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Novel processable precursor for BN by the polymer-derived ceramics route

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Abstract

Novel precursors polymerized from (alkylamino)borazines (AAB) were synthesized and transformation of processable poly-AAB to boron nitride (BN) was researched. The AAB monomers of the type $(BNH)_3(NHR)_3$ were synthesized via ammolysis of 2,4,6-trichloroborazine (TCB) with different propylamines under mild conditions. The specially designed monomers served as molecular precursors for BN by the polymer-derived ceramics route. The processability of the polymeric precursors varied with propylamino-groups of AAB linked with boron atoms on $(BNH)_3$. The good processability of the poly[2,4,6-tris(*iso*-propylamino)borazine] (PTP^iAB) was proven by melt-spinning it into polymer fiber. Furthermore, the PTP^iAB gave a ceramic yield of about 53 wt% in Ar at 1200 °C by TGA. Based on FTIR, Raman, XRD, XPS and elemental analysis, the pyrolytic product of PTP^iAB showed a composition of $BN_{1.07}$. In addition, the BN illustrated excellent oxygen resistance in air.

Keywords: Boron nitride; Poly(alkylamino)borazines; Polymer-derived ceramics method; Oxygen resistance

1. Introduction

In view of their high temperature stability, enhanced oxidation resistance and low density, boron nitride (BN) matrix composites embedded with BN fiber are deemed to be potential candidates for aircraft and space applications [1,2]. However, preparation of BN fiber is difficult using conventional powder routes [3]. The polymer-derived ceramics (PDCs) route [4–7], which offers homogeneous element distribution, low impurity level and good processability, is an elegant method for fabricating BN fiber [8]. It is worth noting that the PDCs method allows the design and control of the reactivity of moleculars to lead to soluble and fusible preceramic polymers. As far as we know (alkylamino)borazine (AAB) monomers synthesized from 2,4,6-trichloroborazine (TCB) were regarded as attractive molecular precursors for BN fiber to date [9–11].

It is known that the processability of polymeric precursors derived from AAB monomers was strongly dependent on the substituent alkylamino groups linked with boron atoms [10,12]. Therefore, it is possible to adjust the processability of the preceramic polymers by substituting chlorine atoms on TCB with different alkylamines. However, it was inconvenient to synthesize AABs using gaseous alkylamines and TCB to lead to processable polymers due to quantitative measurement of these gaseous alkylamines, which need extraordinarily low temperature.

With the aim to facilitate the synthesis, two AABs for BN polymeric precursors have been synthesized using different liquid propylamines and TCB in our earlier work [13], respectively. Importantly, the synthesis of these monomers is under mild conditions without extraordinarily low temperature. In the present work, various polymeric precursors from above two AABs were obtained by thermal condensation. Moreover, processability of these polymers was tested by hand drawing technique. Finally, based on a combination of XRD, elemental analysis (EA), XPS, FTIR and Raman techniques, BN derived from the processable precursor was characterized.

2. Experimental

All samples described in this investigation were manipulated in a dry nitrogen atmosphere. Toluene as a solvent was purified by distillation with sodium.

Two molecular monomers were synthesized by aminolysis of TCB with *n*-propylamine and *iso*-propylamine, respectively, as reported in a previous investigation [13]. In a Schlenk flask,

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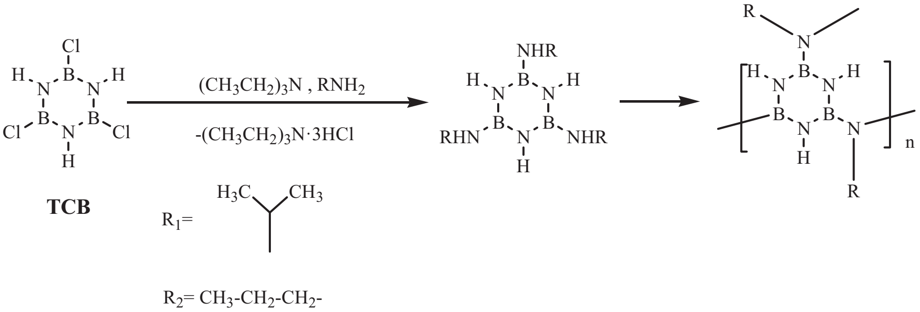

Scheme 1. Synthetic route of poly[2,4,6-tris(*iso*-propylamino)borazine].

