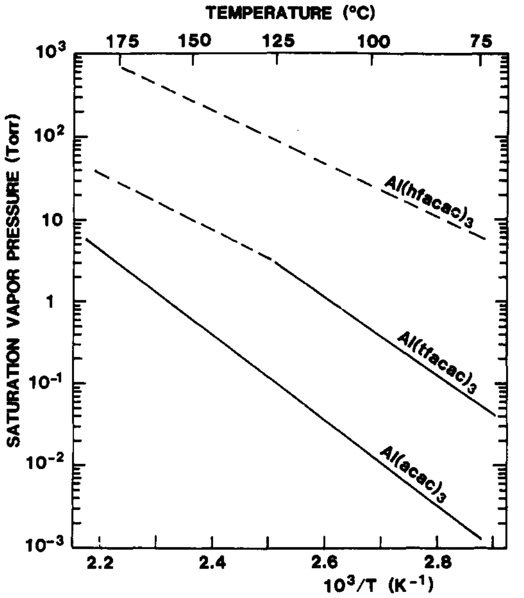

Figure 8. Saturation vapor pressure versus temperature from data given in ref 13 for sublimation (solid line) and evaporation (dashed line) of aluminum(III) β-diketone chelates.

The yields of vaporization corresponding to the sublimation of $Al(acac)_3$ in hydrogen, sublimation of $Al(tfacac)_3$ in argon, evaporation of $Al(hfacac)_3$ in hydrogen at temperatures from 75 to 175 °C, and also the sublimation of $Al(acac)_3$ (or more precisely $Al_2(acac)_6$) in argon between 150 and 175 °C are essentially equivalent. The lowest yields of vaporization are provided by the sublimation of $Al(acac)_3$, i.e., $Al_2(acac)_6$, in argon below 150 °C, and also by the evaporation of $Al(tfacac)_3$ in argon above 125 °C while the saturation vapor pressure of $Al(hfacac)_3$ is higher by a factor of 10 or 100 than that of $Al(tfacac)_3$ or $Al(hfacac)_3$, respectively (Figure 8). The data presented in Figures 7 and 8 can serve as a guideline for the selection of the more appropriate volatile precursor to be used in chemical vapor deposition of aluminum containing films.

Conclusion

The thermogravimetric study of vaporization of aluminum(III) β-diketone chelates such as $Al(C_5H_7O_2)_3$, $Al(C_5H_4F_3O_2)_3$, and $Al(C_5HF_6O_2)_3$ has demonstrated that the major factors affecting the kinetics of vaporization (in addition to the vaporization temperature) are the nature and pressure of the buffer gas as well as the cross-sectional area of the vaporization boat. The kinetics of the vaporization process was limited by the diffusion of these large complex molecules in the buffer gas from the boat to the cold wall of the thermogravimetric analyzer. The apparent activation energy of sublimation of aluminum(III) acetylacetonate was dependent on the nature of the buffer gas, suggesting that dimer $Al_2(acac)_6$ or monomer $Al(acac)_3$ molecules may be evolved by sublimation of the compound in argon or hydrogen, respectively. The values of the activation energy of these vaporization processes were in relatively good concordance with those of the standard enthalpy of sublimation or evaporation reported in the literature and determined by other techniques. The experimental data expressed in terms of number of aluminum atoms provided by vaporization of these metal complexes in combination with the data of saturation vapor pressure can help for the selection of the more appropriate precursor to be used in CVD of aluminum-containing films.

Registry No. $Al(C_5H_4F_3O_2)_3$, 14354-59-7; $Al(C_5HF_6O_2)_3$, 15306-18-0; $Al(C_5H_7O_2)_3$, 13963-57-0.

Mechanistic Studies of the Conversion of Borazine Polymers to Boron Nitride

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The thermal chemistry of thin films of a borazinylamine polymer deposited on KOH-etched aluminum and sapphire has been examined by thermal decomposition mass spectroscopy, thermogravimetric analysis, and Raman spectroscopy. The majority of the gas evolution chemistry is found to occur below 400 °C. All products desorb with the same temperature profile, and the major desorbing species are NH_3 and N_2 (polymer decomposition products) and HCl (side reaction products). The hydrogen remaining in the solid at 400 °C (≈50%) is continuously lost from 400 to 1200 °C. Facile ring-opening steps are evidenced by the complete isotope mixing that occurs for samples in which the ring nitrogens are labeled with ^{15}N. With increasing pyrolysis temperature, the Raman spectra change from that characteristic of the polymer (25 °C) to an intense featureless fluorescence spectrum (up to 400 °C), to an intense three-peak resonance Raman spectrum (≈400 to 1200 °C), and finally to a less intense Raman spectrum characteristic of h-BN superimposed on a fluorescence background at 1600 °C. The implications of these observations to the pyrolysis mechanism are discussed.

Introduction

Soluble or fusible inorganic polymers offer several benefits for the formation of ceramic materials, and they furnish reagents with which to probe the mechanistic aspects of ceramic formation. In addition, polymers provide access to ceramic forms such as fibers, foams, and some coatings not available from classical ceramic processing.[1-3]

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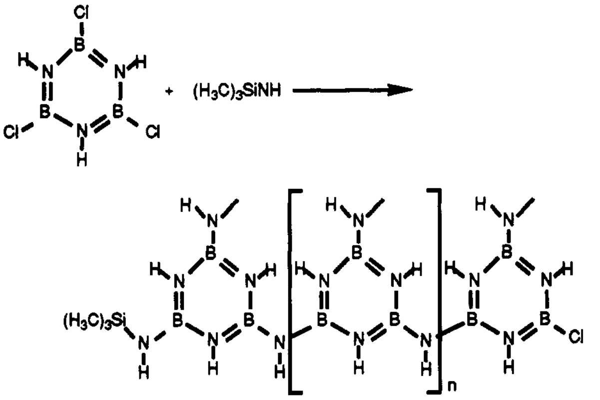
For example, several groups have recently reported preparations of polymers suitable for production of hexagonal boron nitride powders, fibers, coatings, composites, and aerogels,[4-26] and poly(borazinylamine) polymers,[4-6,16-25] prepared by cross-linking borazines, as schematically shown by one example in eq 1, are particularly useful.



