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# Polymeric precursors to boron based ceramics

Larry G. Sneddon*, Mario G. L. Mirabelli, Anne T. Lynch, Paul J. Fazen, Kai Su, and Jeffrey S. Beck

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

*Abstract* – Our recent work is described that has resulted in the production of several new boron-polymer systems, including poly(vinylborazine), poly(vinylpentaborane) and poly(borazylene), that have proven to be high yield precursors to boron ceramics such as, boron nitride and boron carbide.

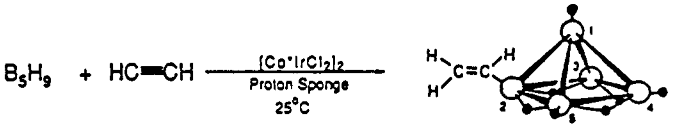
## INTRODUCTION

Because of their high strengths, low weights, high temperature and chemical stabilities, and controllable electronic properties, ceramics and ceramic-composite materials are in the forefront of advanced materials technologies. However, many ceramic applications will require the development of new processable ceramic precursors from which films, coatings, fibers or shaped materials can be formed before the final ceramic material is produced. Thus, as an alternative to conventional high-temperature powder techniques, there has recently been great interest in the development of polymer precursors to ceramic materials. (ref. 1,2) Such routes offer a number of potential advantages, including precise control of ceramic compositions and the ability to form shaped objects. Likewise, a polymer could undergo decomposition at low temperatures, enabling ceramic formation under milder conditions than those used in conventional methods.

There are a number of boron-containing ceramics for which the development of a polymer based synthetic route would be advantageous. Because of their unique mechanical and electronic properties, boron carbide and boron nitride are materials of particular interest. For example, boron carbide has been shown to have excellent promise as a high temperature thermoelectric material, (ref. 3) while h-boron nitride has been proposed as both a dielectric material for semiconductor devices and as a fiber coating which will improve the strength of ceramic composite materials. (ref. 2) We describe in this paper some of our recent work that has led to the development of several new boron polymer systems, derived from pentaborane(9) ($B_5H_9$) and borazine ($B_3N_3H_6$), which have proven to be useful precursors to boron carbide or boron nitride.

## SYNTHESES AND CERAMIC CONVERSION REACTIONS OF VINYLBORANE POLYMERS

Our initial efforts focused on the development of the synthetic routes needed to allow high yield, selective syntheses of vinylborane molecular species, such as vinylborazine and vinylpentaborane, from which new polymeric precursor materials could be derived. We found (refs. 4-7) that certain Ir and Rh complexes are highly active catalysts for borane/alkyne additions which allow the large scale syntheses of the targeted alkenylboranes. Thus, as indicated below, vinylpentaborane may be readily obtained by the $[(\eta\text{-}C_5Me_5)IrCl_2]_2$ catalyzed reaction of pentaborane(9) with acetylene, while vinylborazine may be produced via a $RhH(CO)(PPh_3)_3$ catalyzed reaction of borazine with acetylenes:



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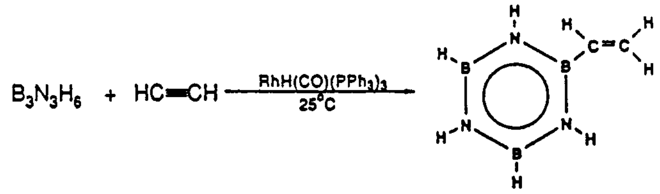
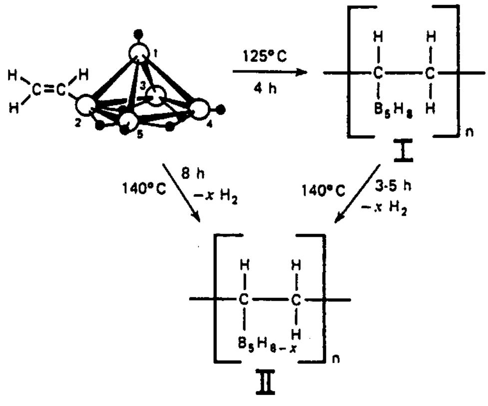


(2)

### Poly(vinylpentaborane): a boron carbide precursor

The 2-(vinyl)pentaborane (ref 8,9) was found to readily polymerize at 125°C to form polymer I in over 90% yield. The poly[2-(vinyl)pentaborane] prepared in this manner is soluble in most common organic solvents and has a broad weight range with fractions up to a molecular weight of ~1000 g/mol.

Further heating of I at 140°C results in loss of ~1.0 mol equivalent of $H_2$ and production of a hard, intractable, crosslinked polymer II. Elemental analysis of II is consistent with an empirical formula of $C_2B_5H_9$ indicating loss of $H_2$ and possible formation of B-B linkages. II can also be formed in high yield (91%) directly from 2-($H_2C{=}CH$)-$B_5H_8$ by heating the olefin at 140°C.



