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Influence of Molecular Precursor Structure on the Crystallinity of Boron Nitride

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Processible polymers have been prepared from borazinic derivatives. They were thermolyzed into boron nitride using an appropriate chemical and thermal treatment in order to obtain a carbon-free ceramic. Despite similar pyrolysis conditions, the crystallinity of the resulting BN was found to be different for each polymer. These differences should be related to the structure of the molecular precursors and of the polymers derived therefrom. Polymers prepared from the borazine, $(HNBH)_3$, always gave the more-crystallized materials. © 2000 Academic Press

Key Words: **boron nitride; borazine; precursor; crystallinity.**

INTRODUCTION

Nonoxide ceramics are usually obtained as powders from high-temperature reactions of simple, inexpensive raw materials. However these classical routes are not suitable to lead to ceramic fibers, matrices, coatings, and binders (1, 2). These forms are usually obtained from processible preceramic polymers. Due to the specific properties of boron nitride, especially as ceramic composites, the BN molecular precursors chemistry has found a renewed interest (1–5). Most of the precursors are built around the borazinic ring, N_3B_3, which is the basic pattern of hexagonal boron nitride. When heated, the borazine (Fig. 1a), $(HNBH)_3$, undergoes a polymerization (6) that leads to an unfusible polycyclic polymer (Fig. 1A) soluble in glyme-like solvents. This polymerization has been showed to be catalyzed by ammonia (7). A spinable polymer can be obtained by bonding dipentylamino groups to the rings (8, 13). A simple method for preparing substituted borazines is to use the ability of the chlorine atoms of 2,4,6-trichloroborazine, $(HNBCl)_3$, (TCB) to be replaced by amino groups, leading to reactive aminoborazines, or to react with silazanes, giving directly a polymer (3, 4, 9–11). Thereby, the reaction of methylamine with TCB leads to the formation of 2,4,6-*tris*(methylamino)borazine (MAB) (Fig. 1b), $(CH_3NH)_3B_3N_3H_3$, which can be transformed into a processible "three-point" polymer when heated (9, 11). To get a "two-point" pseudo-linear polymer, an asymmetric borazine, $\{(CH_3)_2N\}\{CH_3NH\}_2B_3N_3H_3$, (DMAB) (Fig. 1c) can be prepared and polymerized (1, 11, 16). In this work, four kinds of processible polymers have been prepared from the borazines described above: a dipentylamine modified polyborazylene (I), a copolymer resulting from the reaction between borazine and MAB (II), a DMAB-based polymer (III), and a MAB-based polymer (IV). These polymers have been thermolyzed following the same chemical and thermal treatment up to 1800°C. All the polymers led to carbon-free boron nitride but the samples, characterized by X-ray diffraction, exhibited important structural differences induced by the structure of the original polymer.

RESULTS

Polymers Synthesis

All the studied precursors and polymers were highly sensitive to hydrolysis and oxidation. Consequently the handling and the synthesis reactions were always performed under controlled argon atmosphere according to the standard air-sensitive compounds handling (12). The ceramic yield of the polymers were determined by TGA using 100-mg samples and following the chemical and thermal treatment used for the ceramization up to 1000°C.

Polyborazylene modified polymer (I). The synthesis of this polymer has been previously described (8, 13, 14). Borazine, $(HNBH)_3$, was heated in vaccuo at 70°C for 48 h. Then a solution of the reaction product in glyme reacted with dipentylamine at 75°C for 196 h. After glyme removing, a waxy polymer (I) was recovered and characterized by elemental analysis (B, 20.8; N, 31.0; C, 37.2; H, 9.3), DSC, and TGA.

