

Occurrence of Liquid Crystallinity in a Borazine Polymer

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Received September 8, 1993. Revised Manuscript Received January 10, 1994[©]

The first all inorganic mesophase has been prepared by low-temperature processing of a borazine oligomer. Presumably the potential for planar alignment of the aromatic-like molecules can occur leading to the formation of a liquid-crystalline phase. Optical microscopy and XRD clearly show the development of mesophase textures as well as a reversible phase transition between the anisotropic and isotropic phases. Transmission electron microscopy of the solid obtained from further heating, while still in the liquid-crystalline phase, reveals the presence of a polycrystalline microstructure with long-range preferred orientation.

Introduction

Very recently we reported the first successful preparation of a carbon fiber/BN matrix composite using a low-viscosity oligomer of borazine as a precursor to the BN.¹ In one set of experiments using a pitch based carbon fiber it was observed that heating the composite from 1200 to 1500 °C led to a significant increase in mechanical properties. The improved mechanicals observed after heating to 1500 °C suggested that the mismatch in coefficient of thermal expansion (CTE) might not be as great as one would predict based on a highly anisotropic carbon fiber embedded in an isotropic BN matrix. This led us to conjecture that some orientation of the matrix might occur at the interface to the fiber to reduce local stress associated with a mismatch in CTE. The possibility also existed that we might be forming a mesophase in the borazine oligomer similar to that observed in specially treated pitches.² Other evidence pointing in this direction was the fact that the BN prepared from borazine produced a highly graphitic structure (with an interlayer spacing of 3.34 Å) on heating at a temperature of 1500 °C for 2 h. From some of our earlier work it would be expected that in the absence of B₂O₃ one would have to heat BN to 2500 °C to observe an interlayer spacing below 3.4 Å.³ In this paper, we provide conclusive evidence that borazine does form a liquid-crystalline phase during polymerization. To our knowledge this may represent the first completely inorganic liquid-crystalline polymer.

Experimental Section

The borazine oligomer was synthesized as described in the literature.⁴ In a typical reaction, 10 g of borazine was heated in a nitrogen atmosphere at 70 °C in a 3-oz pressure reaction vessel. After 20–25 h, the oligomer attained a viscosity of ~100 cP

measured at 25 °C. The reaction was continued for 35–45 h until the viscosity of borazine became 500–2500 cP. With slightly longer reaction time, viscosities rapidly increased leading to solidification. The polymer was placed in a refrigerator at 0–5 °C for periods of 1 week to a month. To examine thin-film specimens by SEM, the borazine was also polymerized in a thin-walled gold capsule by heating to 700 °C at a rate of 5 °C/min. The sample was cold-sealed under nitrogen.

A Waters 510 gel permeation chromatography (GPC) from Millipore Co. was used to determine the molecular weight distribution of borazine oligomer in anhydrous THF using an Ultrastayragel column with a 500-Å pore size. Differential scanning calorimetry (DSC) was carried out on a duPont thermal analysis system 2910 at a heating rate of 20 °C/min under N₂.

The optical textures were observed using a Leitz Laborlux 12 Pol S polarized light microscope equipped with Linkam THMS 600 heating stage which is controlled down to 0.1 °C by a TMS 90 temperature control system. The sample was placed between two cover slips on the hot stage which was purged by dry nitrogen. Photomicrographs were taken using a SLR 35-mm single-lens reflex camera system. A Carl Zeiss D-7082 optical microscope with auxiliary plates and MC 63 photomicrographic camera was also used for obtaining an interference contrast of the viscous mesophase samples.

The mass spectra were determined using VG 70-VSE mass spectrometer with HP 5890 gas chromatography (MS/GC), controlled by the VGOPUS data system running on a VAXstation 3100 computer. The vaporized borazine oligomer from a fused silica capillary column was ionized by a 70-eV beam of electrons. As the sample was heated to 450 °C, the mass range from 1 to 700 was scanned every 3 °C to provide a computer-generated bar plot.

The borazine mesophase was characterized using a Scintag X-ray diffraction (XRD) instrument with Cu K α radiation. The system has a horizontal tantalum heating mount controlled by an Anton Paar high-temperature attachment HTK 10. The sample chamber including the mounted sample was gently purged by dry nitrogen to remove moisture during measurement.

Internal fine structures and selected area diffraction (SAD) patterns of BN prepolymer samples were determined with the Philip CM 12 transmission electron microscope (TEM). Most of the TEM specimens were prepared by simply grinding the polymer consolidated at 0–5 °C under an inert-gas glovebox. Small granules were adhered to a carbon-coated substrate by dipping into either the powder or a dilute borazine mesophase solution in THF solvent followed by drying in vacuum. The solid borazine polymer was placed on a cold stage to minimize thermal decomposition by 120-kV electron beams (wavelength 0.0335 Å, camera constant 730). The surface morphology of samples formed in the gold tube pyrolysis was examined using a Hitachi S-800 scanning electron microscope (SEM). Prior to viewing, the

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• Abstract published in *Advance ACS Abstracts*, February 15, 1994.

