Molecular and Polymeric Ceramic Precursors

Research Progress Report

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Abstract

The development of new methods for the production of complex materials is one of the most important problems in modern solid state chemistry and materials science. This project is attempting to apply the synthetic principles which have evolved in inorganic and organometallic chemistry to the production of technologically important non-oxide ceramics, such as boron nitride, boron carbide and metal borides. Our recent work has now resulted in the production of new polymer systems, including poly(B-vinylborazine), polyvinylpentaborane and polyborazylene, that have proven to be high yield precursors to boron-based ceramic materials. Current work is now directed toward the synthesis of new types of molecular and polymeric boron-containing species and an exploration of the solid state properties of the ceramics that have been produced in these studies.

Summary of Scientific Progress

Many inorganic polymers exhibit enhanced properties compared to typical organic polymers, including thermal and chemical stability, electronic conductivities and preceramic properties.¹ This project is exploring the synthesis, characterization and applications of new inorganic polymer systems, with a particular interest in the development of processable polymeric precursors to important solid state materials. A major focus of our work in the last three years has dealt with the synthesis and properties of new preceramic polymers.

Because of their high strengths, low densities, high temperature and chemical stabilities, and controllable electronic properties, ceramics and ceramic-composite materials are in the forefront of advanced materials technologies. Although most ceramic materials can already be produced in large quantities via conventional powder techniques, these materials, due to their brittle and refractory properties, are not easily formed into complex shapes. Therefore, applications of advanced ceramics as films, fibers, coatings or other complex shaped materials will require new ceramic synthesis and processing methods. Polymeric-precursors have now proven to be attractive synthetic routes to solid state materials that enable their formation in processed forms. Such methods offer a number of advantages² including: (1) precise control over polymer stoichiometry and composition which can be systematically varied to optimize ceramic properties, (2) the ability to form the polymer into a desired shape or thin-film followed by conversion to the ceramic with retention of form, and (3) low temperature decomposition, enabling ceramic formation under milder conditions than those used in conventional techniques.

There are already several commercialized polymeric precursors to silicon-based ceramics, including the polycarbosilanes³ used to form silicon-carbide "Nicalon" fibers and the polysilazane⁴ precursors to silicon nitride. Because of their technological importance for both structural and electronic applications, our work has focused on the development of new polymeric precursors to boron-based ceramic materials including, boron carbide, boron nitride and metal borides and most recently, composites such as BNC or SiNCB ceramics. As described in the following sections, our work during the last three years has resulted in the development new polymeric precursors to each of these systems.

Polymeric Precursors for Boron Nitride.

Graphite and h-BN exhibit similar strength and ablation properties, as well as anisotropic thermal expansions and conductivities; however, unlike graphite, h-BN is oxidatively stable in air to 900°C and is an electrical insulator. This combination of properties has led to a number of unique structural and electronic applications for h-BN, but many of these uses require the formation of the ceramic in a processed form.⁵ We have now synthesized several new inorganic polymers, including the borazine-

based polymers polyvinylborazine and polyborazylene, and shown that they can be used to obtain boron nitride in a variety of forms, including films and fibers.⁶

Polyvinylborazine. The production of polyvinylborazine, an inorganic analogue of polystyrene, initially required the synthesis of the previously unknown compound vinylborazine, $\text{CH}_2=\text{CH}-\text{B}_3\text{N}_3\text{H}_5$. This was achieved via the metal-catalyzed reaction of borazine with acetylene and this reaction has allowed the large scale production of this monomer.⁷

Insoluble polymeric materials result from thermally induced polymerizations of pure liquid B-vinylborazine, but it was found that solution polymerizations using the free radical initiator AIBN proceed smoothly to form soluble homopolymers. The spectroscopic data support a polystyrene-type structure.⁸

These new polyvinylborazine polymers have now been used to produce, depending upon pyrolysis conditions, a variety of ceramic materials, ranging from black, high carbon content materials to white h-BN. In each case, however, the polymer/ceramic conversion was found to take place with both high ceramic and chemical yields and give materials with B/N ratios of 1.0. Best results for the production of pure h-BN were obtained from the pyrolyses under an ammonia atmosphere, which produced white, crystalline h-BN with only 0.27% carbon and 0.15% hydrogen impurities, corresponding to an empirical formula of $\text{B}_{1.00}\text{N}_{1.01}\text{C}_{0.006}\text{H}_{0.04}$.

