl amine. The long chain alkyl-amine groups improved the plasticity of the polymer, allowing the polymers to be melt-spun. Using a similar approach, we found that new amine-modified polyborazylenes could be readily obtained by the reaction of polyborazylene with secondary amines, including diethyl amine (DEA), dipentyl amine (DPA) and hexamethyldisilazane (HMD). For example, as shown in Eq. 5, reaction of polyborazylene with DPA in glyme solution at 75 °C gave a clear polymeric material in 91% yield with a  $(\text{B}_{3.0}\text{N}_{3.12}\text{H}_{3.9})(\text{NPn}_2)_{0.47}$  composition.



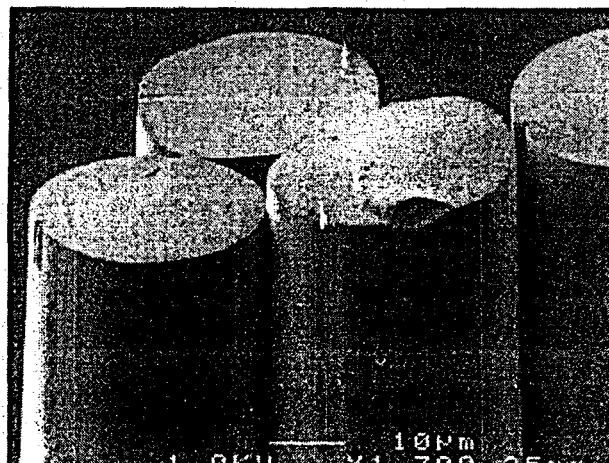
In the case of the **DEA** and **DPA**-modified polymers, spectroscopic studies, model reactions and analysis of volatile by-products indicate modification of the polymer proceeds primarily through dehydrocoupling. In contrast, modification of the polymer with **HMD** occurred primarily through N-Si cleavage reactions, as shown in Eq. 6.



TGA studies of these polymers showed a reduction of low-temperature crosslinking reactions, with the onset of decomposition and weight loss increasing to  $>100^\circ\text{C}$ . DSC studies showed the long-chain alkyl groups of the pendant **DPA** groups serve as efficient plasticizers, reducing the  $T_g$  of the polymer to  $90^\circ\text{C}$ , giving the **DPA**-modified polymers excellent properties for melt-spinning. As shown in the scanning electron micrograph in the Figure (below, left) high quality **DPA** polymer fibers were achieved by the continuous extrusion of polymer melts to give polymer fibers that were flexible, uniform and free of voids.



**Polyborazylene Fiber**



**BN Ceramic Fibers**

Pyrolysis of the cured polymer fibers under ammonia to  $1000^\circ\text{C}$  produced clear, flexible boron nitride fibers of  $\sim 30\ \mu\text{m}$  diameter. SEM micrographs (Figure, above, right) also show these ceramic fibers are smooth, uniform and dense. X-ray diffraction studies on both single ceramic fibers and bulk samples, and powder DRIFT spectra are consistent with the formation of



turbostratic BN. A typical elemental analysis of a bulk sample is  $B_{1.00}N_{1.03}C_{0.00}H_{0.20}$ , while Rutherford Backscattering Spectrographs of single fibers showed a surface composition of  $B_{1.5 \pm 0.3}N_{1.0 \pm 0.2}O_{0.2 \pm 0.1}$  consistent with the formation of a  $B_2O_3$  surface species during the air cure of the fibers.

Preliminary measurements of the mechanical properties of the crude 30  $\mu m$  BN fibers derived from DPA gave typical tensile strengths of 0.18 GPa and elastic moduli of  $\sim 14$  GPa. These values are lower than the poly(aminoborazine)-derived BN fibers reported by Kimura;<sup>10</sup> however, because strengths depend strongly on the fiber diameter and processing parameters, significant increases in the strengths of the DPA-derived BN fibers are expected with the use of a more sophisticated spinning apparatus and higher temperature sintering.