(1) Kim, D.-P.; Economy, J. *Chem. Mater.*, in press.

(2) Honda, H. *Carbon* 1988, 26, 139. Marsh, H.; Walker, P. L. *Chemistry and Physics of Carbon*; Marcel Dekker: New York, 1979; Vol. 15, p 229. White, J. L. *Progress in Solid State Chemistry*; Pergamon: New York, 1975; Vol. 9, p 59. Gasparoux, H. *Mol. Cryst. Liq. Cryst.* 1981, 63, 231.

(3) Economy, J.; Anderson, R. N. *J. Polym. Sci. C* 1967, 19, 283.

(4) Fazen, P. J.; Beck, J. S.; Lynch, A. T.; Remsen, E. E.; Sneddon, L. G. *Chem. Mater.* 1990, 2, 96.

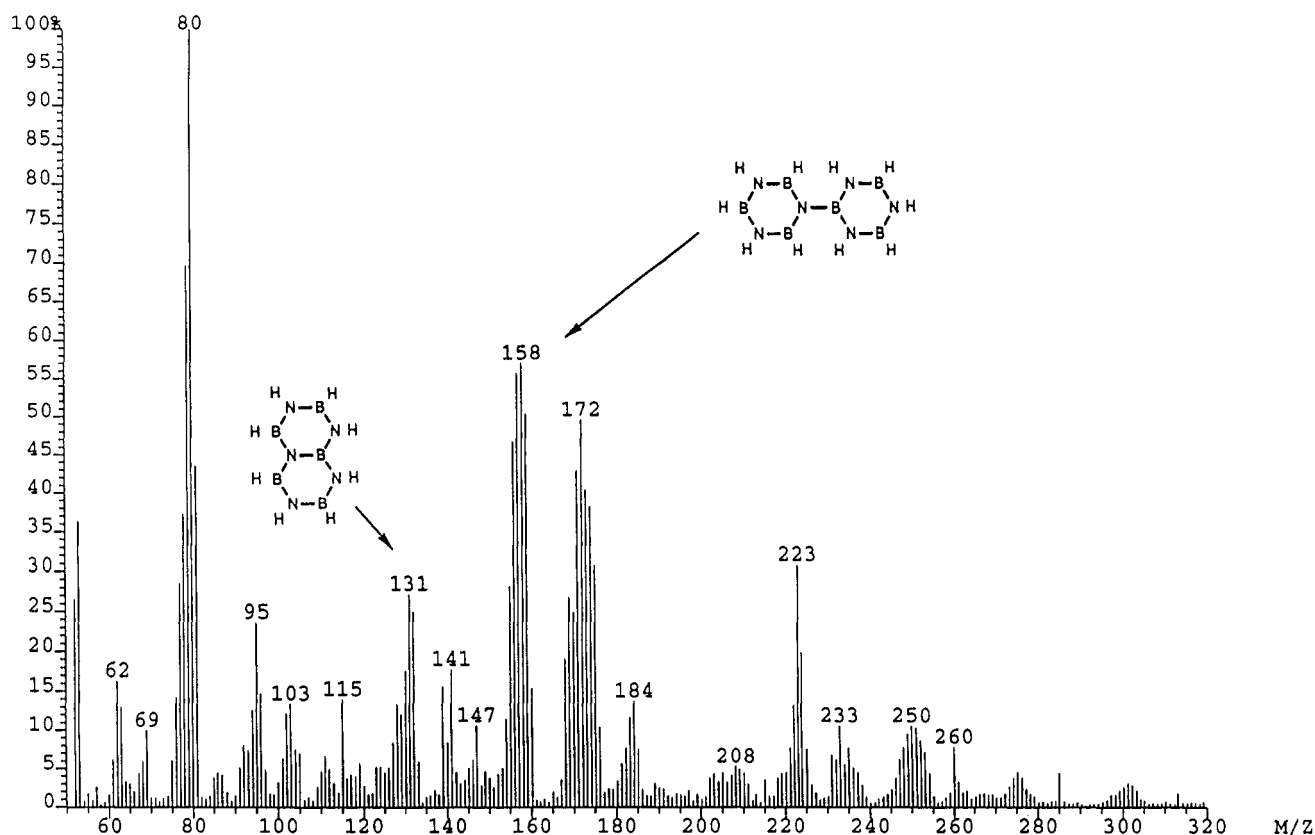


Figure 1. Mass spectrum of borazine polymer reacted at 70 °C for 40 h.

surfaces were covered with a thin gold-palladium layer in a Polaron sputtering chamber.