Polyborazylene. The poly(B-vinylborazine) described in the previous section shows excellent conversions to boron nitride, but because of the carbon backbone this polymer requires pyrolyses under ammonia atmosphere to achieve low-carbon boron nitride. In an effort to develop new boron nitride precursors that would give improved ceramic yields and/or not require the use of ammonia during the ceramic conversion step, we initiated investigations of the syntheses of poly(borazylene) polymers, such as shown in the Figure below, composed of linked borazine rings analogous the organic poly(phenylene) polymers. Such polymers were also of particular interest because of their potentially high ceramic yields (95%) and their close structural relationship to boron nitride.

Initial investigations focused on metal catalyzed synthetic routes; however, during the course of these studies we discovered⁹ that controlled thermolysis of liquid borazine in vacuo at moderate temperatures results in nearly quantitative

dehydropolymerizations to form *soluble* polyborazynes. The resulting polymers are highly soluble in polar solvents with a typical M_w 7,600 and M_n 3,400. Elemental analyses and SEC/LALLS/UV studies support a branched-chain or partially crosslinked structure.

Bulk pyrolyses of the polymer under either argon or ammonia to 1200°C result in the formation of white boron nitride powders in excellent purities and ceramic yields (85-93%).

Studies^{10,11} of the polyborazylene/boron-nitride ceramic-conversion reaction have shown that both polyborazylene and a crosslinked intermediate material obtained by heating at 400°C, exhibit X-ray patterns consistent with a layered structure. This observation suggests a simple process for the conversion of the polymer to boron nitride, involving a dehydrocoupling reaction between the B-H and N-H groups on adjacent polymers resulting in a 2-dimensional-crosslinking of the polymer.

Because of its solubility, low-temperature decomposition, and high ceramic and chemical yields, polyborazylene would appear to be the ideal chemical precursor to

boron nitride and thus enable many important applications. We have now, in fact, employed both polyborazylene and polyvinylborazine for the production of h-BN coatings on alumina, silicon carbide, silicon nitride and carbon fibers by simply dipping yarn in polymer solutions then heating the coated fibers to $>900^{\circ}\text{C}$. Such coatings are of great technological interest since they can enhance the toughness of ceramic-matrix composites by increasing the potential for fiber pullout.

Hybrid Polymers: Precursors to SiNCB and BNC Ceramic Composites

Borazine-Modified Hydridopolysilazanes. Polysilazanes have been shown to be excellent polymeric precursors to silicon nitride or SiNC ceramic materials.⁴ Chemical modification of polysilazanes has been proposed as a means of modifying and enhancing the properties of the polymer and/or the final ceramic materials. For example, the incorporation of boron in the polysilazane has been claimed¹² to decrease the crystallinity of the silicon nitride derived from these polymers and thereby extend the effective use-temperature of these ceramics. Given the potential importance of SiNCB materials, we have investigated in collaboration with Ed Remsen (Monsanto) and Gregg Zank (Dow-Corning) the generation of new classes of hybrid polymers that might serve as processable precursors to such composite ceramics.

We have now found¹³ that the high yield synthesis of hybrid borazine-substituted hydridopolysilazanes can be achieved by the reaction of the preformed silicon-based preceramic polymer, hydridopolysilazane (HPZ),¹⁴ with liquid borazine at moderate temperatures. The amounts of borazine incorporated into the hydridopolysilazane can be readily controlled. For example, polymers of compositions $(\text{B}_3\text{N}_3\text{H}_5)_{0.02}(\text{HSi})_{0.30}(\text{Me}_3\text{Si})_{0.19}\text{NH}_{0.26}\text{N}_{0.23}$ **1** and $(\text{B}_3\text{N}_3\text{H}_5)_{0.07}(\text{HSi})_{0.34}(\text{Me}_3\text{Si})_{0.18}(\text{NH})_{0.13}\text{N}_{0.28}$ **2** 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 that they have retained their hydridopolysilazane backbones, but are substituted with pendant borazines by means of a borazine-boron to polymer-nitrogen linkage. Such linkages may have been formed by either hydrogen or trimethylsilane elimination reactions.