The DPA-modified polyborazylenes are particularly attractive precursors to BN fibers since we have previously developed convenient, high-yield syntheses of both the  $[B_3N_3H_4]_x$  polymer,<sup>4</sup> and its precursor, borazine.<sup>11</sup> Furthermore, it is expected that the properties of the polyborazylene polymer can now be systematically tailored for use in different technological applications by modification with the wide variety of available dialkylamines. For example, as discussed later in the Proposed Research section the HMD polymers ( $\{(R_3Si)_x B_3N_3H_{4-x}\}_y$ ) are now being investigated as potential precursors to oxidation-resistant BNSi hybrid ceramics.

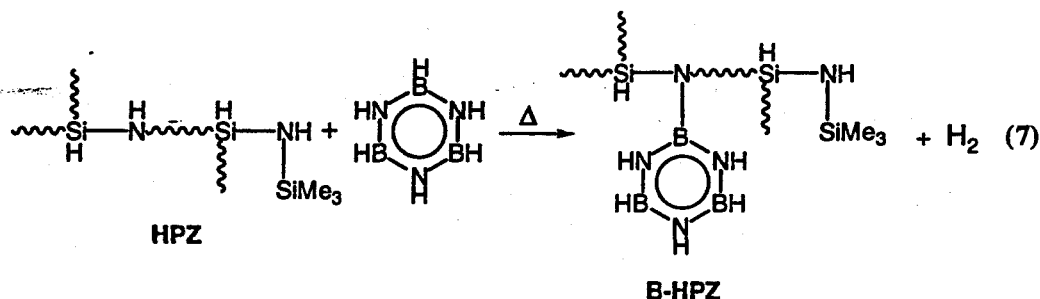
### New Polyborosilazanes: Precursors to SiNCB Composites

Compared to single-component ceramics, ceramic composites often offer many advantages for high performance applications. For example, composite SiNCB ceramics have a number of enhanced properties compared to traditional SiNC ceramics, including higher thermal and oxidative stabilities, controllable thermal expansions, decreased crystallinities and higher ceramic and chemical yields.<sup>12</sup> Likewise, SiNCB ceramics have been shown to function as self-sealing barriers for the oxidation of carbon in carbon-carbon composites.<sup>13</sup> A major accomplishment during the last grant period was our development of several new "single-source" polyborosilazane precursors that allow the formation of compositionally homogeneous SiNCB composites in processed forms.

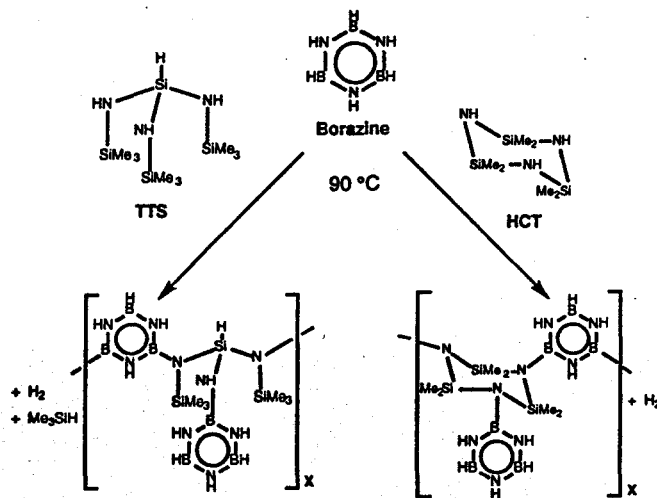
#### *First Generation SiNCB Precursors: Borazine-Based Polyborosilazanes*

