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Pyrolysis behavior of poly[(*n*-propylamino/methylamino)borazine]

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Abstract

A processable poly[(*n*-propylamino/methylamino)borazine] (PPAB) has been pyrolyzed in Ar to study its thermal decomposition behavior. The structural evolution and chemical composition change during pyrolysis were characterized by chemical analysis, thermal gravimetry–mass spectrometry (TG–MS), Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The results indicated that the polymer-to-ceramic transition of PPAB involved two steps. Below 400 °C, the gas species were mainly methane and methylamine, while from 400 to 900 °C those were methane and *n*-propylamine. The PPAB displayed a ceramic yield of 52 wt% at 1000 °C and the pyrolyzed product was amorphous boron nitride (BN) with a small quantity of carbon impurity, in presence as C–C and C–N bonds. Moreover, for the pyrolyzed product, further heat treatment resulted in the occurrence of a transformation from amorphous to turbostratic.

Keywords: Ceramic precursor; Poly[(alkylamino)borazine]; Pyrolysis

1. Introduction

In view of their high melting point, low density and enhanced oxidation resistance, boron nitride (BN) matrix composites embedded with BN fibers are deemed to be potential candidates for aircraft and space applications [1–3]. However, it is difficult to fabricate BN fibers with high purity and good property using conventional powder routes [4]. The pyrolysis of preceramic precursors (PDCs) [5–7] was proved to be an effective way to shaped non-oxide ceramics owing to its high purity, low processing temperature, controllable composition and flexible forming. Further, poly[(alkylamino)borazine]s, possessing B_3N_3 hexagons and alkylamino chains linked with boron atoms on B_3N_3, were attractive precursors to BN fibers [8,9].

To date, different poly[(alkylamino)borazine]s have been developed. By condensation of tri(methylamino)borazine and laurylamine, Kimura et al. [10] prepared BN fibers. Miele and co-workers [11,12] found precursors from asymmetric (alkylamino)borazines exhibited best potentials to BN fibers. However, it was not easy to synthesize asymmetric monomers using gaseous alkylamines and 2,4,6-trichloroborazine (TCB), due to quantitative measurement of gaseous alkylamines.

To facilitate the synthesis, various asymmetric (alkylamino)-borazines have been synthesized using different alkylamines and B-trichloroborazine (TCB) in our earlier work [13,14]. Importantly, the synthesis of these monomers was under mild conditions without extraordinarily low temperature. Among this, [2-*n*-propylamino-4,6-bis(methylamino)]borazine (PAB) derived polymer (PPAB) has become an attractive precursor to BN fibers. Here, evolution of structure and composition of PPAB during pyrolysis was studied to understand the thermal behavior and thermal conversion process.

2. Experimental

All samples described in this investigation were manipulated in a dry nitrogen atmosphere. PPAB was prepared by condensation of PAB using a procedure previously described [14]. The structures of PAB and PPAB were shown below. Pyrolysis of PPAB was under Ar at a heating rate of 5 °C/min.

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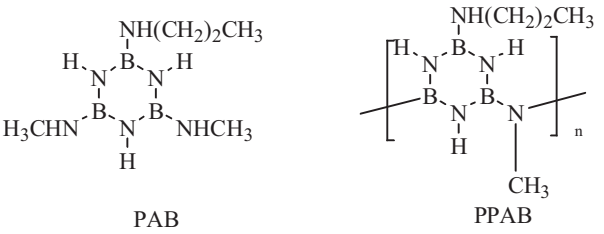
Further heat treatment of pyrolyzed residues obtained at 1000 °C was achieved up to 2000 °C in Ar (holding time, 1 h).



Thermal gravimetry–mass spectrometry (TG–MS) was performed in a Netzsch STA 449F1 equipment with a Balzers Thermo Star™ mass spectrometer (heating rate: 5 °C/min, Ar flow). Boron content was measured by a chemical titration method. Element contents of N, H and C were checked by Leco TCH-600 N/H/O and Leco CS-600 C/S analyzers. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet Avatar 360 spectrophotometer in KBr pellets. The X-ray photoelectron spectroscopy (XPS) spectra were obtained using a VG ESCALAB MKII instrument (Al K_α excitation). The binding energy of C1s at 284.6 eV was as the reference. X-ray diffraction (XRD) patterns were obtained using a powder X-ray diffractometer (Siemens D-5005, Cu K_α radiation).

3. Results and discussion

Fig. 1 gives the FTIR spectrum of PPAB. The very intense absorption at 1410 cm^{-1} and the weak absorption at 718 cm^{-1} can be assigned to ν(B–N) and δ(B–N), respectively [15]. Moreover, strong stretching mode of N–H group at 3443 cm^{-1}, typical bands for alkyl groups between 2800 and 2980 cm^{-1}, C–N group at 1090 cm^{-1} and C–H unit linked with borazinic rings at 1500 cm^{-1} were observed.