n-propylamine (or *iso*-propylamine, the same below) was slowly dropped into the solution of TCB and triethylamine in toluene under vigorous stirring. The white precipitation was noticed upon dropping propylamines into the solution. The molar ratio between *n*-propylamine, TCB and triethylamine were 3:1:3. After stirring at −10 °C for 5 h, the temperature of the slurry was elevated to room temperature under stirring and then lasted for 12 h. Subsequently, the mixture was filtered and washed with toluene to give a light yellow solution. After the solvent was evaporated in vacuo, AAB monomers were obtained. Preceramic polymers were synthesized by thermal condensation of AAB monomers according to a multistep temperature procedure and kept at the target temperature for 5 h. The synthetic route of poly[2,4,6-tris(*iso*-propylamino)-borazine] can be expressed in Scheme 1.

Polymer fiber was prepared using the hand drawing technique in a glove box under dry Ar [14]. Polymer fiber of length exceeding 10 cm was afforded by stretching with a stainless steel needle from the viscous melt. The preceramic polymer was first milled to a fine powder (500 mesh) in a glove box under Ar. Then pyrolysis of the fine powder was under NH_3 gas at a heating rate of 5 °C/min. Further crystallization of pyrolytic residues obtained at 1000 °C was achieved at different temperatures for 1 h in Ar.

Boron content was measured by a chemical titration method. Element contents of N, O, H and C were checked by Leco TCH-600 N/H/O and Leco CS-600 C/S analyzers. FTIR spectra were recorded on a Nicolet Avatar 360 spectrophotometer in KBr pellets. XRD patterns were obtained using a powder X-ray diffractometer (Siemens D-5005, Cu Kα radiation). TGA was performed in Ar or air (heating rate: 5 °C/min, Netzsch STA 449C). The surface of the fiber was analyzed by using a scanning electron microscope (JEOL, JSM-6300). Raman spectra were obtained by using a Bruker SENTERRA spectrometer and excited using the 632.82 nm He–Ne laser. The XPS spectra were obtained by means of a VG ESCALAB MKΠ instrument (Al Kα excitation).

PTPAB: FTIR (KBr/cm^{-1}): 3421/3134/1031 (N–H), 2924/2853 (C–H), 1400 (B–N), 745 (B–N–B), 1078 (C–N). ^{13}C NMR (ppm): δ 8.9 ($-CH_3$), 25.9 ($-CH_2CH_3$), 45.9 ($-NHCH_2$), 55.1 ($-NCH_2$).

PTP^{i}AB: FTIR (KBr/cm^{-1}): 3414/3130/1021 (N–H), 2962 (C–H), 1400 (B–N), 805 (B–N–B), 1092 (C–N). ^{13}C NMR (ppm): δ 19.3 ($-CH_3$), 43.4 (–NHCH), 50.3 (–NCH–).

3. Results and discussion

3.1. Characterization of the polymeric precursors

The synthetic route of poly(alkylamino)borazines was shown in Scheme 1. It was found that both reactions between TCB and different propylamines proceeded as expected [13]. The effect of monomer and reaction temperature on the properties of polymeric precursors was investigated and the results were given in Table 1.

Clearly, there was no visible difference between polymers obtained from TPAB monomer. When the temperature was increased from 150 to 250 °C, they were all light yellow liquid with softening point lower than room temperature. Whereas, polymers polymerized from TP^{i}AB displayed different appearance with temperature increasing from 120 to 180 °C. These polymers from TPAB and TP^{i}AB changed from soluble light yellow rubber to insoluble yellow solid gradually with temperature increasing, indicating that regulation of the poly-AAB's properties were realized by aminolysis of TCB with different propylamines. This also suggested that TPAB

Table 1
Polymerization conditions and properties of the synthesized polymeric precursors.

Monomer	Polymer	Temperature (°C)	Appearance	Solubility	Softening point (°C)
TPAB	TPAB-150	150	Light yellow liquid	Soluble	<r.t.
	TPAB-180	180	Light yellow liquid	Soluble	<r.t.
	TPAB-250	250	Light yellow liquid	Soluble	<r.t.
TPiAB	TPiAB-120	120	Light yellow rubber	Soluble	<r.t.
	TPiAB-150	150	Light yellow solid	Soluble	70
	TPiAB-180	180	Yellow solid	Insoluble	>300

Holding time: 5 h.