Our initial work on SiNCB precursors focused on borazine-based polyborosilazanes, including both borazine-co-silazane backbone polymers and boron-modified hydridopolysilazanes. As shown in the Figure, the borazine-co-silazane backbone copolymers were obtained by the thermal condensation of borazine with two silazanes, 1,1,3,3,5,5-hexamethylcyclo-trisilazane (HCT) and tris(trimethylsilyl-amino)silane (TTS).<sup>14</sup> The freshly prepared polymers are meltable and readily soluble in ethers. Spectroscopic analyses and molecular weight distribution studies indicate both series of copolymers have highly complex, branched structures, with multiple borazine-boron to silazane-nitrogen linkages. Elemental analyses of the B-TTS copolymers are consistent with an approximate  $[(-B_3N_3H_4)NH]_3SiH_x$  structural unit, while the B-HCT copolymers have compositions ranging from  $(B_3N_3H_4)_{1.00}(N)_{1.81}(SiMe_2)_{1.57}(H)_{1.6}$  to  $(B_3N_3H_4)_{1.00}(N)_{1.07}(SiMe_2)_{1.28}(H)_{0.9}$ . Molecular weight studies indicate highly branched structures and relatively low molecular weights with  $M_n = 1,000-2000$  for B-TTS and  $M_n = 3,000-4,000$  for B-HCT. The polymers also have large polydispersities.

Using a second approach, involving the modification of a preformed polysilazane with a boron-containing pendant, borazine-substituted hydridopolysilazanes were achieved by the reaction of hydridopolysilazane (HPZ)<sup>15</sup> with liquid borazine at moderate temperatures (Eq. 7).<sup>16</sup> The borazine-modified hydridopolysilazanes can be prepared with relatively high molecular weights ( $M_n = 5,000-24,000$ ), and a range of boron contents (2-17%). The amount of borazine incorporated into the hydridopolysilazane can be readily controlled. For example, polymers of compositions  $(B_3N_3H_5)_{0.02}(HSi)_{0.30}(Me_3Si)_{0.19}(NH)_{0.26}N_{0.23}$  and  $(B_3N_3H_5)_{0.07}(HSi)_{0.34}(Me_3Si)_{0.18}(NH)_{0.13}N_{0.28}$  were prepared by heating HPZ in excess borazine at 73°C for 2.2 h and 7.0 h, respectively. The spectroscopic data for the new polymers indicate they have retained their hydridopolysilazane backbones and are substituted with pendant borazines by means of a borazine-boron to polymer-nitrogen linkage.



Studies of the ceramic conversions reactions of the three borazine-modified polymers (B-HCT, B-TTS<sup>14</sup> and B-HPZ<sup>16</sup>) demonstrated they are each converted to composite SiNCB ceramic materials in high ceramic and chemical yields, but that each polymer system has its own unique properties. The two copolymer systems yield ceramics having much higher boron-content than the higher molecular weight B-HPZ polymers. Furthermore, even with the similarities in their polymer elemental compositions, structural differences in the two copolymer systems result in different ceramic compositions upon pyrolysis. While the B-HCT copolymers are converted to SiNCB ceramic materials with retention of Si and C to 1800 °C, the facile loss of  $-SiMe_3$  groups from the B-TTS based ceramics yields low carbon content SiNB ceramics at 1400 °C. Further loss of Si from the B-TTS-based ceramics produces dense BN rich materials at 1800 °C. The higher molecular weight B-HPZ polymers, however, yield lower boron content SiNCB ceramics with typical compositions at 1400 °C of  $Si_{1.00}B_{0.09}N_{1.08}C_{0.44}$ . At 1800 °C, the B-HPZ derived ceramics still efficiently retain nitrogen with typical compositions of  $Si_{1.00}B_{0.10}N_{0.47}C_{0.58}$ . In contrast, the ceramics derived from unmodified HPZ are unstable to nitrogen loss, and are nearly pure SiC at 1800 °C, with typical compositions of  $Si_{1.00}C_{0.92}N_{<0.03}$ .