The pyrolytic conversion of PPAB was monitored by TG–MS and the pyrolysis proceeded in two well-resolved stages (Fig. 2). In the first step below 400 °C, PPAB lost 32.6 wt% of its initial mass. The temperature range from 400 to 900 °C marked the second step, occupying 13.8 wt% mass of PPAB.

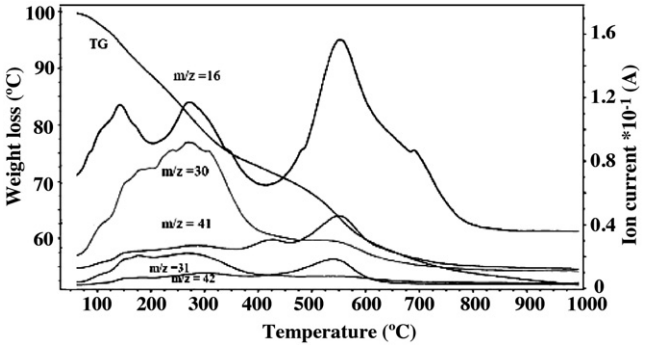


Fig. 2. TG–MS curves for the pyrolytic conversion of PPAB.

From 900 to 1000 °C, the weight loss was less than 1.5 wt%, indicating full conversion of polymer-to-inorganics. Moreover, the ceramic yield at 1000 °C was nearly 52 wt%.

In mass spectra, it is clear that CH_4 ($m/z = 16$) was the most abundant gas phase during whole pyrolysis process. Below 400 °C, CH_4 and $^{\bullet}CH_3NH$ ($m/z = 30$) were the main gas species. Besides, other species such as CH_3NH_2 ($m/z = 31$), $^{\bullet}CH_3CH{=}CH_2$ ($m/z = 41$) and $CH_3CH{=}CH_2$ ($m/z = 42$) were also present. Above 400 °C, evolution of $^{\bullet}CH_3NH$ decreased and CH_4, $^{\bullet}CH_3CH{=}CH_2$ became the main gas species. Hence, volatilization of methylamine was mostly below 400 °C, while that of *n*-propylamine originated from the deamination reaction was mainly between 400 and 900 °C. These data illustrated that methylamino groups were more active than *n*-propylamino groups. Considering that during synthesis of PPAB from PAB monomers, gaseous methylamine evaporated while *n*-propylamino units reserved [11], it should be reasonable that symmetric structure of PAB molecular monomer favors the formation of PPAB's quasi-linear structure to provide good melt-processability for preparing BN fibers.

To get a clear understanding about the chemical composition change in PPAB during pyrolysis, the different atomic ratios were plotted as a function of temperature (Fig. 3). Before pyrolysis, the composition in PPAB was (wt%): B (22.79), N (44.71), C (22.64) and H (7.87). The H/B, C/B and N/B atomic ratios were 3.59, 0.92 and 1.57, respectively. With increasing

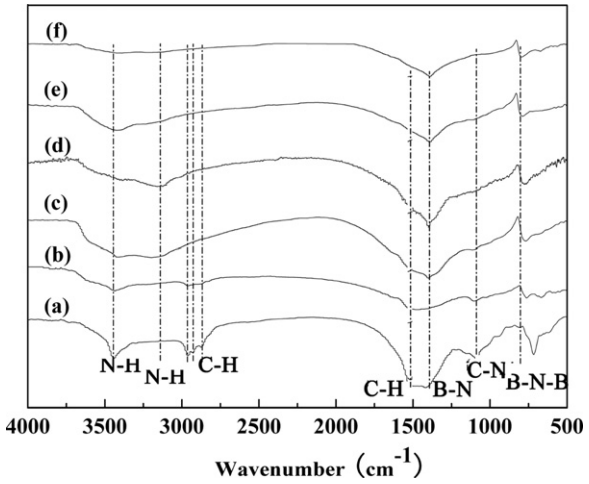


Fig. 1. FTIR spectra of (a) PPAB and products obtained at: (b) 400, (c) 600, (d) 800, (e) 1000 and (f) 1500 °C in Ar.