Results and Discussion

Background. It is generally accepted that molecular size and structure are the controlling factors in determining the formation of a mesophase from the aromatic components of pitch.² An important criterion is the formation of large, flat aromatic molecules capable of stacking to form a liquid-crystalline structure. Figure 1 shows a representative mass spectrum of borazine polymer prepared by heating at 70 °C for 40 h. The spectrum is consistent with earlier work showing that the major components in the polymer are biphenyl type (158 *m/e*) and naphthalenic type (131 *m/e*).⁵ Intensities of mass spectra cannot be directly related to concentrations in the original polymer sample because of the different vapor pressures of the molecular components and different efficiencies of ion production. In contrast, the pyrolysis of benzene at much higher temperatures forms only phenyl intermediates as opposed to borazine which also produces the naphthalenic unit at relatively low temperature.⁶

It is well-known that biphenyl and its homologues such as triphenyl benzene give nongraphitizable carbons while naphthalene or anthracene produce graphitizable carbons through formation of a mesophase.⁷ It is also reported that mixtures of the nongraphitizable biphenyl with at least 50% graphitizable naphthalene or anthracene show

anisotropic morphologies.^{7,8} Hence it appears that polymerization of borazine to oligomeric structures has the potential to create the necessary concentration of disk-shaped graphitizable units to permit mesophase formation as suggested in Figure 2.

Mesophase Formation. In carbon manufacture where a high degree of orientation is desired, it is particularly important for development of a mesophase, that a balance be achieved between the chemical rate of formation of suitably shaped molecules and the mobility or diffusional characteristics in the plastic phase.² In the case of the borazine polymer, which is best described as a thermosetting system,⁹ a slowdown in the initial rate of polymerization is necessary to maintain the necessary mobility to facilitate stacking of the incipient disk-shaped molecules. When polymerization is carried out with application of heat, a borazine mesophase is not observed. For example, even room-temperature polymerization for a few hours leads to a highly porous, nonmelting solid state. The porosity arises from hydrogen evolution which leads to foaming of the solid. On the other hand, processing at 5 °C for 2 weeks leads to mesophase formation, with no foaming.

In Figure 3 is shown hot-stage XRD data demonstrating liquid-crystalline order in the borazine polymer melt which was treated at 5 °C for 2 weeks. The borazine melt shows the (002) peak which is somewhat reversible after heating rapidly to 70 °C and cooling to room temperature. After heating to 100 °C, the peak becomes permanently broadened indicating further polymerization primarily of the isotropic state. The XRD data show conclusively that a

(5) Mamantov, G.; Margrave, J. L. *J. Inorg. Nucl. Chem.* **1961**, *20*, 348. Laubengayer, A. W.; Moews, P. C.; Porter, R. *J. Am. Chem. Soc.* **1961**, *83*, 1337.

(6) Fitzer, E.; Mueller, K.; Schaefer, W. *Chemistry and Physics of Carbon*; Marcel Dekker: New York, 1971; Vol. 7, p 237.

(7) Marsh, H.; Dachtler, F.; Melvin, J.; Walker, P. L. *Carbon* **1971**, *9*, 159. Marsh, H.; Foster, J.; Hermon, G.; Iley, M. *Fuel* **1973**, *52*, 234.

(8) Mochida, I.; Kudo, K.; Fukuda, N.; Takeshita, K.; Takahashi, R. *Carbon* **1975**, *13*, 135.

(9) Kim, D.-P.; Economy, J. *J. Am. Ceram. Soc.*, in press.