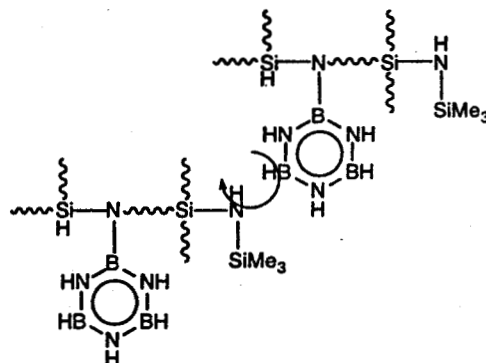
XRD studies of the ceramics obtained from all three types of borazine-based polymers showed they are largely amorphous to 1400°C. At 1800 °C, crystallization of  $\beta$ - $Si_3N_4$ ,  $\beta$ -SiC and

elemental Si begins. In contrast, initial crystallization of  $\alpha$ - $\text{Si}_3\text{N}_4$  in polysilazane derived ceramics such as HPZ-ceramics is usually observed near 1400 °C. Above 1600 °C, the ceramics begin to decompose with loss of nitrogen, and both  $\alpha$ - $\text{Si}_3\text{N}_4$  and  $\beta$ -SiC crystallize. By 1800 °C, nitrogen loss is complete and only crystalline  $\beta$ -SiC is usually observed by XRD.

Thus, the above results clearly demonstrate that addition of boron to the silazane systems serves to both inhibit crystallization and improve the thermal stability of the derived silicon based ceramics. The differences in the composition of the ceramics derived from these systems allow for significantly different potential applications. While the B-HCT based ceramics could serve as effective precursors to high BN content SiNCB ceramic matrix materials, the efficient elimination of both Si and C from the B-TTS based copolymers suggest they may be better suited as precursors for amorphous BN coatings on carbon and/or ceramic fibers. The B-HPZ polymers serve as an excellent higher molecular weight precursors to lower boron content SiNCB ceramics.

### Second-Generation SiNCB Precursors

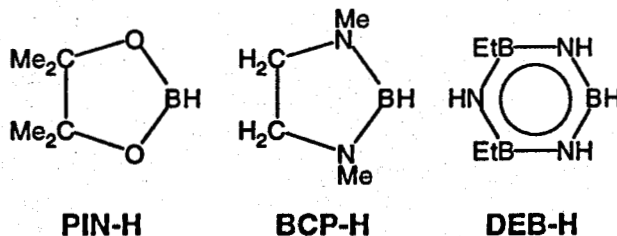
While the B-TTS, B-HCT and B-HPZ polymers are suitable precursors to SiNCB matrix materials and/or coatings, many other potential applications require much greater control of structure and reactivity than is available in these systems. Due to the latent reactivity of the B-H groups on the pendant borazanyl rings, these polymers continue to react and build molecular weight in their melts by the crosslinking reaction in the Figure. Therefore, these polymers are not suitable for processes that require stable melt viscosities, as, for example, in the generation of polymer fibers by melt-spinning.



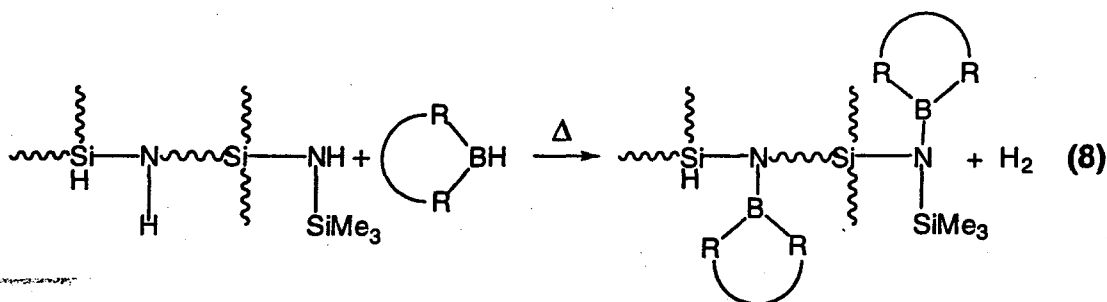
As was the case for the polyborazylene polymer, we felt that the key step needed to retard the crosslinking reaction of the polyborosilazane polymers was to remove or block any reactive B-H groups. We have now designed and synthesized new second-generation hydridopolysilazanes derived from *monofunctional* boranes<sup>17,7</sup> that do not contain reactive B-H groups and thus cannot undergo the crosslinking reactions occurring in the borazine-based polymers.