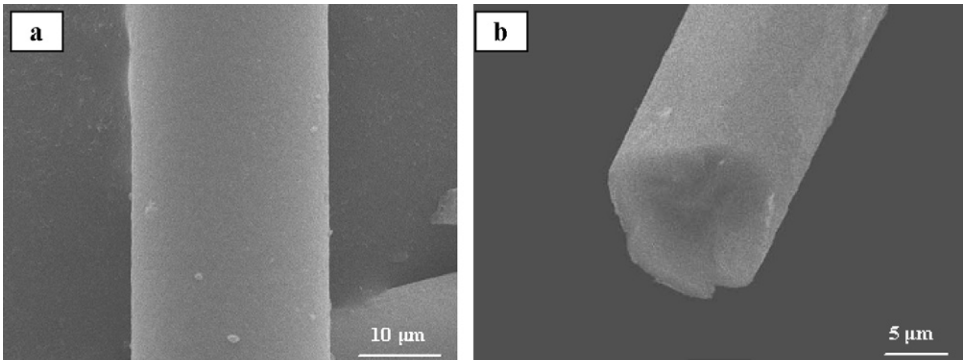

Fig. 1. The typical morphology of (a) the polymer fiber and (b) the as-obtained BN fiber.

monomer possessed a relatively lower reactivity compared to TP^{i}AB under thermal conditions. As expected, a soluble and fusible polymer (TP^{i}AB-150) was obtained after holding at 150 °C for 5 h. Indeed, effect of the substituent's steric bulk in AAB monomers such as methylamino- and dimethylamino-groups in adjusting poly-AAB's processability was reported in recent papers [10,12].

The difference in the property of two polymers is directly reflected in melt-processability. The low viscosity of liquid PTPAB indicated its inability to be melt-spun. Contrarily, TP^{i}AB-150 provided polymer fiber by hand drawing in glove box filled with Ar, as reported in literature [14]. The fiber exhibited a smooth surface with no flaw and a diameter of about 20 μm, as Fig. 1(a) illustrated. Even so, the polymer fiber was very fragile and cannot endure any mechanical shock, just like polycarbosilane fiber [15]. When the temperature of the viscous melt was too high, a high degree of polymerization happened and it was difficult to obtain polymer fiber.

The elements in TP^{i}AB-150 were characterized by the elemental analysis (wt%): B (12.37), N (35.80), C (37.2), H (9.3) and small quantity of oxygen. The presence of oxygen can be related to partial hydrolysis of TP^{i}AB-150 with H_2O during handling and measurements, leading through –B–O– groups to the tiny incorporation of oxygen impurities.

The ceramic yield of TP^{i}AB-150 in Ar was examined by TGA, as shown in Fig. 2. The weight loss mainly occurred below 800 °C (almost 45 wt%). The weight decrease was only about 2 wt% in the region from 800 to 1200 °C, indicating full conversion of polymer-to-inorganics. Moreover, the ceramic yield at 1200 °C was almost 53 wt%. It is worth pointing out that a higher ceramic yield can be obtained through further crosslinking of TP^{i}AB-150 in NH_3, as reported in a previous investigation [16].

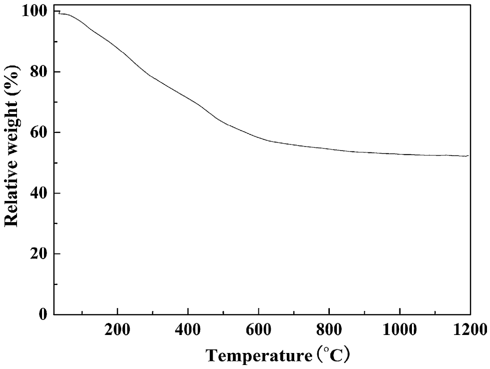

Fig. 2. TGA curve of PTP^{i}AB in Ar.

