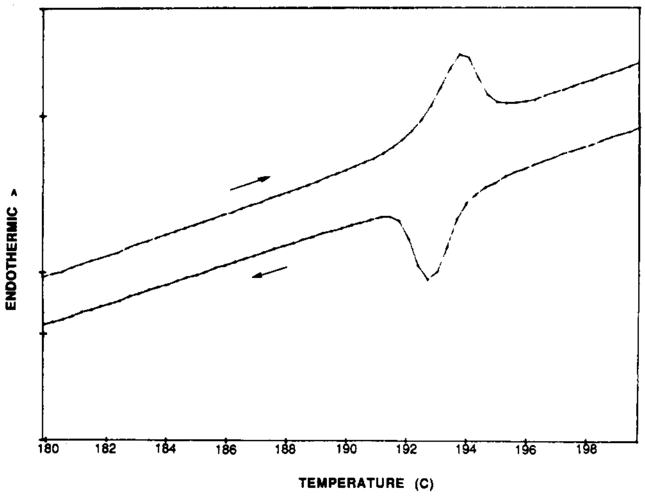

Figure 3. DSC of Hg_xTiS_2 showing the reversible thermal event near 193 °C. The event is endothermic on heating and exothermic on cooling. The absolute value of the associated enthalpy is 0.49 ± 0.02 kcal/mol of Hg and is independent of x for $0.27 \le x \le 1.29$.

will be published in the near future.

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Boron Nitride Fibers Processed from Poly(borazinylamine) Solutions

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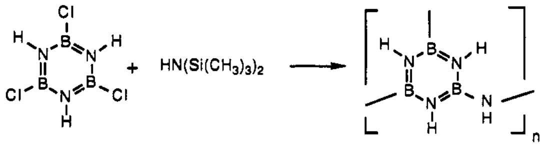
During the past 25 years, carbon fibers and filaments obtained from organic polymer solutions and melts have been intensively studied[1] due to their technological importance that is derived largely from the very high strength-to-weight properties found in carbon fiber/resin composites. Boron nitride, with a graphite-like structure, should be amenable to similar fiber and composite production with appropriate precursors. Indeed, the increasing utility of the polymer precursor approach to fiber research is illustrated by the development of other nonoxide fiber materials such as SiC,[2a–e] Si_3N_4,[2c–g] and AlN.[3] Further, the resistance of boron nitride to oxidation at high temperatures[4] and its dielectric properties offer foreseeable advantages over carbon fibers in certain applications. Despite their potential benefits, BN fibers are comparatively less studied than their carbon counterpart, and this is a direct consequence of a shortage of appropriate processible sources. However, recent progress in the development of boron nitride precursors including those obtained from decaborane cross-linked by amines,[5] nitrided poly-B_2O_3 melt-drawn filaments,[6] soluble borazinyl oligomers,[7] and poly(borazylene)[8] now permits more fruitful studies of BN fibers.

An amino-bridged borazine polymer developed in our group and illustrated in eq 1 is a useful precursor to BN



(1)

ceramics.[9] It is soluble in liquid ammonia, and the concentrated solutions have favorable rheological properties for fiber production. Since the preceramic polymer is moisture sensitive, all manipulations of materials prior to pyrolysis were conducted under a dry atmosphere of N_2. The white gel polymer[9] was isolated by vacuum evaporation of volatiles and then transferred to a simple fiber-pulling jig. The jig consisted of a solution reservoir into which a glass rod with six drawing tips was lowered and raised on a pulley to draw fibers. A 30 wt % solution of the polymer in $NH_3(l)$ was obtained by condensation of anhydrous ammonia into the jig reservoir containing the polymer. The polymer/NH_3 solution was rapidly stirred at −78 °C, and the NH_3 was subsequently evaporated to

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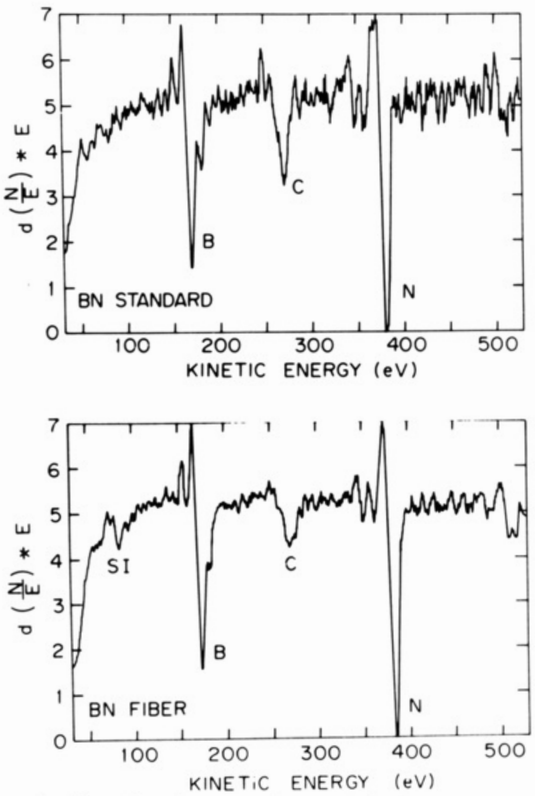