(1)

Borazine Gel

Unfortunately, very little is known about the structures of the preceramic BN precursors or the mechanisms for polymer decomposition and conversion to solid-state product.

In the present report, thermal decomposition mass spectroscopy (TDMS), thermogravimetric analysis (TGA), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) are used to identify the major thermal decomposition products produced from pyrolysis of thin poly(borazinylamine) coatings and to explore the pyrolysis mechanism. A preliminary report on a portion of this work has appeared.[24] The TDMS and TGA results suggest that there are two important temperature regimes for the pyrolysis chemistry. At low temperatures (<400 °C), borazine ring-opening processes dominate along with loss of NH_3, N_2, and HCl. These *chemical processes apparently are not rate limiting in the thermal conversion of borazinylamine polymers to h-BN.* The limiting step is suggested to involve sterically hindered dehydrogenation of the remaining NH units and, as suggested by Raman spectra, diffusion-limited volume reduction. These processes lead to the growth of large delocalized fused ring fragments and eventually h-BN.

Experimental Section

Polymer Synthesis and Coating. The Al substrates (11 mm × 11 mm × 0.76 mm) were etched in hot KOH. XPS analysis of the Al substrates prior to polymer deposition showed them to be oxidized with O(1s) the dominant XPS peak. Sapphire substrates were used without cleaning prior to deposition. Two polymeric precursors were employed, and their preparations were accomplished as described in the literature.[18] Samples of the first were prepared by combination of trichloroborazine and hexamethyldisilazane (1:1.5 ratio) in diethyl ether at −78 °C. The solution was warmed to 20 °C and transferred under dry nitrogen to a flat-bottom 100-mL glass vessel containing the substrates to be coated. After 12 h, solvent, unreacted hexamethydisilazane, and reaction by-products were removed by vacuum evaporation. The coating substrates were removed from the vessel and placed in a transfer tube. These samples are referred to as deposited samples.[28]

A second set of samples was prepared by a similar reaction, except that the reaction solvent was tetrahydrofuran (THF). Evaporation of THF left a colorless granular solid that was redissolved in liquid NH_3 at −40 °C. The resulting polymer solution ($\approx$30 wt %) was used to dip coat substrates. These are referred to as dipped samples. The dipped and deposited samples gave basically the same results, and the results presented here will in general refer to the deposited samples; where differences exist these are noted.

Experimental Measurements. The ultrahigh-vacuum (UHV) system used for XPS and TDMS studies has been described previously[29] and will only be summarized here. It consists of an UHV system with a double-pass cylindrical-mirror analyzer (operated at 50-eV pass energy), a Mg/Al X-ray source for XPS, and a quadrupole mass spectrometer mounted in a separate snouted container for direct line-of-sight TDMS measurements. The quadrupole is computer controlled, allowing collection of complete mass spectra at near the maximum scan rate. Individual samples are mounted on a transportable sample plug-in assembly containing a heater and thermocouple. The samples are clamped against the surface of the heater block with the thermocouple spot welded to the block. As a result the temperatures reported here are those of the heater block; the actual polymer temperatures are expected to be somewhat lower due to heat transfer limitations. Typical heating rates were roughly 0.9 °C/s. All sample loading and transfer steps were done in an Ar-filled glovebag in order to minimize air exposure. Despite these precautions, XPS spectra always gave an appreciable O(1s) peak.

Thermogravimetric analyses were performed on a Perkin-Elmer Model 3700 analyzer: sample sizes 5–20 mg, heating rate, 10 °C min^{-1}, and argon flow rate 25 cm^3 min^{-1}. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Raman Spectra. Raman spectra were obtained by using a computer-controlled, scanning, double monochromator equipped with holographic gratings and a photon-counting photomultiplier tube. The monochromator was operated at 6-cm^{-1} resolution.

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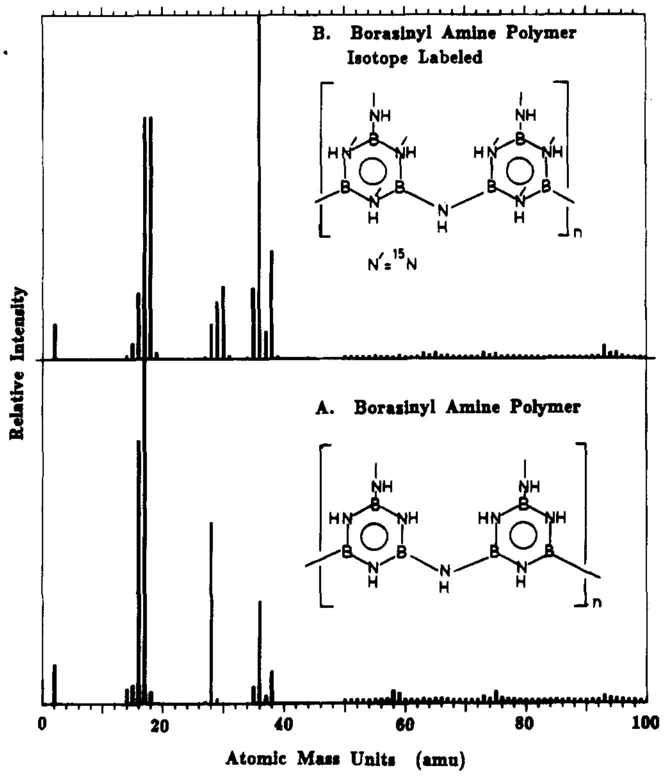

Figure 1. Mass spectra obtained at the maximum rate of release of decomposition products. Spectrum A: film obtained by direct synthetic reaction onto a Al substrate. Spectrum B: polymer similar to A but with borazine ring nitrogens labeled with ^{15}N.

Bulk poly(borazinylamine) polymer samples were illuminated with the 457.9-, 488.0-, 514.5-nm argon laser lines and with the 647.1-nm krypton laser line. Not all of these spectra are shown. Films of poly(borazinylamine) polymer on aluminum were illuminated primarily with the 514.5-nm argon laser line. For poly(borazinylamine) polymer films on sapphire, the 457.9-nm argon laser line was utilized, since excitation at this wavelength minimizes Al_2O_3:Cr fluorescence from the substrate.