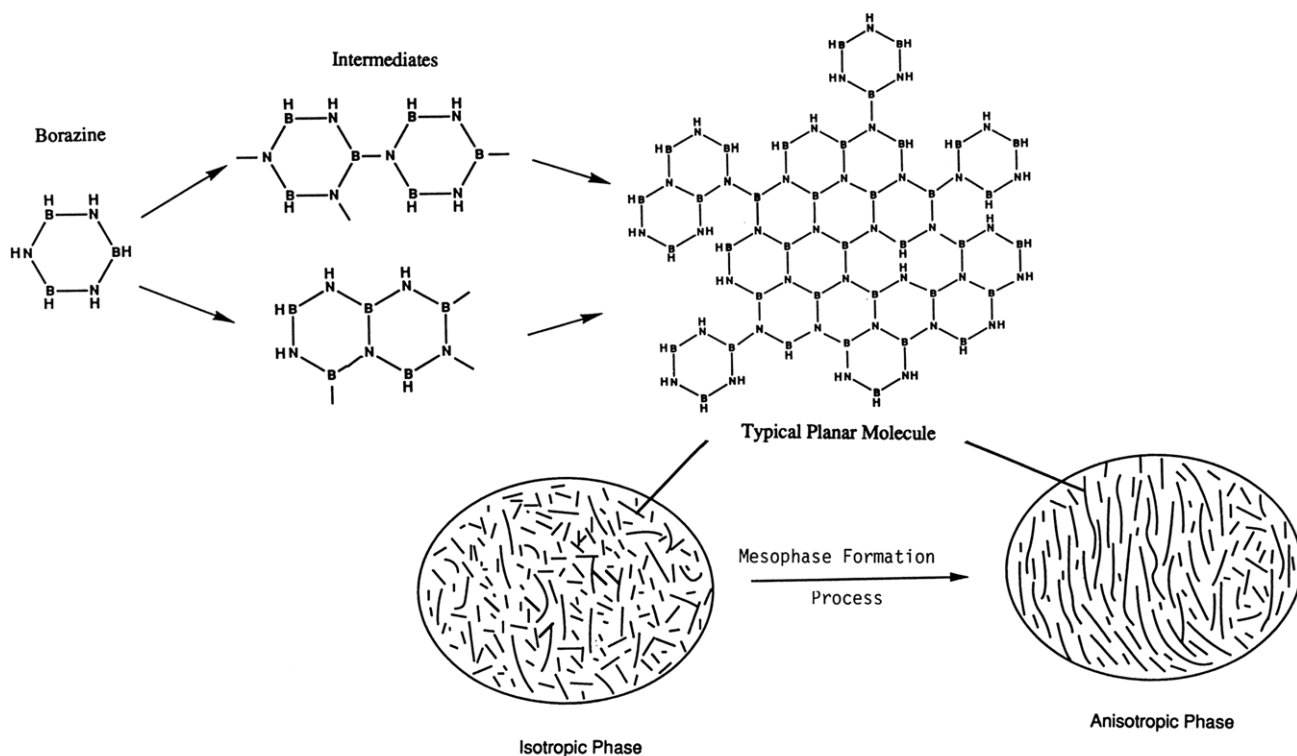


Figure 2. Schematic process for borazine mesophase formation.

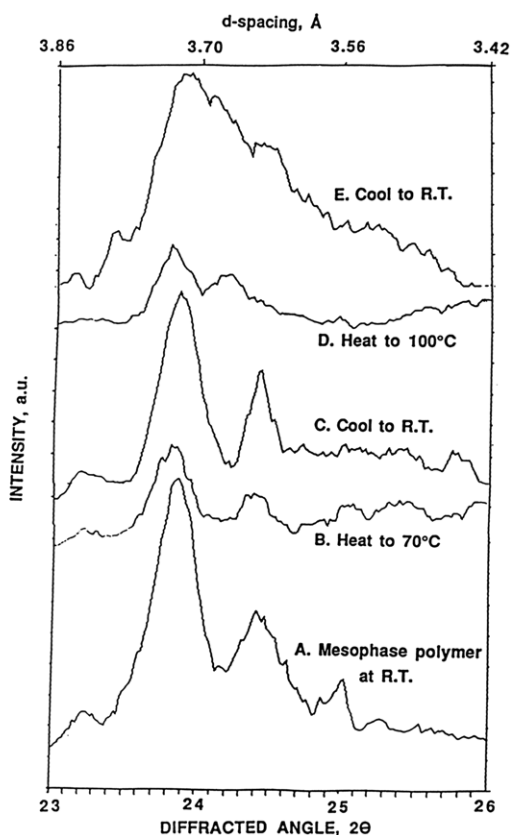


Figure 3. XRD of borazine mesophase on the hot-stage: (a) room temperature, (b) heat to 70 °C, (c) cool to room temperature, (d) heat to 100 °C, (e) cool to room temperature.

considerable degree of order (mesophase) is present in the polymer melt. It is noteworthy that after 1 week of processing at 5 °C the presence of a mesophase was barely detectable by optical microscopy. It appears that, during the low-temperature process, the constituent compounds

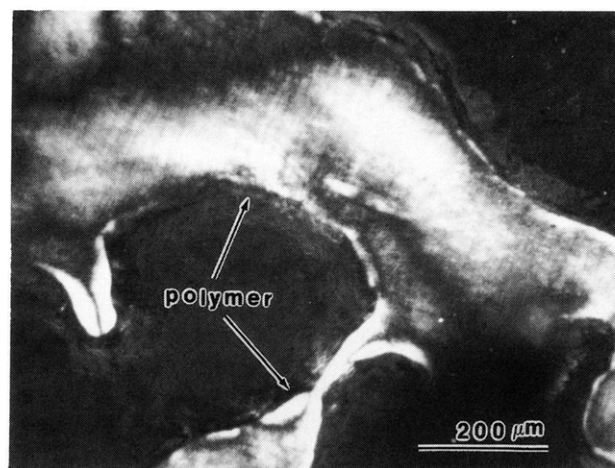


Figure 4. Striplike anisotropic texture of the early stage of borazine mesophase.

can slowly assemble to produce lamellar shapes which presumably have the necessary aspect ratio to induce phase separation into a liquid-crystalline structure.

Optical Anisotropy. After the low-temperature treatment at temperatures between 0 and 5 °C for 1 week, the isotropic borazine polymer began to transform to an optically anisotropic phase (Figure 4). This incipient anisotropy could be detected as anisotropic patches with a striplike texture which is more predominant when the polymer is placed under a low shear stress between glass slips.