Figure 1. Scanning Auger analyses of (top) commercial BN powder and (bottom) BN fiber pyrolyzed at 1650 °C.

a point where the viscosity of the solution was sufficient to draw fibers. Stirring was discontinued during fiber pulling. The green fibers were harvested in a drybox, transferred to a quartz tube, and pyrolyzed at 1200 °C for 12 h under flowing anhydrous ammonia. The resulting fibers were pliable and amorphous to X-rays. They were subsequently transferred to an alumina tube and pyrolyzed under UHP argon at 1650 °C for 8 h, and fragile white fibers 5–50 μm in diameter were obtained.

Scanning Auger microscopy (SAM) was used to examine the chemical composition of the fibers. The analysis was performed at 2 keV at a high tilt angle, and the ion gun was used to provide the sample with positive ions. These conditions were helpful in preventing charging of the sample that typically occurs when analyzing an insulating material. The AES spectra illustrated in Figure 1 show that the fibers heated at 1650 °C have similar peak height ratios for boron and nitrogen as a commercial sample of BN powder (Ventron). The fibers contain small amounts of carbon and silicon on the surface, but this was removed by brief ion sputtering prior to the Auger analysis. Auger maps of B and N also indicate that the surface of the fibers is homogeneous.

X-ray powder diffraction analysis of the fibers processed at 1650 °C indicates that the fibers are crystalline BN [$d(002) = 3.37$ Å]. The average crystallite size (L_c), calculated by the Scherrer formula[10] on the (002) reflection, is on the order of 12 nm. This value resembles that for carbon fibers obtained at similar pyrolysis temperatures.[11] The IR spectrum shows absorbances at 790 and 1380 cm^{-1} that are characteristic of BN.[12] A very weak vibration centered at 3400 cm^{-1} is indicative of residual NH groups remaining in the BN structure.[12]

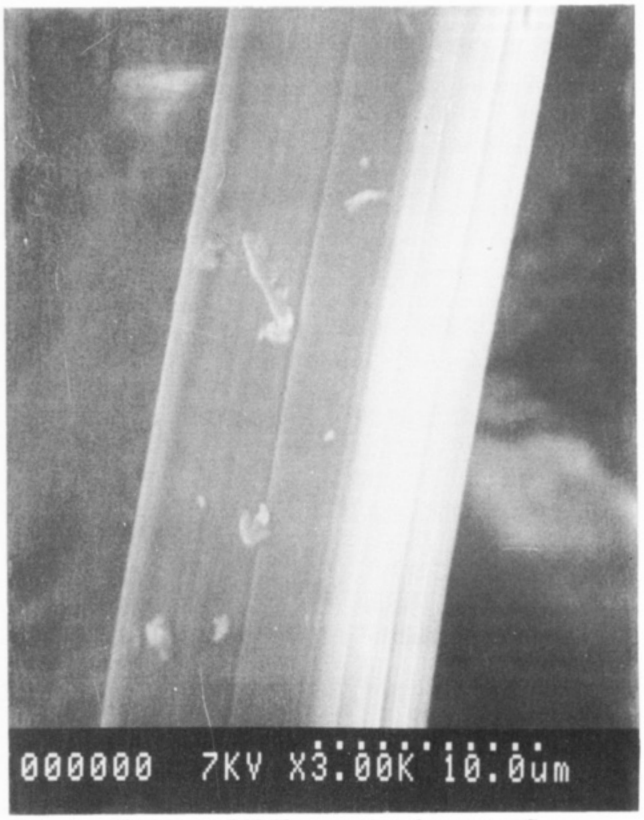

Figure 2. SEM of a BN fiber pyrolyzed at 1650 °C.

Figure 3. SEM of a fiber end showing cross-sectional detail.

A sample suitable for SEM analysis was prepared by embedding fibers in an epoxy resin plug which was then ground with carborundum grit to expose fibers at the surface. The surface was polished on a napped wheel with 1-μm Al_2O_3 grit suspension. A few drops of DMSO/HNO_3 solution were placed on the plug overnight to etch the surface and further expose the fiber surfaces.[13] The plug