Our initial studies with borane reagents such as 9-BBN and catecholborane demonstrated these monofunctional boranes are not sufficiently stable to achieve a processable polymer. However, as shown in the Figure, we have now identified several different mono-functional boranes that are both reactive with HPZ and thermally stable at the temperatures needed for melt processing.

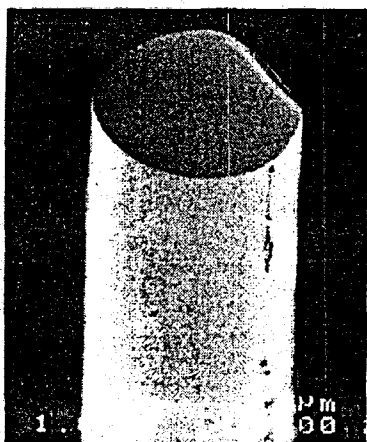
All three boranes may be readily synthesized. PIN-H<sup>18</sup> and BCP-H<sup>19</sup> may be prepared by reacting  $\text{BH}_3 \cdot \text{THF}$  with pinacol or N,N'-dimethylethylenediamine, respectively. DEB-H may be synthesized by the catalyzed hydroboration of borazine,  $\text{B}_3\text{N}_3\text{H}_6$ .<sup>6</sup> Many monofunctional boranes are unstable toward disproportionation, redistribution, isomerization, or elimination reactions,<sup>20,21</sup> but the PIN, BCP, and DEB do not decompose under the conditions required for polymer modification or subsequent polymer processing.



Boron-modified polymers, **PIN-HPZ** and **DEB-HPZ**, were readily prepared as shown in Eq. 8, by heating solutions of **HPZ** dissolved in each borane at 60-100 °C.<sup>17,7</sup> The degree of modification can be easily controlled by the duration of the reaction, with typical boron content of ~1-3%. The resulting polymers were soluble in common organic solvents, including ethers and hydrocarbons.



Studies of the polymer to ceramic conversion reactions showed the modified polymers yield SiNCB ceramics containing ~1-3% boron at 1400 °C, with the highest boron content in the **PIN-HPZ** derived samples. At 1800 °C, the **PIN-HPZ** derived ceramics exhibited improved thermal stability with nitrogen contents of up to 23%, compared to the ceramics obtained from unmodified-**HPZ**, which usually retain less than 4% nitrogen at this temperature. Furthermore, the **PIN-HPZ** derived ceramics were amorphous to 1600 °C, and at 1800 °C showed only weak diffraction from  $\beta$ -SiC. Thus, the **PIN-HPZ** based ceramics have properties equivalent or better than those obtained from the **B-HPZ** polymer. However, unlike the **B-HPZ** polymers which show initial weight losses due to crosslinking below 80 °C,<sup>16</sup> TGA studies of the **PIN-HPZ** and **DEB-HPZ** samples showed that the crosslinking reaction that results in the low-temperature weight loss in the **B-HPZ** polymers has been suppressed in the **PIN-HPZ** and **DEB-HPZ** polymers. Thus, in contrast to the **B-HPZ** polymers, the **PIN-HPZ** and **DEB-HPZ** polymers were found to be stable as melts and it was possible to continuously melt-extrude polymer fibers. Scanning electron micrographs of the **PIN-HPZ** polymer fibers show they are smooth and uniform (Figure, left). After a brief cure with  $\text{Cl}_3\text{SiH}$ , pyrolysis under an argon atmosphere to 1200 °C produced black SiNCB ceramic fibers (Figure, right) that were dense and uniform.