Data as to the degree of polymerization at the point of phase separation (after 2 weeks) of the mesophase can be obtained through a comparison of the molecular weight distributions determined by GPC. In Figure 5 two curves for an isotropic phase and a mesophase-containing polymer indicate that both phases contain varying concentrations of species with almost the same molecular weight. But the mesophase appears to have a higher concentration of

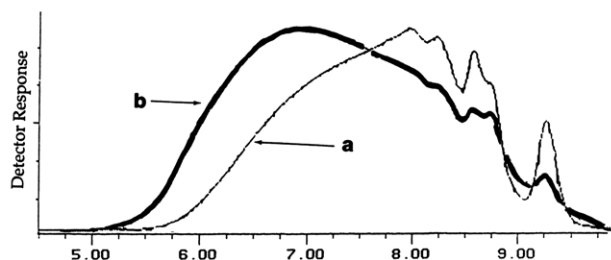


Figure 5. Molecular weight distributions for (a) an isotropic phase, (b) a mesophase-containing borazine polymer.

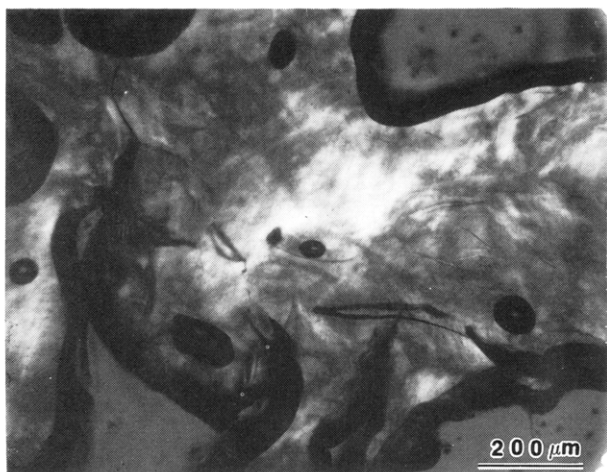


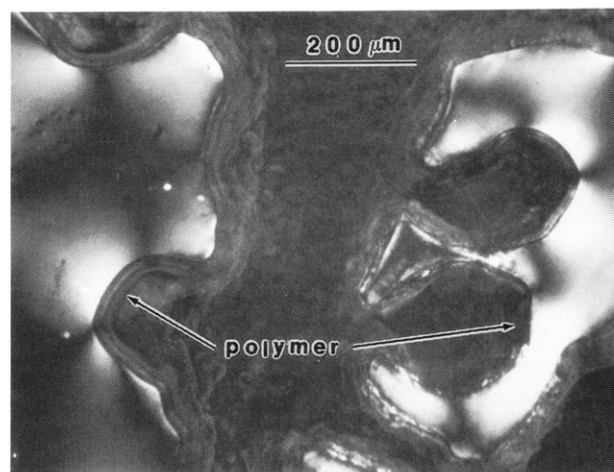
Figure 6. Optical anisotropy of borazine mesophase, treated at 0–5 °C for 2 weeks.

large molecules. On the basis of molecular weight data from other workers,⁴ it appears that the molecular weight distribution of the borazine mesophase is comparable to that of a carbonaceous mesophase which is in the range 400–3000.²

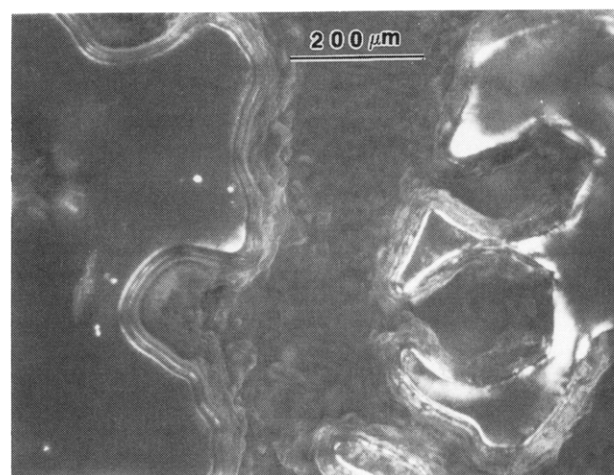
In Figure 6 is shown the texture of the borazine polymer treated after 2 weeks at 5 °C as viewed through cross-polarizers. Much larger anisotropic patches can be detected with layers lying either parallel or perpendicular to the plane of polarization of the incident light. The specific orientation of particular regions in the patches was distinguished by use of a sensitive-tint plate. The isochromatic areas of the anisotropic domains changed to blue, yellow, or magenta indicating molecular orientations with different optical axial directions. Interestingly the migration of bubbles trapped in the polymer melt resulted in extended orientation parallel to bubble flow.

When the above samples were heated rapidly up to 100 °C followed by fast cooling (at a rate of 50 or 100 °C/min), it was found that the specimens displayed Schlieren textures, with cross and node defects as observed in conventional nematic liquid crystals (Figure 7). When the specimen was rotated, the extinction contours were observed to sweep over the surface.