Note that both fluorescence and Raman bands occur in the spectra. Fluorescence bands are generally broader than Raman bands and are fixed in wavelength irrespective of the excitation wavelength. Raman bands are the result of inelastic scattering processes between a photon and a phonon. For a given vibrational mode, the Raman band occurs at a fixed shift from the frequency of the excitation line. Raman spectra are plotted in terms of a Raman shift, which is the difference in frequency units (cm^{-1}) between the plotted wavelength and the wavelength of the laser line used for excitation. In terms of Raman shift, the positions of fluorescence bands vary with excitation wavelength. Because of the sensitivity of the polymer samples to moisture, all samples were contained in quartz tubes; all heating steps and spectral measurements were conducted in these tubes either under an Ar atmosphere or under vacuum.

Results

XPS spectra[27] for the as-deposited films show the presence of B, N, C, Cl, Si, and O and the complete absence of substrate peaks. The only major change that occurs on heating to ≈400 °C is the complete loss of the Cl peaks and a slight relative reduction of the Si peaks. With use of reported sensitivity factors[30] the N:B ratio is estimated to be 1:1 while the ratio expected from the initial polymer stoichiometry is 1.5:1. The Si, Cl, and C probably result from the trimethylsilyl chloride polymerization coproduct, although they may also arise from anticipated polymer chain termination groups.

Figure 1 contains representative mass spectra obtained at a temperature near where the maximum gaseous product release occurs. Spectrum A is for a deposited sample on Al, and spectrum B is the same except that the borazine ring nitrogens have been labeled with ^{15}N. Consider first spectrum A. The major products are in order as follows: NH_3, identified from the mass 16 to 17 ratio; N_2, identified from the isolated mass 28 peak; HCl, identified from the mass 36 to 38 ratio. Other possibilities for the fragment at 28 amu are CO or a BNH_x species such as aminoborane (H_2BNH_2), but the fragment at mass 12 is at least a factor of 2 too small for CO and the anticipated fragments around mass 28 are missing for species such as aminoborane.[31] The identification of the mass 28 peak as due to N_2 is further confirmed by the isotope-labeled mass spectrum in Figure 1B, where masses 28, 29, and 30 are observed. In addition to confirming the identification of the N_2 product, this distribution shows that borazine ring NH and bridging NH groups are both sources of N atoms in the N_2 product, consistent with isotopic exchange between the ring nitrogens and the bridging amine nitrogens. Similarly, both mass 17 and 18 are observed for NH_3. Unidentified, much less intense fragments are observed at higher mass. There is a slightly greater (20%) NH_3 release for the samples obtained by dipping the substrate in an ammonia solution of the polymer and nearly a factor of 4 decrease in HCl release. The polymer–liquid ammonia dissolution step may lead to trapping of solvent (NH_3) in the resulting solid film or to solvolysis of residual B–Cl bonds with production of terminal NH_2 end-capping groups on the polymers.[32] The byproduct of the solvolysis reaction is expected to be NH_4Cl, small amounts of which also may be retained in the dipped samples. The majority of NH_4Cl, however, would deposit on the larger surface area of the coating container as the liquid NH_3 solvent is evaporated.

The release rate of the pyrolysis products can be more clearly seen from the TDMS spectra of the individual mass fragments. By recording mass spectra and the sample temperature as a function of time, the intensity variation of a single mass species as a function of temperature can be extracted. For a polymer film directly deposited onto Al, Figure 2 contains the change in mass spectrometer ion signal for NH_3 (mass 17), N_2 (mass 28), and HCl (mass 36). In this case the product distribution is $NH_3 > N_2 \simeq HCl$, and all products are generated over the same temperature range (≈125–350 °C), with small variations in the relative amounts of the two peaks. All other products appear at much lower intensity levels. The results for the dipped samples are identical with those in Figure 2, but the product distribution is $NH_3 > N_2 > HCl$.[27] While the use of ion currents instead of calibrated partial pressures is a source of possible error, this is not expected to change the relative product distributions. From the information given by UTI, Inc., on ionization efficiencies and multiplier gain for the model 100C quadrupole mass analyzer, we estimate that the N_2 (mass 28) curve in Figure 2, relative to NH_3 (mass 17), should be decreased by a factor of $^1/_2$ and the HCl (mass 36) by a factor of $^1/_3$.

That complete exchange occurs between the ring and amine nitrogens is shown by the TDMS data given in Figure 3 for the three N_2 mass peaks in mass spectra such as in Figure 1B. There is some contribution from CO to the mass 28 spectrum as evidenced by the shoulder at ~90

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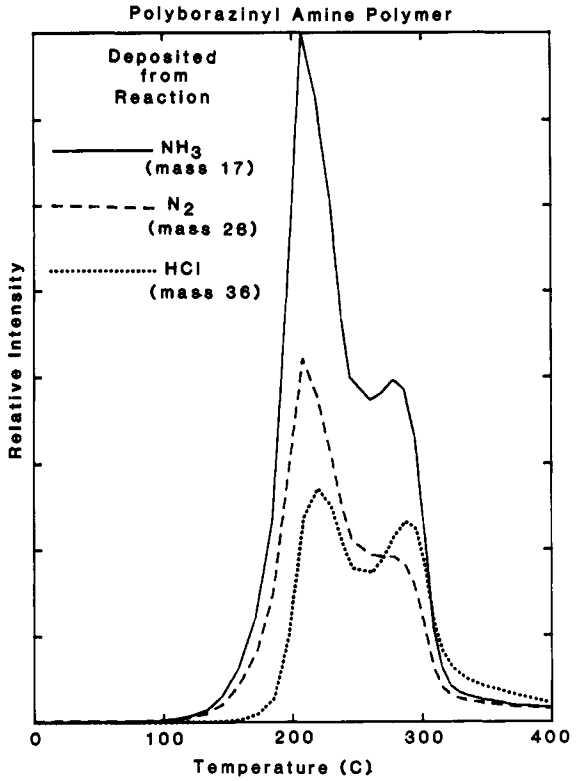

Figure 2. Thermal decomposition spectra for NH_3, N_2, and HCl obtained from mass spectral data as in Figure 1A.