Upon pyrolysis both I and II were found to be excellent, high yield, precursors to boron carbide. For example, the conversion of II to $B_4C$ was accomplished by heating a sample of the polymer to 1200°C under argon for 8 h. Boron carbide prepared in this manner was isolated in 77.0% ceramic yield and 97.1% chemical yield according to the following equation:

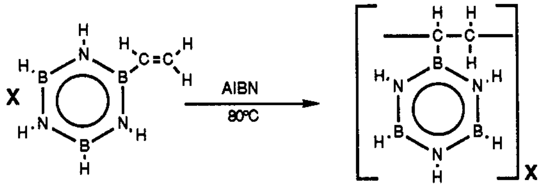
$$[\text{-}CH_2\text{-}CH(B_5H_8)\text{-}]_x \xrightarrow{1200^\circ C} 5/4\ B_4C + 3/4\ CH_4 + 3\ H_2 \qquad (3)$$

Elemental analyses of the ceramic product are consistent with an empirical formula of $B_{4.02}C$ and the material exhibited a density of 2.0 g/mL. Crystalline $B_4C$, as determined by X-ray powder diffraction, was obtained by heating the amorphous ceramic at 1455°C under argon for several days. The density of the material increased from 2.0 g/mL to 2.3 g/mL, thus approaching the theoretical value of 2.5 g/mL.

These studies clearly demonstrate that oligomeric vinylpentaboranes are excellent precursors to $B_4C$. Furthermore, the fact that polymer I appears to undergo crosslinking at low temperatures indicates that it might be useful for applications where thermosetting behavior is desired.

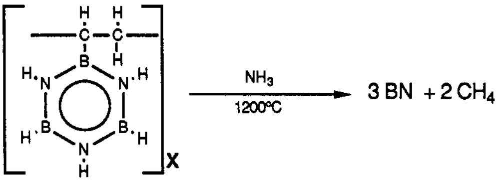
### Poly(vinylborazine)

We have also found that B-vinylborazine can be readily polymerized either thermally (ref. 7) or with the aid of free radical initiators (ref. 10) (Eq. 5) to produce soluble forms of the new polymer, poly(B-vinylborazine): the inorganic analogue of poly(styrene).



(4)

These new poly(B-alkenylborazine) polymers satisfy a number of the criteria previously identified for preceramic materials and their use as precursors to boron nitride was investigated. It was found that depending upon the polymer and pyrolysis conditions, a variety of ceramic materials may be produced, ranging from black, high carbon 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.



(5)

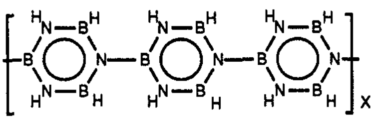
Best results for the production of pure h-BN were obtained from the pyrolyses of soluble poly(vinylborazine) under an ammonia atmosphere at 1200-1400°C. This produced white, crystalline materials with only 0.27% carbon and 0.15% hydrogen impurities, corresponding to an empirical formula of $B_{1.00}N_{1.01}C_{0.006}H_{0.04}$. The product also exhibited the density, DRIFT and X-ray diffraction spectra, and oxidative stabilities characteristic of h-BN.

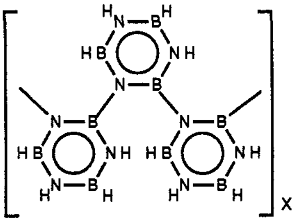
We are currently exploring both the generation of higher molecular weight poly(vinylborazines) and new poly(vinylborazine/styrene) copolymers, as well as the applications of poly(vinylborazines) for the formation of boron nitride coatings and fibers.

## Poly(borazylene)

Poly(B-vinylborazine) shows excellent conversions to boron nitride, but because of its carbon backbone, it requires pyrolysis under an ammonia atmosphere in order to achieve low-carbon boron nitride. In an effort to develop new boron nitride precursors that give improved ceramic yields and/or do not require the use of ammonia during the ceramic conversion step, we initiated investigations of the syntheses of alternative types of borazine based polymers.

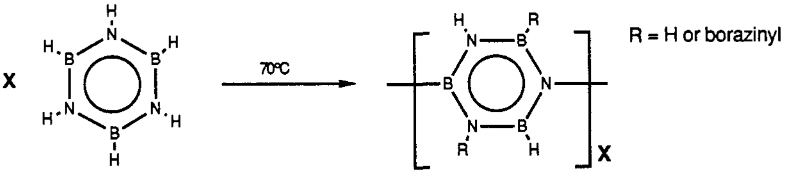
Poly(borazylene) polymers, such as shown below, composed of linked borazine rings analogous the organic poly(phenylene) polymers, were of particular interest because of their potentially high ceramic yields (95%) and their close structural relationship to boron nitride.





Small dehydrodimers and oligomers of alkylated borazine have previously been prepared; however, only the N-B coupled dimer 1:2'-$[B_3N_3H_5]_2$ has been obtained from the parent $B_3N_3H_6$ system. (refs. 11-13) Several studies (refs. 11,14) of the stability of liquid borazine have also reported the formation of white low volatile (perhaps polymeric) solids, but these materials were not identified. Thus, no tractable dehydrocoupled polymers derived from the parent borazine had previously been characterized.