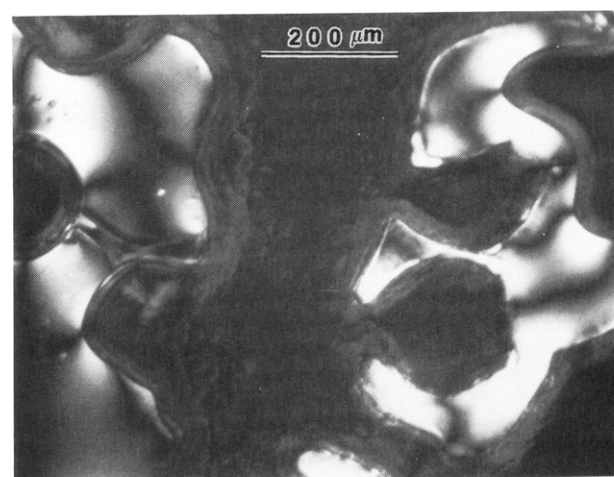
When the mesophase is heated at 100 °C, the anisotropy begins to convert to the isotropic phase and this is accompanied by foaming (see Figure 7b). The reversibility of this transition is influenced by the tendency of the oligomers to continue to polymerize. On cooling to room temperature, under conditions where the XRD pattern of the mesophase is recovered, we observe from optical microscopy a somewhat stronger birefringence (Figure 7c). On heating at or above 100 °C for several minutes, the



a



b



c

Figure 7. Optical texture of borazine mesophase, (a) Schlieren texture, at room temperature, (b) heated to 100 °C, (c) cooled to room temperature.

ordered phase can no longer be recovered on cooling because of increased cross-linking. Pitch mesophases also display an irreversible consolidation on longer heating at somewhat higher temperatures.

Neither borazine nor the carbonaceous mesophase show phase transitions in DSC measurements.² The enthalpy for conversion of a nematic phase to an isotropic phase may be too small to be detected or possibly the transitions are smeared over a broad temperature range.

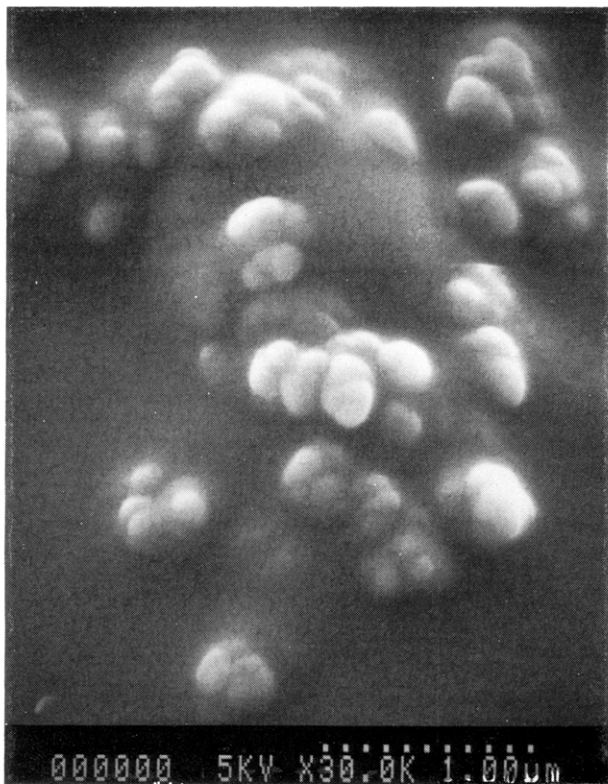
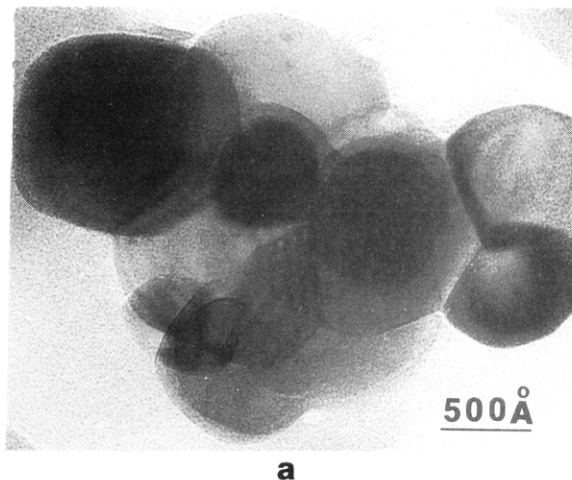


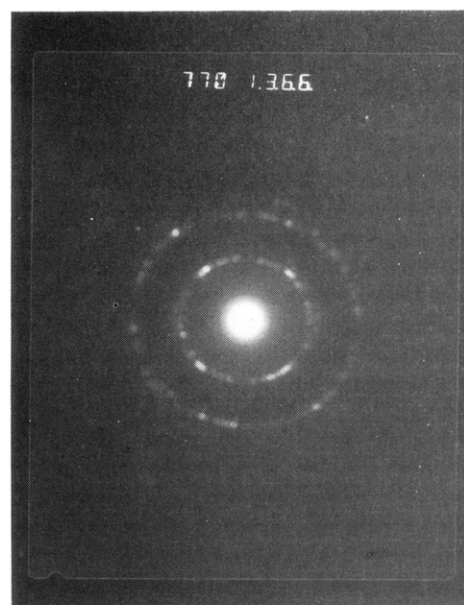
Figure 8. High-resolution SEM for BN spheres produced in a sealed gold tube.