3.2. Ceramization of TP^{i}AB-150

The XRD patterns of TP^{i}AB-150 annealed at various temperatures were illustrated in Fig. 3. As seen, the sample annealed at 1200 °C were fully amorphous, suggesting that microcrystalline phases are absent in the samples pyrolyzed below 1200 °C. The result was in good agreement with the study on BN derived from poly(borazinylamine) [17]. While the XRD pattern of the sample annealed at 1500 °C changed a lot, implying a great development of phase composition occurred in the temperature range from 1200 to 1500 °C. A sharp peak at $2\theta = 26.4°$ and a diffuse hump at $2\theta = 41.6°$ attributed to the (0 0 2) and (1 0) plane of turbostratic-BN were noticed, respectively [18]. For the sample annealed at 1800 °C, two diffuse peaks ascribed to the (1 0 1) and (0 0 4) plane of hexagonal BN (*h*-BN) were observed. The value of $d_{0\,0\,2}$ (0.334 nm) was close to that of *h*-BN (0.333 nm) [19], indicating a high degree of crystallinity for BN obtained at 1800 °C in this work.

FTIR and Raman spectrum of BN obtained at 1800 °C were shown in Fig. 4. The FTIR spectrum of the BN was close to that of *h*-BN [Fig. 4(a)]. Two main absorption peaks at around

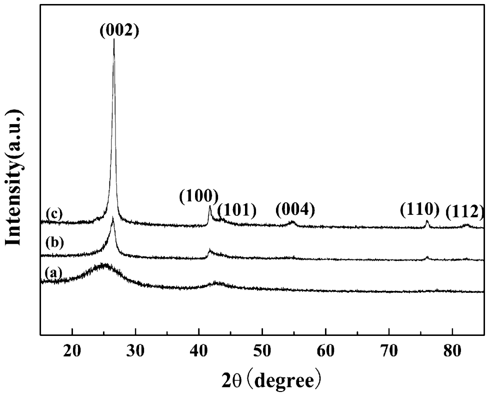

Fig. 3. XRD patterns of the products obtained at different temperatures: (a) 1200 °C (b) 1500 °C and (c) 1800 °C.

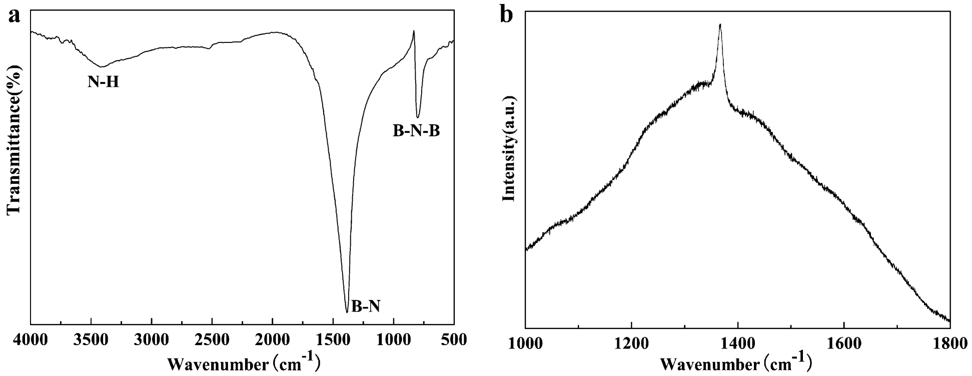

Fig. 4. FTIR spectra (a) and Raman spectra (b) of BN obtained at 1800 °C.

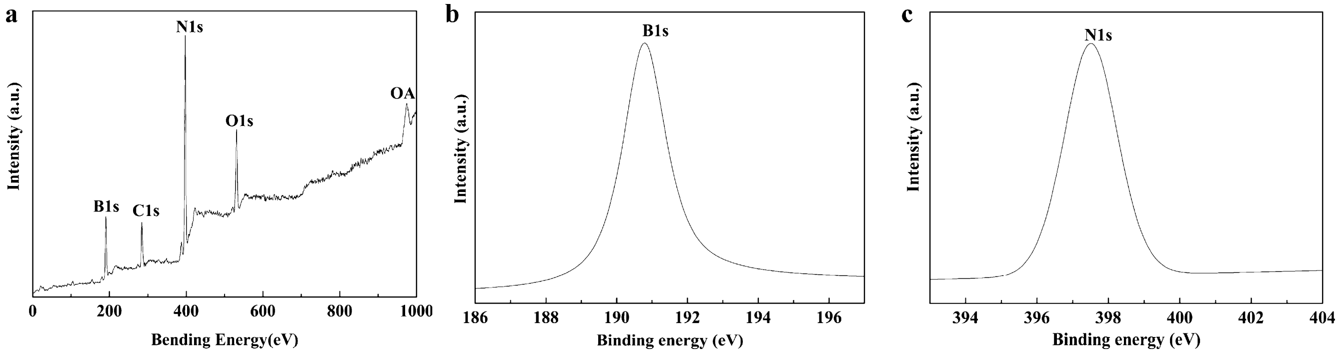

Fig. 5. XPS spectra of the BN sample: (a) survey spectrum; (b) B1s region; (c) N1s region.