PIN-HPZ Polymer Fiber



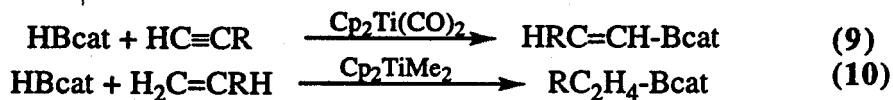
SiNCB Ceramic Fiber

## Metal Catalyzed Reactions of Polyboranes

An essential part of both our past success in inorganic polymer synthesis and our proposed future research described in the later sections of this proposal has been our continuing development of new transition metal catalyzed reactions of polyboranes. These reactions have allowed the high yield selective functionalization of polyboranes, such as borazine and decaborane, that are the key components in many of the inorganic polymers. Some of our most important recent results involving new titanium- and platinum- catalyzed reactions are described in the following sections:

### Titanium Catalyzed Reactions

Our previous work has shown that a variety of late transition metal complexes can be used to catalyze the reactions of polyboranes with olefins and acetylenes to yield alkyl or alkenyl-substituted products. Recently, however, early transition metal complexes have also been found to catalyze olefin and acetylene hydroborations with monoboranes such as catecholborane (HBcat).<sup>22</sup> For example, Hartwig has recently reported<sup>22a</sup> that  $\text{Cp}_2\text{Ti}(\text{CO})_2$  catalyzes the hydroboration reactions of HBcat with acetylenes, while  $\text{Cp}_2\text{TiMe}_2$  is an effective catalyst in reactions of HBcat with olefins.

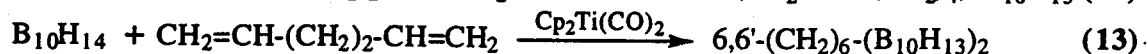
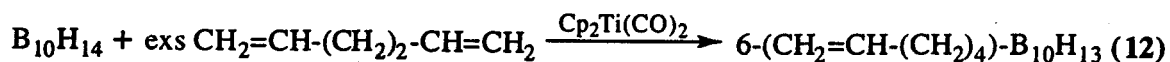


These reports suggested that early metal metallocene catalysts might also be useful for reactions involving polyboranes with the possibility of new types of activities and selectivities. We have therefore begun to explore the use of these early metal catalysts for a variety of borane reactions. Our initial studies<sup>23</sup> have already led to the discovery of a remarkable titanium catalyzed reaction that has allowed the systematic high-yield synthesis of monoalkyldecaboranes.

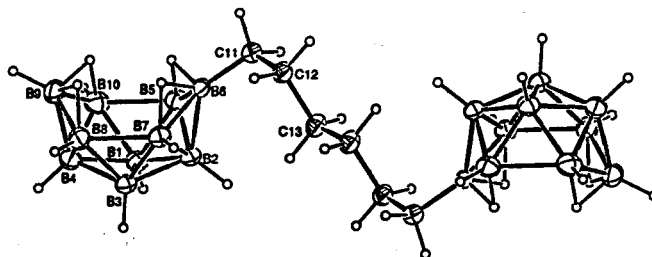


We have previously reported<sup>24</sup> that platinum complexes will catalyze decaborane olefin-hydroboration to give dialkyldecaboranes,  $6,9\text{-(RC}_2\text{H}_4\text{)}_2\text{B}_{10}\text{H}_{12}$ , in high yields, but the titanium catalyzed reactions give exclusively *monoalkyldecaboranes*,  $6\text{-(RC}_2\text{H}_4\text{)B}_{10}\text{H}_{13}$  products. Even with forcing conditions and long reaction times, no dialkylproducts are formed. Gaines<sup>25</sup> has recently reported multi-step synthetic routes to monoalkyldecaboranes, but the titanium catalyzed reactions are a significant improvement, since they provide simple, high-yield, one-step routes to such compounds directly from decaborane. Reactions are typically carried out without solvent at 80-90°C, with an excess of olefin and ~5 mol% catalyst and give greater than 90% isolated yields. The catalyst is long-lived with reactions being carried out for more than 12 days showing no significant decrease in rate.