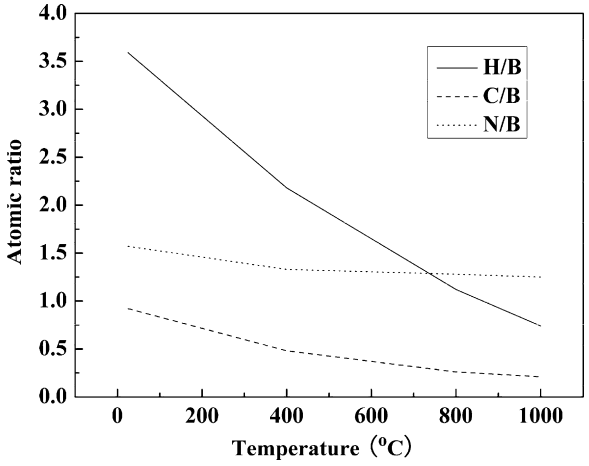
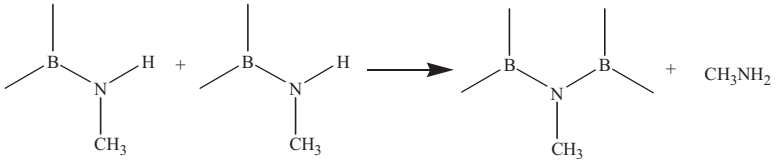


Fig. 3. H/B, C/B and N/B atomic ratios in pyrolyzed samples at different temperatures.

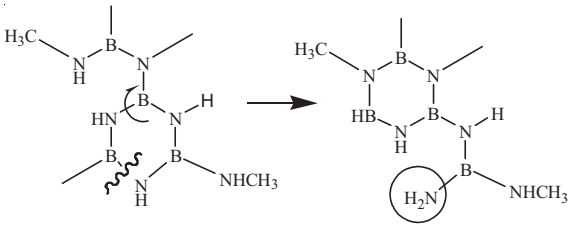
temperature, the C/B and N/B atomic ratios reduced gradually, while that of H/B decreased much more quickly due to evolution of alkylamine and methane discussed above. At 1000 °C, the H/B, C/B and N/B atomic ratios decreased to 0.72, 0.20 and 1.22, respectively.

The structural evolution of PPAB during pyrolysis analyzed by FTIR was given in Fig. 1. With increasing temperature, the organic groups decreased gradually. The 400 °C sample displayed a reduction in the intensity of N–H, C–H and C–N bands, caused by loss of methane and methylamine according to Eqs. (1) and (2) [16]. At 600 °C, a weak N–H band attributed to NH_2 was observed near 3200 cm^{-1}, originated by intra macromolecular mechanism with B_3N_3 ring opening due to Eq. (3) [15].

(1)



(2)

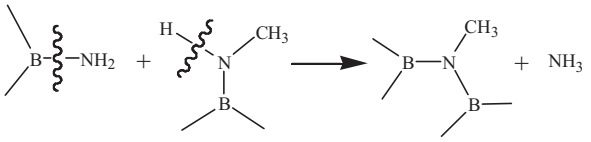


(3)

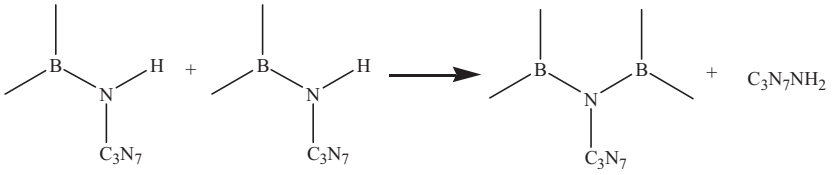
Above 600 °C, the intensity of C–N and N–H bands kept on decreasing due to reactions of Eqs. (4) and (5). At 1000 °C, the C–N band became very weak. The 1500 °C sample exhibited only two absorptions at 1395 and 805 cm^{-1}, which were typical peaks of hexagonal-BN (*h*-BN) [12]. It was also noticed that these two bands shifted frequency during pyrolysis, which was correlated to the modification of atomic environment and crystallization process.

Further evidence for the surface composition of the sample pyrolyzed at 1000 °C can be obtained from the XPS spectra. The wide scan XPS spectrum (Fig. 4(a)) showed the presence of B, N and C elements. A small quantity of oxygen was also noticed, originated from the absorption of CO_2 and O_2 on the sample's surface. From the split B1s and N1s spectra (Fig. 4(b) and (c)), the B1s peak at 190.7 eV and N1s peak at 397.6 eV indicated BN [6]. Also, the presence of carbon was studied, as Fig. 4(d) displayed. The C1s peak was split into double peaks at 284.2 and 285.4 eV corresponding to the C–C and C–N bonds, respectively [17,18]. The result confirmed that the sample obtained at 1000 °C was BN with carbon impurity.