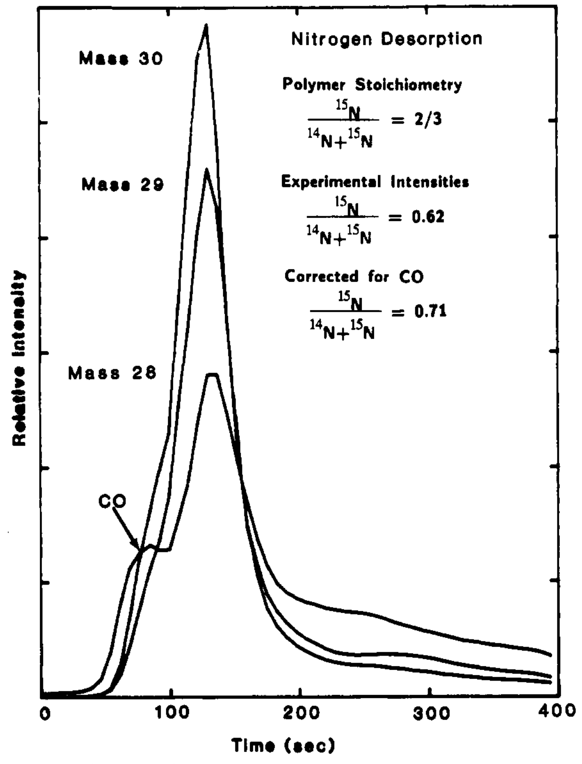

Figure 3. Thermal decomposition spectra for masses 28, 29, and 30 from mass spectral data as in Figure 1B.

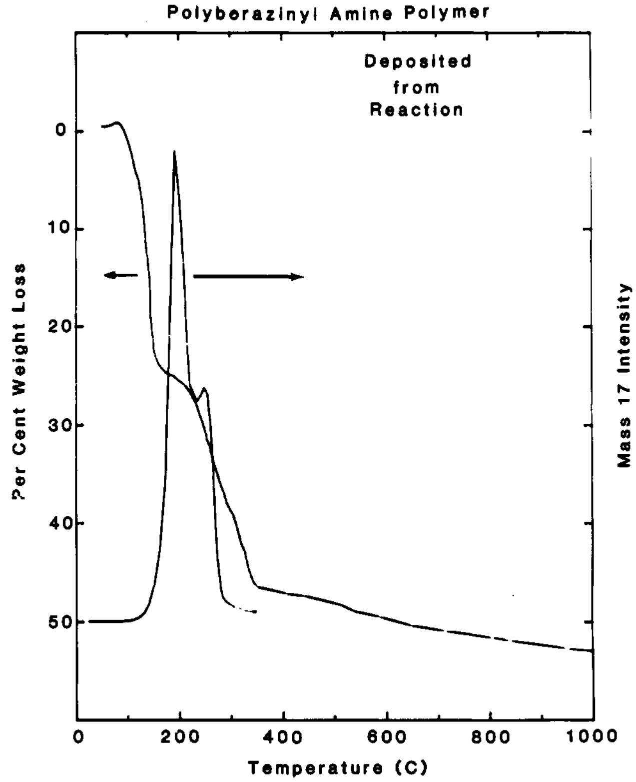

Figure 4. Ammonia thermal decomposition spectrum from Figure 2 directly compared to a thermal gravimetric analysis curve.

°C and the absence of this shoulder in the mass 29 or 30 spectra. Although the exact polymer stoichiometry and structure are unknown, it is assumed that the repeating unit is that shown in Figure 1. This structure and an assumption of complete mixing would lead to the prediction of a value of $^2/_3$ for the ratio $^{15}N/(^{14}N + ^{15}N)$. The experimental value based on the maximum intensities is 0.62, and if the mass 12 to mass 28 ratio for CO is used to remove the CO contribution to mass 28, the experimental ratio becomes 0.71. Despite the uncertainty in polymer structure it is clear that there is complete statistical scrambling in the nitrogen and NH_3 produced, and this requires that borazine ring-opening processes are prevalent in the low-temperature thermal chemistry. One might suspect catalytic reactions on the Al substrate as a potential source of the isotope mixing. However, while we know of no information about the interaction of borazine with Al, it is known that NH_3, the major product of pyrolysis of the polymer, interacts with Al and Al_2O_3 only by weak van der Waals interactions.[33]

That the loss of material below ~400 °C observed in the TDMS experiments represents the temperature regime where most of the volatile material is lost is further shown by a direct comparison of the TDMS data with weight loss (TGA) data. Figure 4 contains the mass 17 TDMS spectrum from Figure 2 directly compared to the TGA data for an as-deposited polymer sample. The data are comparable in that both show two sharply differentiated decomposition steps at relatively low temperature. Furthermore, the TGA data given in Figure 4 show that the majority of the weight loss occurs below 350 °C; nearly 90% of the total weight loss (52%) achieved by 1000 °C occurs in the low-temperature regime (<400 °C) while only 10% occurs in the high-temperature regime, 350–1000 °C. Similar results are obtained for NH_3-dipped samples. Thus, one can draw the same conclusions from both the TDMS and TGA data; gas evolution from pyrolysis of films directly deposited onto Al occurs mainly in two distinct steps in the low-temperature regime below approximately 400 °C.