Studies of the thermolytic reactions of the polymers demonstrated that they are converted in high ceramic and chemical yields to composite SiNCB ceramic materials. The ceramic yields ($\sim 70\%$) to 1400°C are increased over that observed for the unmodified HPZ ($\sim 57\%$) due to both the retention of boron and nitrogen in final ceramic, and a borazine-crosslinking reaction which retards the loss of polymer backbone components. It is also very significant that, in contrast to the ceramic

materials obtained from unmodified **HPZ**, the borazine-modified polymers yield ceramics that are amorphous to 1400°C.

As shown in the Table, pyrolyses carried out to higher temperatures also demonstrated that the boron-modified ceramics are significantly more stable with respect to nitrogen loss than the ceramic derived from the unmodified **HPZ**.

High Temperature Pyrolysis Results.

HPZ

<u>Temp.(°C)</u>	<u>Char yield (%)</u>	<u>Composition</u>
1400	62.3	C _{1.00} N _{2.35} Si _{2.43}
1500	61.3	C _{1.00} N _{2.42} Si _{2.48}
1600	55.5	C _{1.00} N _{1.66} Si _{2.23}
1700	44.1	C _{1.00} N _{0.13} Si _{1.15}
1800	42.4	C _{1.00} N _{0.03} Si _{1.06}

Polymer 1

<u>Temp.(°C)</u>	<u>Char yield (%)</u>	<u>Composition</u>
1400	68.8	C _{1.00} N _{2.42} B _{0.20} Si _{2.25}
1500	69.9	C _{1.00} N _{2.36} B _{0.21} Si _{2.25}
1600	62.9	C _{1.00} N _{2.24} B _{0.21} Si _{2.21}
1700	59.1	C _{1.00} N _{1.66} B _{0.21} Si _{1.94}
1800	51.1	C _{1.00} N _{0.80} B _{0.18} Si _{1.72}

Significant differences in the onset, phases and extent of crystallization in the ceramic products obtained from **HPZ** and the modified polymers were also observed. The ceramics resulting from the borazine-modified polymers do not show any major crystallinity until 1700°C, at which temperature a mixture of α -Si₃N₄, β -Si₃N₄ and β -SiC is observed. In contrast, the ceramic derived from **HPZ** shows substantial amounts of crystalline α -Si₃N₄ at 1500°C, both α -Si₃N₄ and β -SiC at 1600°C and only β -SiC above 1700°C.¹⁵

Because of their ease of synthesis and processability, as well as the increased thermal stabilities and reduced crystallinity of their derived ceramics, these new hybrid borazine-modified hydridopolysilazanes polymers may prove to be reasonable precursors for enhanced SiNCB fibers, matrices for ceramic-ceramic or carbon-carbon composites and/or binders for nitrogen based ceramic powders. These applications are presently under investigation.

Poly(styrene-co-B-vinylborazine) Copolymers. The discovery that soluble poly(B-vinylborazine) homopolymers could be readily formed in solution at 80 °C with the aid of AIBN initiation has enabled the systematic production of a new soluble organic/inorganic hybrid polymers. In our initial studies⁸ we demonstrated the production of a new family of poly(styrene-co-B-vinylborazine) copolymers.

Elemental analyses and the spectroscopic data are consistent with their styrene-co-B-vinylborazine formulations. By adjusting the monomer feed ratios and the initiator concentrations, copolymers ranging in composition from 10 to 90% styrene and molecular weights from ~1,000 to >1,000,000 can be produced. The use of these AIBN initiated olefin copolymerization reactions are now being explored as routes to a wide variety of borazine-containing hybrid organic polymers.

Precursors to Metal Borides and Metal-Boride/Nitride Composites

Decaborane-Based Metal Boride Precursors. Metal borides¹⁶ are high-melting, extremely hard solids with high thermal stabilities and chemical inertness. Many also have metallic like conductivity and/or unusual magnetic properties. One common powder method of making bulk metal borides has been the reduction of the metal oxide with boron carbide. However, this reaction is not useful for the syntheses of coatings or shaped materials since neither the MO₂ or B₄C are soluble or melt at reasonable temperatures. Since soluble processable polymeric precursors to boron carbide have now been developed, we felt that a processable precursor to a metal boride could be obtained by dispersing a metal source such as MO₂ or M(OR)₄ in such a precursor polymer. Heating the mixture could then result in the *in situ* generation of boron carbide followed by reaction to produce the boride.