The XRD patterns of PPAB treated at different temperatures were given in Fig. 5. As seen, the 1400 °C sample was fully amorphous. While for the 1800 °C sample, the XRD patterns changed a little, indicating the development of phase composition. A sharp peak at $2\theta = 26.4^\circ$ and a diffuse hump at $2\theta = 41.6^\circ$ attributed to the (0 0 2) and (1 0 0) planes of *h*-BN were noticed, respectively. Moreover, a diffuse peak ascribed to the (1 1 0) plane was also observed. When the temperature was enhanced to 2000 °C, the full width half maximum (FWHM) of the (0 0 2) peak became much narrower and a diffuse (0 0 4) peak was also seen, suggesting an improvement of crystallization. The unresolved (1 0 0) and (1 0 1) reflections indicated the sample's turbostratic structure [19]. While it should be mentioned that poly[(alkylamino)borazine] pyrolyzed in ammonia exhibited a higher crystallinity [16], which may be due to the fact that the carbon impurity in the sample pyrolyzed under inert atmosphere limited BN's crystallization. A detailed study about the effect of atmosphere on the composition and structure of poly[(alkylamino)borazine]-derived materials will be reported elsewhere.



(4)



(5)

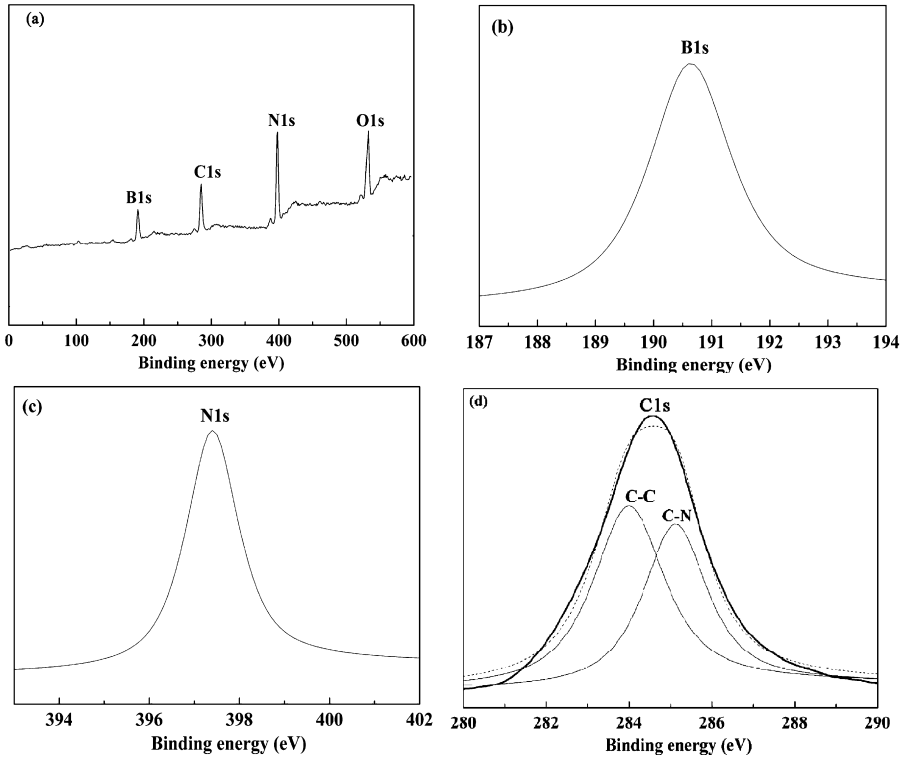


Fig. 4. Wide scan (a), B1s (b), N1s (c) and C1s (d) XPS spectra.

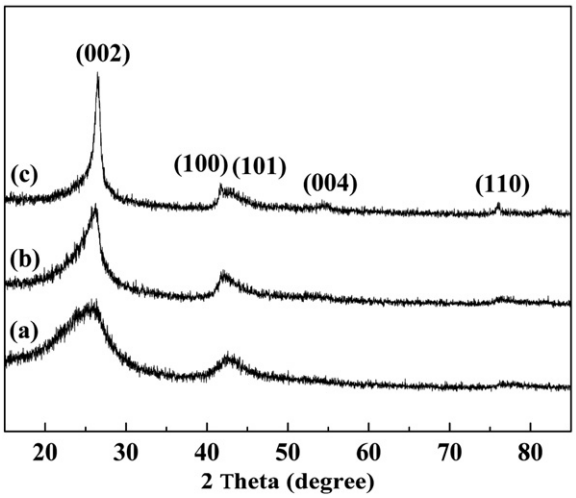


Fig. 5. XRD patterns of pyrolyzed PPAB at: (a) 1400, (b) 1800 and (c) 2000 °C.

4. Conclusions

The thermal behavior of a processable polyborazine was studied and the evolution of structure and composition was characterized. During pyrolysis, methane and methylamine were the main gas species below 400 °C while those above 400 °C were methane and *n*-propylamine. Moreover, the product pyrolyzed at 1000 °C was amorphous BN with a small quantity of carbon impurity, in presence as C–C and C–N bonds. Furthermore, the sample further heat-treated at 2000 °C exhibited a turbostratic structure.

Acknowledgments

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