At high pressures the nematic to isotropic transition shifts to a higher temperature and the range of the nematic phase is broadened to a higher viscosity permitting formation of a spherical morphology.¹⁰ In the borazine polymer, the formation of mesophase spherules was also observed in the polymerization in the sealed gold tube at 700 °C. However, only small microphases ($\sim 0.3 \mu\text{m}$) were observed on the inner surface of the tube (see Figure 8). In a separate study, a Japanese researcher also observed the BN spheres ($2\text{--}3 \mu\text{m}$) formed by the direct pyrolysis of borazine under various pressures and temperatures.¹¹

TEM Microstructure. In general the microstructure of liquid crystals in the direction of the local preferred orientation varies continuously in space with occasional discontinuities.¹⁰ In Figure 9a is shown the polydomain structure of borazine mesophase with moiré fringes, prepared from a dilute solution in THF. The polycrystallinity is clearly evident from the presence of grain boundaries with relatively large domain size. In Figure 9b is shown a SAD pattern from a sample ($\sim 1\text{-}\mu\text{m}$ granule powder) which has solidified after being kept at 5 °C for more than 1 month. The diffuse 002 reflections indicate stacking of a few layers, while the slight occurrence of high-order 00l reflections indicate some parallelism of the BN layers. The elliptical shape of SAD pattern in Figure 9 is close to an oblique pattern indicating that the BN layers are roughly parallel to each other.¹² Some amorphous regions were observed presumably due to thermal



a



b

Figure 9. Polycrystalline TEM of consolidated borazine mesophase, (a) image for polydomain microstructure, (b) SAD pattern.

decomposition by the electron beam. When this ordered structure is annealed at 300 °C, the SAD lines sharpen due to the growth of lattice diameter and thickness of the stacks, although the pattern corresponds to a turbostratic structure (Figure 10a). There is a preferred orientation inside in which a majority of layers maintain the same orientation over large regions although the fragile long-range order is disrupted by grinding during TEM sample preparation (Figure 10b). Inside the oriented zone, a wrinkled layer can be detected with a characteristic zigzag structure as represented in a schematic model of carbon.¹³

On further heating to 1800 °C, one observes a high degree of crystalline order. The continuous increase in crystallite size along the *a* and *c* axes can be attributed to improvements in parallel stacking of the lamellar structure toward the ideal BN structure as demonstrated by the single crystalline SAD patterns and the lattice fringes (Figure 11). Clearly the early presence of a mesophase facilitates formation of this highly ordered BN at relatively low temperatures.

(10) Jackson, C. L.; Shaw, M. T. *Inter. Mater. Rev.* 1991, 36, 165.; Whang, P. W.; Dachille, F.; Walker, P. L. *High Temp. High Press* 1974, 6, 137.

(11) Hirano, S.; Yogo, T.; Asada, S.; Naka, S. *J. Am. Ceram. Soc.* 1989, 72, 66.

(12) Oberlin, A. *Chemistry and Physics of Carbon*; Marcel Dekker: New York, 1989; Vol. 22, p 1. Oberlin, A. *Carbon* 1984, 22, 251. Oberlin, A.; Endo, M.; Koyama, T. *J. Cryst. Growth* 1976, 32, 335.

(13) Oberlin, A.; Villey, M.; Combaz, A. *Carbon* 1980, 18, 347.