Elemental analysis of deposited samples heated to 400 °C is in qualitative agreement with both the TDMS and TGA results. Samples are typically found to contain

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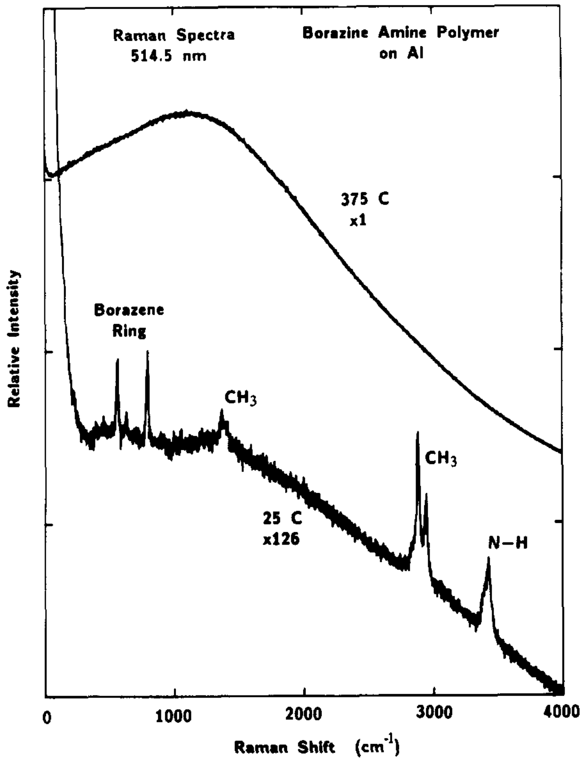

Figure 5. Raman spectra for borazinylamine polymer deposited onto Al. The lower curve is the polymer at room temperature, and the upper curve is the same polymer film after heating to 375 °C and immediately cooling to room temperature.

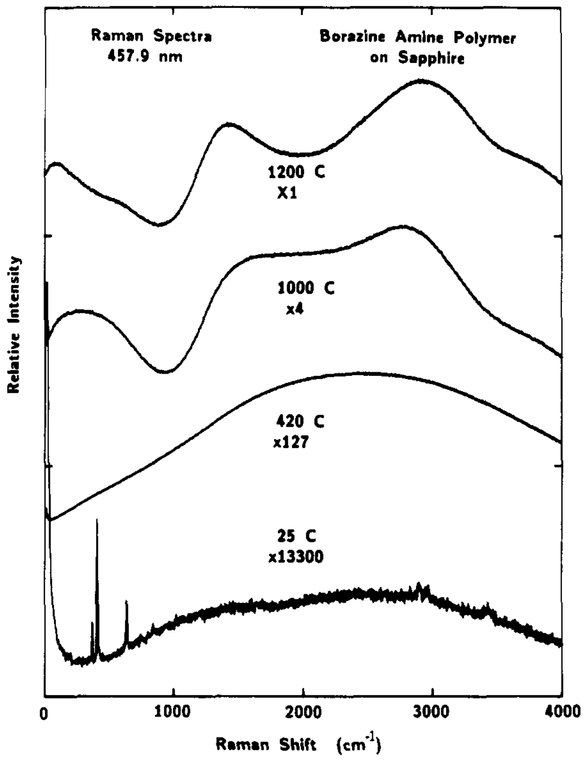

Figure 6. Raman spectra for borazinylamine polymer deposited onto sapphire. Each spectrum is obtained at room temperature after heating to the indicated temperature for approximately 20 min. Heating was conducted in a closed quartz container under Ar.

weight percents of 3.05% C, 2.79% H, 52.17% N, and 34.59% B. If the composition of the carbon bearing species is ignored for simplicity, the analytical composition corresponds to a hypothetical stoichiometry of $B_1N_{1.1}H_{0.85}$. If we assume that the starting material contained only the polymer with stoichiometry $B_1N_{1.5}H_{1.5}$, this would correspond to a total loss of $N_{0.4}H_{0.65}$ for heating to 400 °C. In contrast the maximum loss would be $N_{0.5}H_{1.5}$ if the polymer were converted completely to h-BN. While these assumptions are approximate, they are in qualitative agreement with the TGA results; the fraction of the maximum weight loss from the elemental analysis is 0.74, while the fraction of the total weight loss from the TGA experimental results that occurs by 400 °C is 0.9. Moreover, this analysis shows that ≈80 atom % of the maximum nitrogen loss has occurred by 400 °C, in contrast to only a 43 atom % loss of hydrogen, in qualitative agreement with the TDMS results, which identify NH_3 and N_2 as the decomposition products instead of just NH_3, the expected stoichiometric product if the polymer were converted completely to BN.

By pyrolysis temperatures of the order of 400 °C, the great majority of the chemical steps (material loss and ring-opening reactions) necessary for BN production have occurred, and the stoichiometry of the remaining material is approaching that of h-BN, but with excess hydrogen. The remaining hydrogen is slowly and continuously lost over an extremely large temperature range (400 °C to temperatures in excess of 1200 °C). However, crystalline h-BN is not produced until ≈1200–1600 °C.

The volatile product analysis approach, which depends on monitoring gas-phase products, however, is limited to sample/substrate temperatures below 400 °C by experimental constraints and by the absence of further significant gas evolution at higher temperatures. To probe the complete range of pyrolysis temperatures, we have obtained Raman spectra of the polymer and its solid pyrolysis products as a function of temperature. Figure 5 contains the Raman spectrum for the polymer as deposited from reaction on an etched Al substrate at room temperature. The assignments of the Raman bands are indicated in the figure. The borazine ring vibrations and the N–H vibrations are assigned to the borazinylamine polymer, but the CH_3 bands most likely result from reaction byproducts, e.g., $(CH_3)_3SiCl$, or from $(CH_3)_3SiNH$ end-capping groups. Heating briefly to only 375 °C leads to complete loss of these characteristic Raman bands and appearance of an intense fluorescence spectrum; note that the room-temperature spectrum in Figure 5 has been enhanced by a factor of 126 for direct comparison with the 375 °C spectrum.

Higher temperatures could not be achieved with the Al substrate; therefore, similar polymer films were deposited on sapphire substrates. The Raman analyses of these films, after heat treatments up to 1200 °C, are shown in Figure 6. Note that these spectra were recorded by using a different exciting Raman frequency than that employed to obtain the spectra shown in Figure 5. The same general trends are observed in Figures 5 and 6. Upon heating to 420 °C the characteristic room-temperature Raman spectrum is replaced by an intense fluorescence band; that this feature is due to fluorescence is suggested by the change in Raman shift of the peak intensity between Figures 5 and 6 with change in the laser excitation wavelength. Further heating leads to the development of broad features at ≈200, ≈1400, and ≈2900 cm^{-1}, which become more clearly developed with increasing temperature.