Such precursor systems were obtained¹⁷ by dispersing metal oxides, such as TiO₂, in the decaborane dicyanopentane polymer, (-B₁₀H₁₂NC-(CH₂)₅-CN-)_x. Subsequent pyrolysis of the dispersions at temperatures above 1400°C afford metal borides, including TiB₂, ZrB₂, NbB₂, TaB₂ and HfB₂ in high chemical and ceramic yields.

Elemental analyses of the TiB₂, ZrB₂, NbB₂, TaB₂ and HfB₂ materials showed excellent purities. The metal borides powders were found to be highly crystalline and with grain sizes in the submicron range at 1400°. Based on ceramic conversion studies of both the polymer and the dispersions, the reaction is proposed to involve the *in situ* generation of boron carbide and carbon followed by solid state reduction of metal oxides to produce the borides.

We have also found that, depending upon the metal oxide particle size and the polymer solution viscosity, the metal oxide particles will stay suspended in the solution

and that this precursor mixture may then be used for the generation of excellent metal boride coatings. We have, for example, achieved TiB_2 coatings on graphite with this method. Such coatings are of great potential technological importance for the protection of carbon from attack by molten aluminum in Hall cells and for the protection of carbon fibers in metal matrix composite materials. We are now in the process of expanding our coating work to include a variety of substrates and metal borides.

Polyborazylene-Based Precursors to TiB_2/TiN Composites. The results described in the previous section, yielding metal borides from a boron-carbon based polymer, suggested that the reactions of a metal with a boron-nitrogen polymer, such as polyborazylene, might lead to incorporation of both polymer boron and nitrogen atoms to produce new composite metal-nitride/metal-boride materials, which may have improved properties over individual metal borides or nitrides.

Such a titanium boride/titanium nitride precursor system was made¹⁸ by dispersing titanium powder into polyborazylene. Final ceramic materials were prepared by pyrolysis of either powders or shaped green bodies under inert atmosphere.

Shaped green bodies were made by isostatic pressing of polymer/titanium dispersions. Ceramic bars with excellent shape retention in observed ceramic yields of 91-96%, were then achieved by heating the green bodies to 1450°C. X-ray diffraction and TEM studies¹⁹ of the ceramic conversion reaction have shown that the material goes through several changes in composition and crystallinity as the processing temperature is increased. Up to 800°C there is little reaction between the polymer and the titanium metal. As the temperature is increased, 25-50 nm size crystals of TiN nucleate. At 1200°C crystalline TiB_2 is observed to form. The final morphology contains homogeneous distribution of 500 nm size grains with residual amorphous phase at triple points and along grain boundaries.

The preparations of TiB_2/TiN and $\text{TiB}_2/\text{Ti(CN)}$ composite materials by sintering TiB_2 and TiN or TiCN powders at high temperatures have previously been reported.²⁰ TiB_2/TiN composite coatings have also been achieved by CVD methods.²¹ The new polymer route discussed above is, however, the only direct chemical method that can be used to produce shaped titanium boride/nitride composites, consisting of intimately mixed polycrystals with grain sizes on the order of nanometers, in high ceramic and chemical yields. The dependence of the crystal size and distribution on the reaction/sinter temperature, the evolution of microstructure and the properties of the final composite material, such as conductivity and hardness, are currently under investigation. We are also exploring the reactions of polyborazylene with other metals and soluble metal complexes with the goal of developing a range of new metal boride/nitride precursor systems that will allow the formation of both shaped bodies and coatings.

New Boron-Nitrogen Clusters (Jointly sponsored by DOE and DFG)

During the last year we have initiated investigations of new synthetic routes to nitrogen containing boron-clusters. Such boron-nitrogen clusters could, because of their expected thermal and hydrolytic stabilities, might prove an attractive alternative to borazine for the incorporation of boron and nitrogen into a polymer. Our initial studies focused on the reactions of polyhedral boron compounds with azides and imines and have resulted in the synthesis and structural characterization of the first example of a new class of hybrid fused ring-cluster triazene-thiaborane compound,²² *m*₂(4,exo-9)-(1-SiMe₃-3-H-N₃)-*arachno*-6-SB₉H₁₀ and the production of a series of new imine substituted boranes,²³ such as *endo*-9-((*t*-Bu)MeC=NH)-*arachno*-6-SB₉H₁₁. We are presently exploring new reactions of polyhedral boranes with both saturated and unsaturated nitrogen ligands as possible routes to new hybrid boron-nitrogen clusters and aza-cage/ring compounds.

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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.

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