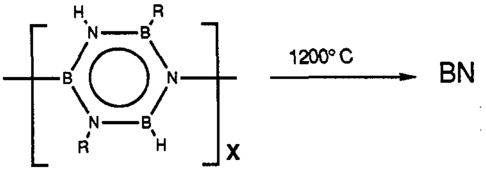
Our initial investigations (ref. 15) of the synthesis of poly(borazylene) focused on metal catalyzed synthetic routes; however, during the course of these studies we discovered (ref. 16) that simply heating liquid borazine in vacuo at moderate temperatures results in a dehydrocoupling reaction to produce *soluble* polymeric materials in excellent yields.



(6)

The polymer is isolated as a white powder that is highly soluble in polar solvents, such as THF and glyme, and that, according to size exclusion chromatography (SEC)/ low angle laser light scattering (LALLS) analysis has $M_w$ 7,600 g/mol and $M_n$ 3,400 g/mol. Elemental analyses of the polymer are consistent with the empirical formula of $B_3N_3H_3$, (linear poly(borazine) □ $B_3N_3H_4$) suggesting the formation of a branched-chain or partially crosslinked structure. Evidence of chain branching was also found in the SEC/LALLS/UV studies. The detailed structure of the polymer has not yet been established; however, since small amounts of both the N:B coupled dimer (1:2'-$(B_3N_3H_5)_2$) and borazanaphthalene ($B_5N_5H_8$) were isolated in the volatile materials from the reaction, the polymer may have a complex structure, having linear, branched, and fused chain segments.

Because of its composition, high yield synthesis, and excellent solubilities, poly(borazylene) would appear to be an ideal chemical precursor to boron nitride. Indeed, bulk pyrolyses of the polymer under either argon or ammonia to 1200°C were found to result in the formation of white boron nitride powders in excellent purities and ceramic yields 85-93% (theoretical ceramic yield, 95%).



(7)

We are presently exploring the use of both poly(vinylborazine) and poly(borazylene) as precursors for the formation of boron nitride films, coatings and fibers. Because of its technological importance, one application that we have been particularly interested in is the use of polymeric precursors for the formation of boron nitride coatings on ceramic fibers in ceramic matrix composite materials. Boron nitride coated ceramic fibers have been shown to enhance the strength of a ceramic fiber/ceramic composite by decreasing the interfacial shear strength between the fiber and matrix and thus increase the potential for fiber pullout (toughness). We have achieved the formation of excellent quality boron nitride fiber coatings by simply dipping ceramic fiber bundles in glyme solutions of either poly(vinylborazine) or poly(borazylene) then heating the fiber under either an ammonia or argon atmosphere to ~900°C. Scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) studies of the resulting fibers have indicated that excellent BN coatings can be achieved on alumina, silicon carbide, silicon nitride or carbon fibers. For example, SEMs of coated alumina fibers are shown in the Figure where uniform BN coatings of ~0.2-0.4μ are clearly evident.

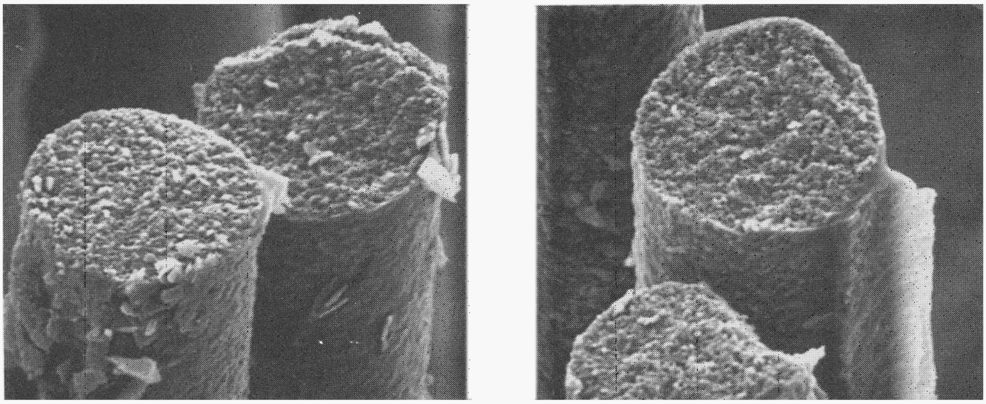


**Fig. Scanning Electron Micrographs of Boron Nitride Coatings on Alumina Fibers Derived From Poly(vinylborazine) and Poly(borazylene)**

## CONCLUDING REMARKS

The success of the polymer precursor approach in producing nonoxide ceramic materials, such as the Nicalon silicon carbide fibers, strongly suggests that such routes have the potential to produce a wide variety of boron ceramic materials in forms that were previously unattainable using conventional metallurgical techniques. It also is clear from our work, described above, as well as that emanating from other laboratories (ref. 1,2) that the key advance that is needed to realize this promise is the design of a wider range of processable boron polymer systems with controllable chemical and physical properties.

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