To ensure that these Raman results do not in some way reflect the thin-film nature of the samples, Raman spectra for samples of the bulk polymer as a function of temperature are presented in Figure 7. Small quantities of the polymer were placed in quartz tubes, heated under vacuum to the indicated temperatures, and then sealed off under

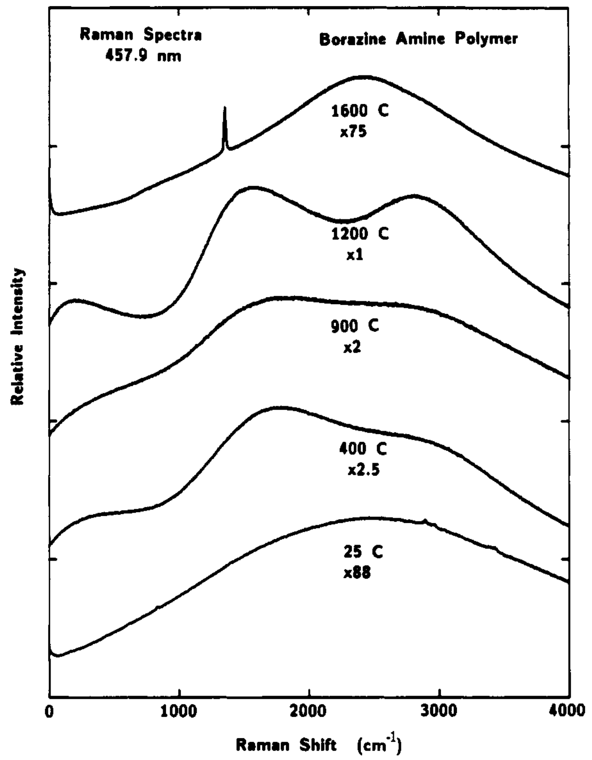

Figure 7. Raman spectra for solid borazinylamine polymer. Individual samples were heated under vacuum in a quartz tube for approximately 12 h at the indicated temperature. The quartz tubes were sealed under vacuum for the Raman measurements.

vacuum. These solid samples were heated at the indicated temperatures for up to 12 h while the thin-film samples were heated for approximately 20 min. As a result the spectral features are more fully developed in the bulk samples than in the thin films at equivalent temperatures. The spectra of the bulk polymer samples show the same general trend as the thim films. The spectrum of the bulk sample heated to 1200 °C shows the same three different distinct bands as are present in the spectrum of the polymer films heated to 1200 °C. By 1600 °C sufficient crystal growth has occurred to produce the sharp Raman line at 1365 cm^{-1} characteristic of h-BN superimposed on a broad feature due to fluorescence.[34] Raman spectra of samples of bulk pyrolytic BN are similar to the 1600 °C spectrum in that they contain both the sharp Raman feature at 1365 cm^{-1} and the broad fluorescence.[34]

The broad features in the spectra of the 25 and 375 °C polymer films on Al (Figure 5), the 25 and 420 °C polymer film on sapphire (Figure 6) and the 25 and 1600 °C bulk polymers (Figure 7) are characteristic of fluorescence processes since the Raman shifts of their peak positions are different for different laser excitation wavelengths. However, the broad feature near 1400 cm^{-1} in the 1200 °C spectra of Figure 6 and 7 appears to have its origin in Raman processes. A feature with similar peak position and bandwidth occurs in spectra of both the 1200 °C film and 1200 °C bulk polymer obtained with 458-, 488-, 514-, and 647-nm excitation. This evidence indicates that the feature is a Raman band. The proximity of this band ($\approx$1400 cm^{-1}) to the 1370-cm^{-1} Raman intralayer B–N stretching band characteristic of h-BN[35,36] suggests a structural similarity between the source of the $\approx$1400-cm^{-1} band of the pyrolysis product and h-BN. However, the large width of the $\approx$ 1400-cm^{-1} band is characteristic of an amorphous material. Thus, the material responsible for the 1400-cm^{-1} band appears to represent a noncrystalline precursor to h-BN. The intensity of the $\approx$1400-cm^{-1} band is orders of magnitude too high for a simple Raman process and implies that resonance enhancement is occurring. Resonance enhancement[37] may occur when the laser excitation wavelength is coincident or nearly coincident with an absorption band of a material and when there is coupling between the electronic and phonon states of the material. Through this coupling a Raman process may be enhanced by the absorption process. If the $\approx$1400-cm^{-1} feature is a Raman band, then the feature at 2900 cm^{-1} is its overtone, and the feature at $\approx$200 cm^{-1} is probably due to low-frequency Raman transitions. The same three-band pattern is present in the spectra of samples heated to temperatures between $\approx$400 and 1200 °C.

Discussion

It has been demonstrated previously that polymers such as represented in eq 1 form amphorous or microcrystalline boron nitride upon pyrolysis at 900 °C and crystalline h-BN at higher temperatures;[16-25] therefore, it is of interest to consider in more detail how the nitrogen- and hydrogen-rich poly(borazinylamine) might be converted to the final solid-state ceramic material.

As mentioned earlier, the exact structure of the room-temperature polymer, schematically illustrated in eq 1, is not known. However, previous studies in our group provide some information. Cryoscopic molecular weight measurements in benzene solution of the polymer prior to gelation indicate that the number of borazine rings in the structure is 8–12. The polymer is not very soluble in benzene, and it gels and precipitates as the polymer grows. Nonetheless, it may be proposed that the room-temperature polymer described in this study contains $\approx$12 or more borazine rings coupled through NH bridge units. It is also thought that this relatively low molecular weight polymer has a rather flat, two-dimensional structure perhaps with some "ruffling". This conclusion is based upon the observation that model compounds such as $[(Me)_3N_3B_3(Me)_2]_2NH$ display a trigonal planar (sp^2) geometry at the bridging N(H) group between the borazine rings.[38] Further, the exo B–N bond distance, 1.442 (5) Å, is identical with the average borazine rings distance, 1.438 Å. These features suggest that there is a degree of π overlap in the exo B–N bonds, and it also may be expected that the exo B–N and ring B–N bonds have similar bond orders and bond strengths. The molecular structure of the model compound also reveals a twist of the borazine rings with respect to each other (58°) that results from inter-ring N–Me steric interactions. These will be absent in the polymer; however, it is expected that the inter-ring N–H repulsion might produce a ruffled structure.