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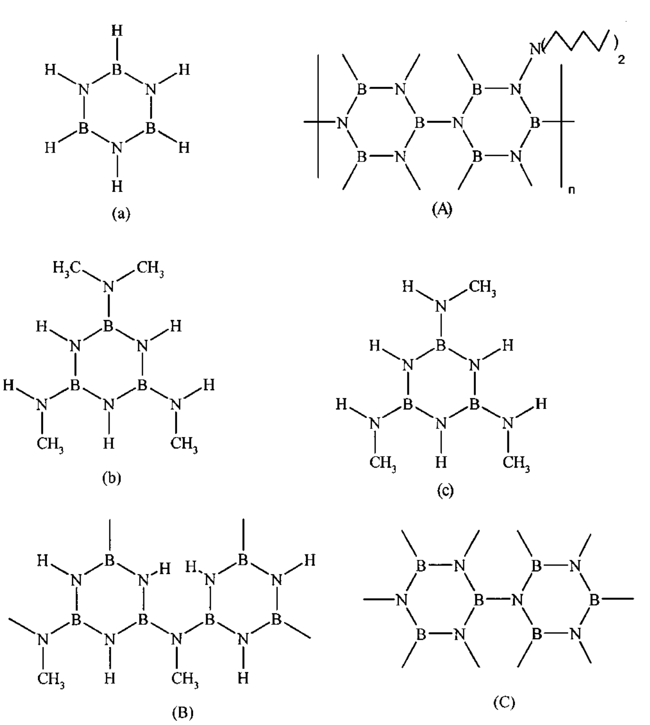

FIG. 1. Molecular precursor (a, b, c) and polymerization schemes (A, B, C) of the tested polymers.

Copolymer borazine–MAB (II). Since borazine is liquid at room temperature, 10 wt% of solid MAB was added to the borazine under vigorous stirring. The reaction mixture was heated up to 75°C for 36 h under low pressure. After cooling at room temperature, a solid opalescent polymer (II) was recovered and characterized using DSC, TGA, and elemental analysis (B, 37.4; N, 52.9; C, 3.8; H, 5.7).

DMAB-based polymer (III). The 2-di(methyl)amino-4,6-bis(methylamino)-borazine was prepared by reacting TCB with a mixture of methylamine and dimethylamine (in a 2:1 molecular ratio). Then DMAB was polymerized by heating for 8 h at 160°C under an argon stream (16). A light-brown, glassy polymer was obtained after cooling and characterized using DSC, TGA, and elemental analysis (B, 20.8; N, 47.7; C, 24.6; H, 5.5).

MAB-derived polymer (IV). Following the same thermolysis conditions described above, the polymerization of 2,4,6-tri(methylamino)borazine led to a processible polymer. After cooling, a glassy polymer was recovered and characterized using DSC, TGA, and elemental analysis (B, 23.7; N, 45.7; C, 18.2; H, 6.8).

The physical characteristics of these polymers (glass transition temperature and ceramic yield) are given in Table 1.

TABLE 1
Properties of the Polymers

Polymer	I	II	III	IV
Glass transition (°C)	− 21.7	22.5	65.0	77.3
Ceramic yield (%)	45.3	77.5	51.7	55.8

Chemical and Thermal Treatment

As it has been widely pointed out, the role of ammonia was very important during the reticulation step and for the stripping of the carbon-containing moieties of the polymers (6, 8, 11, 15) to obtain carbon-free BN. Two successive treatments were performed in two different furnaces. During the first one (preceramization), the polymers were heated up to 600°C (heating rate 50°C.h^{-1}) under an ammonia flow (10 ml.mn^{-1}) and then heated under a nitrogen atmosphere up to 1200°C (heating rate 100°C.h^{-1}). In order to stabilize the BN powders obtained, an annealing of the samples was performed up to 1800°C under nitrogen (heating rate 250°C.h^{-1}). The obtained white powders exibited similar elemental composition determinated by XPS (within the measured error) wt.% B, 46.7 $\pm$ 3.5; N, 49.5 $\pm$ 4.5; O, 3.5 $\pm$ 0.5; C, $<$ 2 (calculated for BN: B, 43.5; N, 56.5). The lack of nitrogen in the samples could be related to the presence of oxygen, corresponding to the formation of a small amount of boron oxide during the pyrolysis.