1384 cm^{-1} and 805 cm^{-1} were identified as the TO modes of the sp^2-bonded *h*-BN, corresponding to plane ring vibration (E_{1u} mode) and out of the plane ring vibration (A_{2u} mode), separately [1]. In Fig. 4(b), the Raman band near 1367 cm^{-1} was attributed to the typical vibration frequency of *h*-BN caused by E_{2g} symmetric vibration mode [20].

Further evidence for the composition information of the pyrolyzed sample can be obtained from the XPS spectra, as shown in Fig. 5. The survey spectrum [Fig. 5(a)] reveals the presence of B and N elements. Small quantity of C and O were also detected, which may be caused by the absorption of C and O on the surface of the sample. The split B1s and N1s spectra were shown in Fig. 5(b) and (c), respectively. Obviously, the B1s peak at 190.8 eV and the N1s peak at 397.7 eV indicated BN [21].

According to elemental analysis, the carbon content in the BN sample was less than 0.1 wt%. And the B/N molar ratio was 1:1.07, which agreed well with the chemical stoichiometric relation between B and N. This clearly demonstrates the successful preparation of BN without carbonaceous impurities by pyrolyzing alkylamino-containing precursor in NH_3.

The typical surface micrograph of the BN fiber obtained at 1500 °C was shown in Fig. 1(b). The BN fiber has a very smooth surface without any observable flaws and a diameter of about 15 μm. It is apparent that the fiber retained its shape during pyrolysis without fusion.

3.3. Oxygen resistance of as-obtained BN

The materials for high temperature applications in oxygen-containing environments must embody excellent oxidation resistance [22,23]. The TGA curve of as-obtained BN in air is illustrated in Fig. 6. As seen, almost no detectable weight change happened before 800 °C. Moreover, extended time oxidation studies of BN at 800 °C in air also revealed the BN's good oxidative resistance. The BN displayed only a small weight gain when furthermore exposed in air up to 400 min and the weight increase was less than 2 wt%. The weight gain is owing to a little amount of BN's oxidation to B_2O_3, as Eqs. (1) and (2) illustrated [24].

$$4BN + 3O_2 \rightarrow 2B_2O_3 + 2N_2 \qquad (1)$$

$$2BN + 3H_2O \rightarrow B_2O_3 + 3H_2 + N_2 \qquad (2)$$

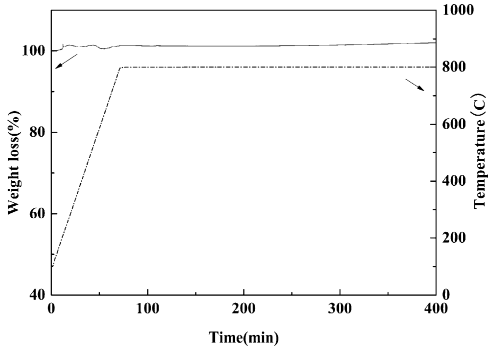

Fig. 6. TGA curve of as-fabricated BN in air at 800 °C (10 °C/min to 800 °C then held).

4. Conclusions

Two poly(alkylamino)borazine precursors were synthesized by thermal condensation of different 2,4,6-tris(propylamino)borazines. Moreover, the properties of the preceramic polymers such as softening point and solubility were greatly effected by polymerization temperature. The processability of these two kinds of polymers was significantly influenced by propylamino-groups linked with boron atoms due to the steric hindrance effect. Furthermore, the poly[2,4,6-tris(*iso*-propylamino)borazine] demonstrated good melt-processability and a ceramic yield of 53 wt% in Ar at 1200 °C. In addition, the sample pyrolyzed at 1800 °C showed characteristics of *h*-BN and a near-stoichiometric composition. Finally, as-obtained BN displayed good oxidation resistance in air. Research is currently under way to investigate the thermolysis of polymer fiber and mechanical properties of the BN fiber.

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