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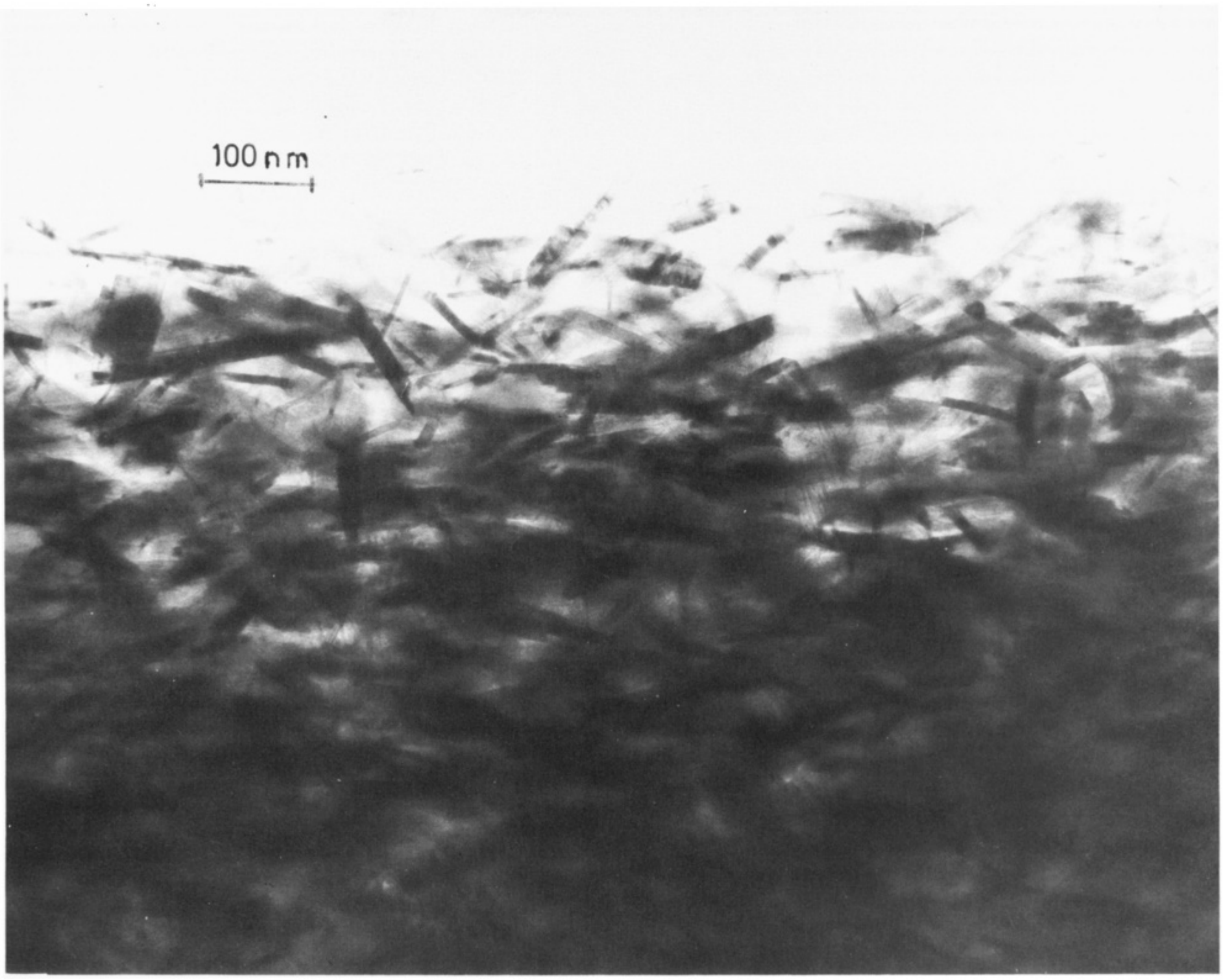

Figure 4. TEM of a BN fiber edge showing detail of partially ordered crystallites.

was then rinsed clean with water and acetone. A typical fiber surface illustrating external striations that run parallel to the fiber axis is shown by the SEM view in Figure 2. The shaded area on the left side of the fiber indicates formation of a "PAC-man" defect,[14] wherein a green fiber, with an initially circular cross section, partially collapses during the loss of volatile material. A cross-sectional view of a larger fiber is shown in Figure 3. Small pores are evident on the cross sectional surface of the fiber, and these may originate in the drawing stage from trapped ammonia bubbles or from gas bubbles produced during green fiber pyrolysis.

The morphology of the fibers was further examined by transmission electron microscopy analysis (Figure 4)[15] and found to be similar to the morphology of high modulus graphite fibers. The electron diffraction pattern originating from the center of the fiber fragment is a diffuse ring, whereas the diffraction from the fiber axis edge shows some preferred orientation. Thus, the ordering of cyrstallites along the fiber axis appears to be higher on the fiber skin than that of the interior. The preferred orientation of the surface crystallites, which in carbon fibers increases with increasing temperature, may be estimated from the (002) reflection of a diffracted X-ray beam from a single fiber edge.[16] The mean misorientation angle using the fwhm of the (002) reflection, arising from a single fiber edge, was determined to be 24°, which is comparable to the values obtained for carbon fibers heated to the same temperature.[11]

These preliminary results show clearly that oriented fibers of crystalline BN with microstructures similar to graphite fibers may be obtained from processing poly(borazinylamine) solutions. The solutions should be amenable to die extrusion fiber spinning. The microstructural similarities with carbon filaments suggest that processing conditions of **1** could be varied to provide BN fibers with mechanical properties comparable to the various types of carbon fibers. Although the use of ammonia as a solvent may appear to introduce complications, the polymer NH_3 syrup is in fact easily handled. Conditions that slow the drying rate of the fibers during the drawing stage should minimize fiber flaws and improve the mechanical properties of the fibers.

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