The results from the present study demonstrate that the polymer decomposition and gas evolution chemistry occur in two distinct temperature regimes. The degradation processes in these regimes are complex and clearly different. However, some definitive conclusions may be drawn. In the low-temperature regime (<400 °C) facile

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(34) The sharp Raman line at 1365 cm^{-1} can be confidently assigned as originating from h-BN and not from graphite impurities. Previous studies have shown that highly crystalline graphite displays a strong Raman band at 1580 cm^{-1} and a weak band at 1380 cm^{-1}. Less crystalline graphite samples typically display bands at 1590 and 1360 cm^{-1} with more nearly equal intensities.

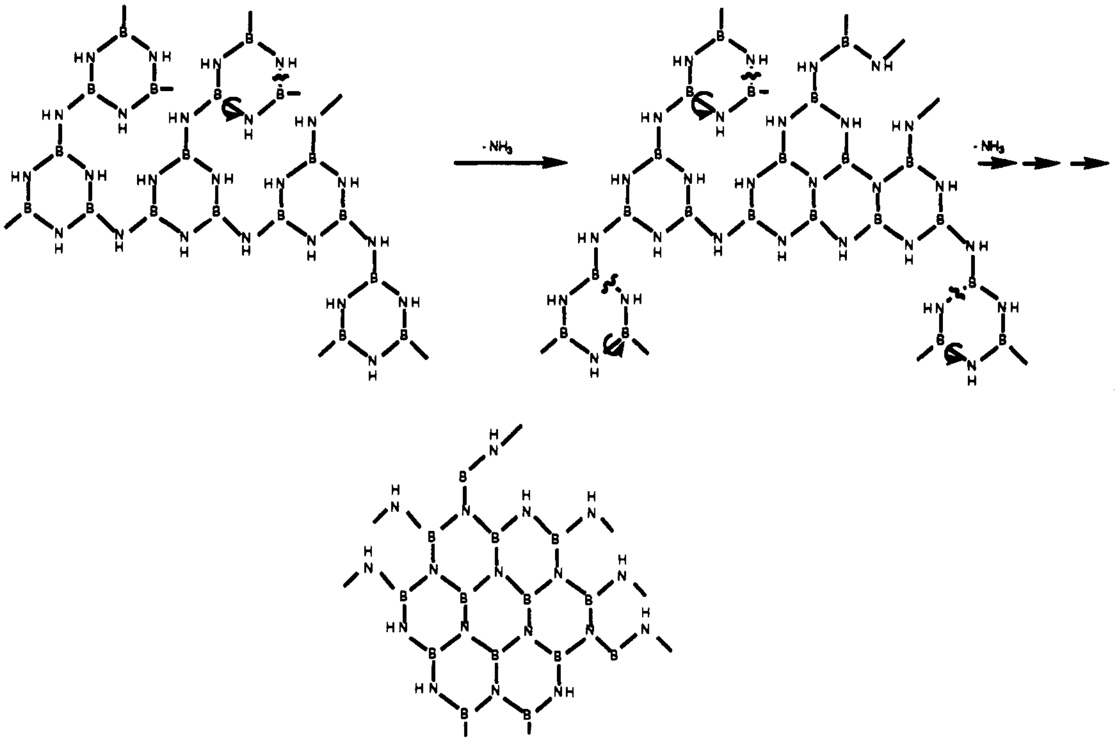
(35) Geick, R.; Perry, C. H.; Rupprecht, G. *Phys. Rev.* **1966**, *146*, 543.

(36) Nemanich, R. J.; Solin, S. A.; Martin, R. M. *Phys. Rev. B* **1981**, *23*, 6348.

(37) Long, D. A. *Raman Spectroscopy*; McGraw-Hill: London, 1977.

(38) Narula, C. K.; Lindquest, D. A.; Fau, M. M.; Borek, T. T.; Duesler, E. N.; Datye, A. K.; Schaeffer, R.; Paine, R. T. *Chem. Mater.* **1990**, *2*, 377.

Scheme I



borazine ring opening, as evidenced by isotope scrambling, and gas evolution chemistry appear to dominate. The loss of NH_3, N_2, and HCl take place in a narrow temperature range between 125 and 350 °C in at least two discernible steps, both of which produce the same gaseous products. Unfortunately, the available data do not unambiguously identify the precise nature of the reactions, although ring-opening processes would certainly generate reactive, terminal NH groups that should "scavenge" hydrogen from other borazine ring NH sites or from exo-bridging NH sites with subsequent expulsion of NH_3 as a dominant product. The resulting solid may be considered to be a thermally cross-linked polymer that contains a slight excess of nitrogen over that needed or BN and a ≈50% excess of hydrogen. The source of the HCl is likely from cleavage of end-blocking B–Cl groups on the polymer which were not aminated in the original polymer synthesis. The reaction source of the N_2 is not clear. In contrast, the high-temperature regime displays loss of mostly H_2, and it is evolved slowly over a wide temperature range, ≈350–1200 °C. The source of the hydrogen is most likely from dehydrogenation of terminal NH groups left isolated during the low-temperature regime cross-linking process. These NH bonds must be broken in order to achieve full consolidation of the BN planar structure and maximum ceramic density.