Of most interest is the fact that titanium catalyzed decaborane reactions with nonconjugated diolefins, such as 1,5-hexadiene, give, depending upon reaction conditions and stoichiometries, high yields of either monosubstituted (88%) or linked-cage products (92%).



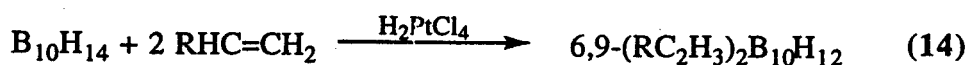
A crystallographic study has confirmed the linked-cage structure in the Figure for 6,6'-(CH<sub>2</sub>)<sub>6</sub>-(B<sub>10</sub>H<sub>13</sub>)<sub>2</sub> where the two decaborane cages are linked at the 6-boron vertex on each cage by the 6-carbon chain.



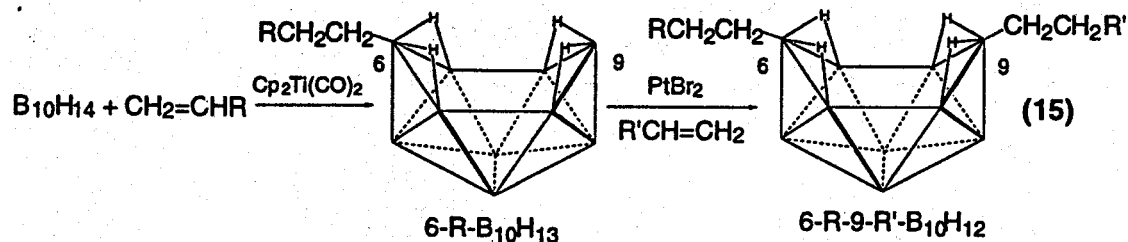
As illustrated in Eqs. 12 and 13, the titanium catalyzed reactions provide simple, efficient entries into two new classes of important polyborane clusters. The linked cage compounds, such as 6,6'-(CH<sub>2</sub>)<sub>6</sub>-(B<sub>10</sub>H<sub>13</sub>)<sub>2</sub>, are expected to serve as starting materials for the construction of new types of chelating polyborane ligands that are needed for the construction of multi-cage metallaborane or metallacarborane arrays. As discussed in much more detail in the Proposed Research section, the polymerization of olefin-substituted compounds, such as 6-(H<sub>2</sub>C=CH-(CH<sub>2</sub>)<sub>4</sub>)-B<sub>10</sub>H<sub>13</sub>, are now being investigated as building blocks of new decaborane-polyolefin polymers.

#### *Metal Catalyzed Routes to Asymmetrically-Substituted Dialkyldecaboranes*

As mentioned above, our earlier work showed that either chloroplatinic acid or platinum dibromide will catalyze decaborane olefin-hydroboration to give dialkyldecaboranes in high yields.<sup>24</sup>