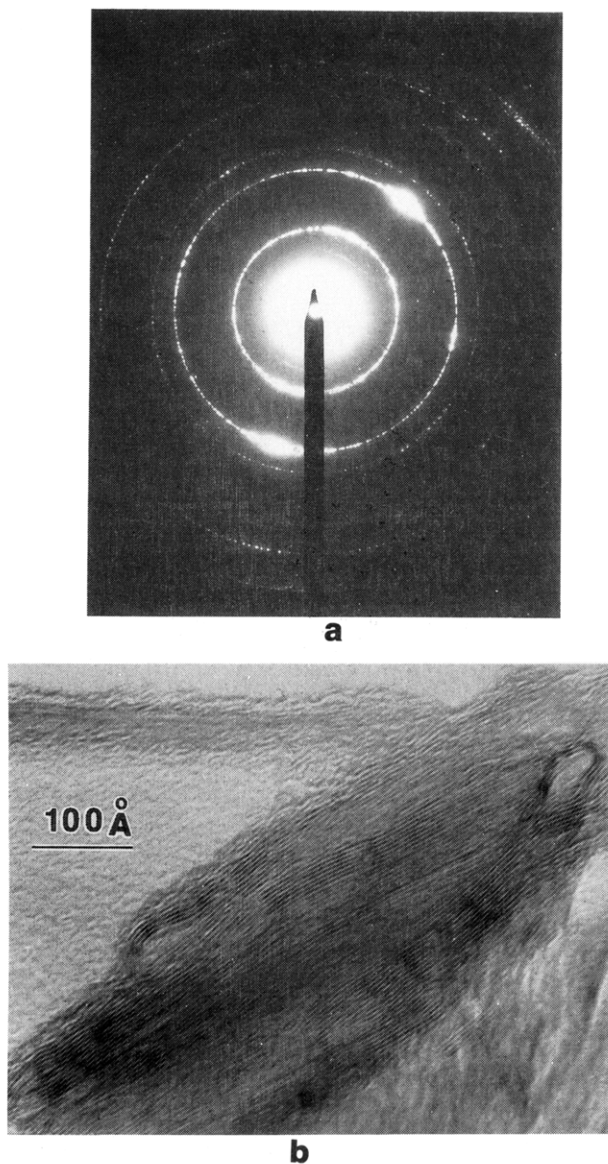


Figure 10. Turbostratic TEM microphotographs of borazine mesophase annealed at 300 °C, (a) SAD pattern, (b) lattice image.

Conclusion

It has been shown that the borazine oligomer when kept at 5 °C for 2 weeks forms a mesophase similar to that derived from pitch. It seems reasonable to propose that the naphthalenic intermediates formed during reaction of borazine lead to large planar aromatic-like molecules, which is a necessary condition for mesophase formation. All the analytical techniques used in this study indicate that we have prepared a mesophase of borazine oligomer. This may be the first example of an all inorganic

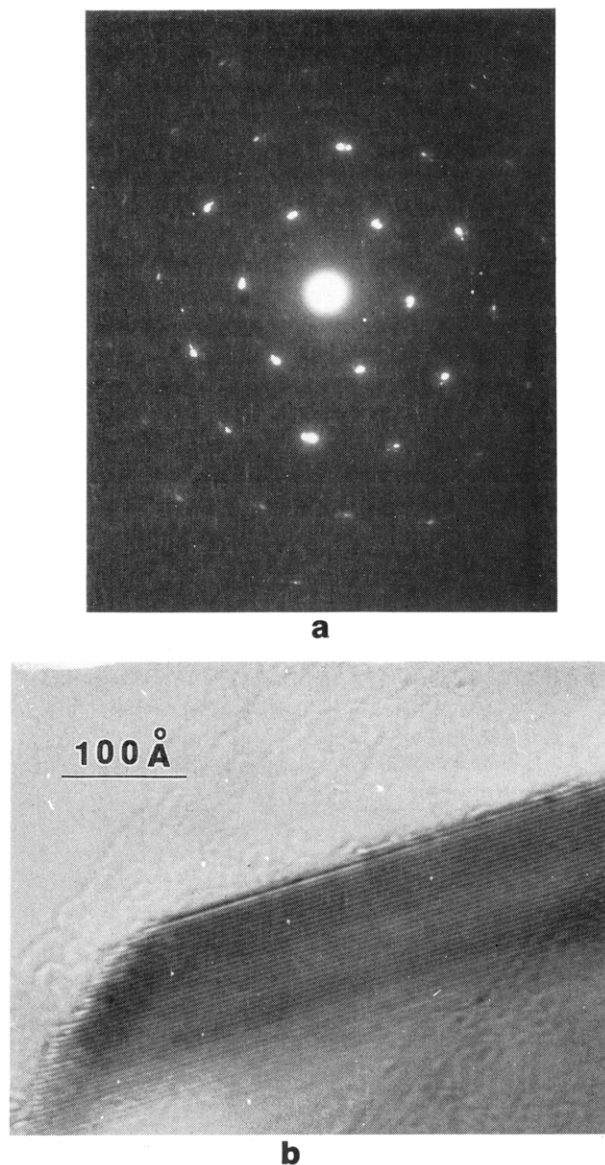


Figure 11. Occurrence of single-crystal BN inside a turbostratic matrix on annealing at 1800 °C, (a) SAD pattern, (b) lattice fringe.

mesophase. The formation of such liquid-crystalline phase helps to explain the excellent mechanical properties of the C/BN composites heated to 1500 °C.

Acknowledgment. The authors gratefully acknowledge the contributions of Mr. R. Milberg of Mass Spectrometry Laboratory and Ms. P. Mochel of the Center for Microanalysis of Materials in University of Illinois at Urbana for their practical assistance to access MC/GC and TEM instruments. This study was carried out with financial support provided by ARPA/ONR.