Given these observations, it is appropriate to briefly speculate on low-temperature regime reaction steps that may account for the conversion of the original polymer via NH_3 loss to the BN precursor. One proposal is summarized in Scheme I. The reader should not conclude that the specific fused ring structure shown in Scheme I is necessarily formed. Instead, a distribution of fused ring structures is likely formed from a series of thermally promoted borazine ring openings,[39] followed by B–N bond rotation that brings the newly generated, reactive B–N(H) fragments in the vicinity of terminal, saturated borazine ring NH, or bridging NH groups. Subsequent hydrogen transfer, expulsion of NH_3, and ring closure would result in efficient formation of fused-ring fragments. As mentioned earlier, these chemical steps are not expected to be rate limiting in the polymer-to-ceramic conversion process. It should be noted that the larger the number of central B_3N_3 rings formed in the fused ring structure, in the low-temperature regime, the smaller the amount of "excess" hydrogen that must be lost in the high-temperature regime. It is also pointed out that the idealized $B_{12}N_{12}H_{12}$ unit closely approximtes the stoichiometry of the polymer obtained after pyrolysis at ≈400 °C.

Further consolidation of these fused-ring units into h-BN will be a much more demanding process since diffusion of the relatively large and probably interconnected fragments is more restricted, and the residual hydrogen resides in more sterically congested regions that should hinder dehydrogenation processes. Thus, it would appear reasonable for diffusion and dehydrogenation of these fragments to be the kinetically limiting feature in the second stage of pyrolysis.

Although the Raman spectra cannot be fully interpreted, the trends observed are consistent with the model described above where the initial development of small fused-ring systems is followed by diffusion-controlled consolidation of the fused ring systems into h-BN. Although the chemical steps that occur are complex, it is possible to extract some understanding of the key features if an analogy is drawn to the equivalent carbon system. Borazine has a bonding and structural similarity with benzene and h-BN with graphite. In the benzene-derived condensed ring systems such as naphthalene, anthracene, etc., the increased delocalization allows absorption and fluorescence in the visible region; naphthalene is inactive in the visible region while pure anthracene has a blue fluorescence.[40] The intense fluorescence that we observe

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[39] Ring-opening reactions promoted by thermal processing of borazine rings has been proposed previously: Toeniskoetter, R. H.; Hall, F. R. *Inorg. Chem.* **1963**, *2*, 29. Some additional discussion is provided in ref 4.

[40] Brewster, R. Q.; McEwen, W. E. *Organic Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1961; p 680.

after heating the polymer to temperatures of the order of 400 °C suggests that by this temperature larger delocalized fragments that may produce fluorescence have formed. Although there is some double-bond character associated with the B-amine bridge bond,[22,38] the room-temperature polymer should be considered as delocalized only to the extent of the individual borazine rings. Of course, one cannot draw the conclusion that fused borazine rings have been produced only on the basis of the fluorescence evidence, but the existence of the fluorescence as well as the higher temperature resonance-enhanced Raman activity suggests that pyrolysis leads to the development of larger delocalized fragments. The development and growth of such fragments is, of course, a necessary step in the development of h-BN.

The line broadening and peak shifts observed by Nemanich and co-workers[36] for Raman spectra of a variety of crystalline h-BN samples as a function of particle size apparently results from a different range of particle sizes than that obtained in our work. Although they do observe line broadening with decreasing particle size, all spectra display the intralayer Raman band at ≈1365 cm^{-1} characteristic of h-BN. Further, apparently no major changes in intensity were observed comparable to those reported here. Nemanich and co-workers[36] also report luminescence from their samples, but this disappears after several hours of laser irradiation. In contrast, the fluorescence observed in the present Raman spectra, which does not disappear with extended irradiation, appears prior to crystallization and increases in intensity as the polymer is converted to amorphous BN and finally crystalline BN. It is tempting to speculate that the large line broadening and frequency shift that we observe at high temperature (≈1200 °C) may reflect the extremely small particle limit of the trends observed by Nemanich.[36]

One point clear from the present study is that the Raman spectra are very sensitive to changes in the material over the entire temperature range of pyrolysis. X-ray diffraction, for example, does not give information until some crystallinity has been established at temperatures above 900 °C. Thus, Raman spectroscopy promises to be a sensitive probe of the chemical and/or physical changes that occur during pyrolysis, and we have experiments planned to investigate the effect of different starting materials.

Summary

A combination of thermal decomposition mass spectrometry, thermogravimetric analysis, Raman spectroscopy, and X-ray photoelectron spectroscopy has been used to investigate the pyrolysis of polyborazinyl amine polymers with the following conclusions:

Two important temperature regimes exist for the pyrolysis chemistry: below 400 and 400–1200 °C.

With the exception of ≈50% of the initial hydrogen all gaseous products form below 400 °C.

Decomposition products below 400 °C are NH_3, N_2, and HCl. NH_3 and N_2 are from decomposition of the polymer and HCl is from byproducts or from incompletely reacted starting material.

Isotope labeling shows that complete exchange occurs between the ring and bridging amine nitrogens at temperatures below 400 °C.

Conversion of the poly(borazinylamine) polymer to h-BN in the low-temperature regime involves deamination and ring-opening reactions, and in a high-temperature regime, diffusion-controlled N–H dehydrogenation and volume reduction steps. Diffusion is the most likely thermal limiting step.

Raman spectra give evidence for the formation of larger delocalized fragments during pyrolysis of the type necessary for h-BN formation.

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Characterization of Polyester Films Modified with N_2O/Ar Plasmas

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Poly(ethylene terephthalate) film that has undergone plasma pretreatment with a mixture of argon and nitrous oxide exhibits the effects of surface cleansing and surface functionalization at low-to-moderate plasma exposure. X-ray photoelectron spectroscopy has detected a new oxygen species resulting from the plasma/polymer interaction. The new oxygen species has been identified as primarily aldehydic, although small amounts of surface carboxylic acid may also be present. Decreasing amounts of ester oxygen and carbonyl carbon have also been detected, which suggests that dissociation of the ester functionality has occurred. With longer plasma exposure, significant amounts of oxygen are lost from the surface with a concomitant increase in surface carbon concentration.

Introduction

The performance of metalized plastic film or articles occasionally suffers due to poor metal-to-polymer adhesion. Over the years researchers have studied and developed numerous procedures to enhance the adhesion between the polymeric substrate and the deposited metal. Two distinct methodologies have been commercially applied to improve metal/polymer adhesion. The first method is to apply a

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