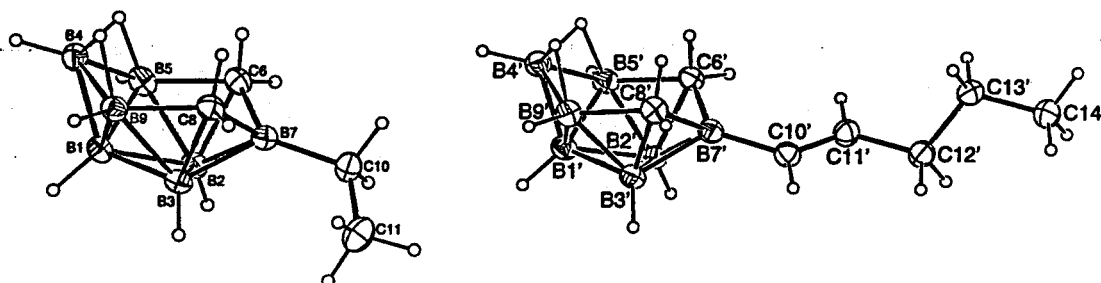
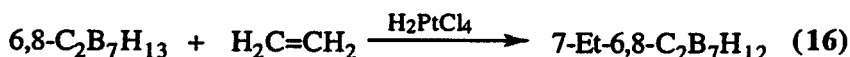
We have now found<sup>26</sup> that asymmetrical dialkyldecaboranes can be readily synthesized in high yields by sequential use of Cp<sub>2</sub>Ti(CO)<sub>2</sub> and PtBr<sub>2</sub> catalysts:



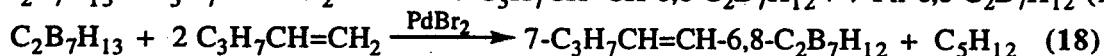
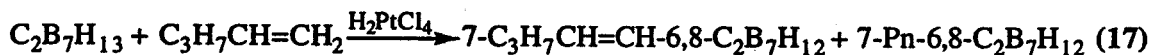
For example, the reaction of 6-octyldecaborane, prepared by the titanium catalyzed reaction, with excess allylbenzene and 3.5 mol% platinum dibromide for 4 h gave 97% isolated yield of 6-(C<sub>8</sub>H<sub>17</sub>)-9-(PhC<sub>3</sub>H<sub>6</sub>)-B<sub>10</sub>H<sub>12</sub> product. These reactions thus give a systematic way of making tailored decaborane derivatives.

### Platinum and Palladium Catalyzed Carborane Reactions

The above results on platinum-catalyzed decaborane reactions, as well as other recent reports that chloroplatinic acid can effect o-carborane alkylations,<sup>27</sup> suggested that platinum based catalysts could prove very useful for reactions involving other larger cage systems. Indeed we have now found<sup>28</sup> that the  $\text{H}_2\text{PtCl}_4$  catalyzed reaction of 6,8- $\text{C}_2\text{B}_7\text{H}_{13}$  with ethylene,  $\text{Me}_3\text{SiCH}=\text{CH}_2$  and  $\text{Cl}_3\text{SiCH}=\text{CH}_2$  give quantitative yields of 3-R- $\text{C}_2\text{B}_7\text{H}_{12}$  products, as shown in the ORTEP plot of 3-Et- $\text{C}_2\text{B}_7\text{H}_{12}$  below (left).



However, reactions with longer chain olefins, such as 1-pentene, result in olefin substitution to give predominately 7-alkenylcarboranes along with lesser amounts of alkylcarboranes. As seen in the ORTEP diagram (above, right) the double-bond is adjacent to the cage. Reactions of these olefins with a  $\text{PdBr}_2$  catalyst gives exclusively 7-alkenylcarboranes.



The production of equivalent amounts of alkane in the reaction indicates a mechanism involving a hydrogen transfer step. We had already observed that  $\text{PdBr}_2$  catalyzes a similar olefin-substitution with pentaborane, yielding alkenylpentaborane.<sup>29</sup> But, the reaction in Eq. 18 is the first example for a larger cage system. We plan to investigate the use of Pt and Pd catalysts for a variety of olefin-substitution and -alkylation reactions as potential routes to both alkenyl and alkylpolyboranes.

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## DOE Sponsored Publications (Published or In Press) During the Last Grant Period (1996-present)

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#### Statement of Unexpended Funds

It is estimated that no funds will remain unexpended or uncommitted at the end of the final budget period.