XRD Determinations

The samples were characterized using XRD powder diffraction. A diffraction pattern was recorded for each sample after heating at 1200 and 1800°C. The diffraction patterns recorded on the powder obtained from polymer I are presented in Fig. 2 and clearly show the crystalline changes induced by the sample annealing. At 1200°C, the diffraction pattern is consistent with that described for turbostratic BN

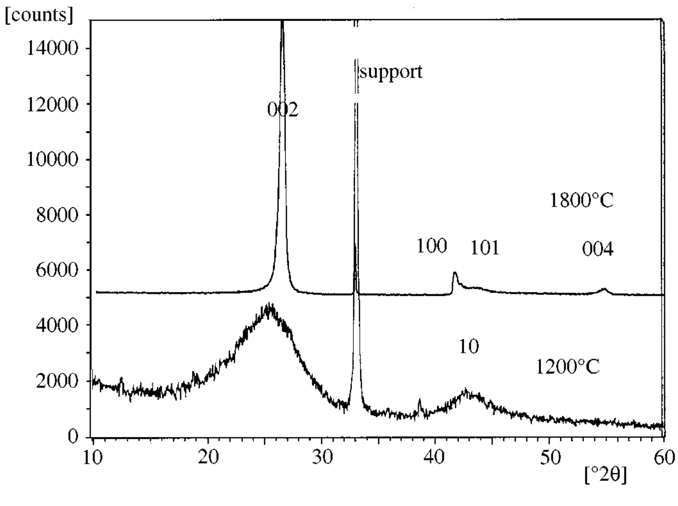

FIG. 2. XRD spectra of the ceramic obtained from polymer I after thermolysis at 1200 and 1800°C.

TABLE 2
X-Ray Diffraction Data for the Samples after a 1200°C Pyrolysis

	Reflection					
	(002)			(10)		
Sample from	2θ	d(Å)	L_c(Å)	2θ	d(Å)	L_a(Å)
Polymer I	25.7	3.46	12.7	42.5	2.12_5	52.8
Polymer II	25.7	3.46	15.5	42.5	2.12_5	45.8
Polymer III	24.05	3.69	10.6	43.0	2.10	43.5
Polymer IV	24.6	3.61	10.3	43.0	2.10	39.6

(17, 18), and two broad diffraction maxima attributed to (002) and (10) (abbreviated value of (*hk*) reflections) are only visible. Table 2 gives the diffraction data of samples obtained from polymers I–IV after a preceramization up to 1200°C. The differences between the four samples can be outlined from the values of the crystallite lengths L_a and L_c, respectively, following the *a* and *c* axis, using the classical Scherrer equation (17). The boron nitride obtained had a turbostratic structure formally analogous to the structure of turbostratic carbon blacks (19) in a naphtalenic form, stacked roughly against each other but showing random rotation and translation about the layer normal. The differences between the samples were not very important, but the BN powders obtained from polymers I and II, which were derived from borazine-based polymers, already appeared to be more crystallized, especially following the *a* axis. The crystallite size was only on average 4 BN layers following the *c* axis and 20 BN hexagons following the *a* axis. This value is worth about 21 for polymer I and 15 for polymer IV. The crystallites appeared to have grown, particularly following the *a* axis, which is consistent with the ceramic conversion scheme described for borazines (6, 9, 14, 20).

The crystallographic values measured for the four samples after annealing up to 1800°C are given in Table 3. The peak position of the two-dimensional (*hk*) reflections decreases with the average diameter L_a. As shown in Fig. 2, the (100) and (101) diffractions are not resolved. Moreover the (102) diffraction required to evaluate the graphitization index (GI) of the boron nitride (17) could never be observed under the experimental conditions. Even using polymer I, the ceramic organization was always lower than that obtained directly from the borazine precursor NH_3BH_3 when pyrolyzed (21). The poor graphitic structure of the BN powders obtained could be related to the low ability of these polymers to be transformed into "graphitized BN" as observed in the carbon chemistry for several carbon fiber precursors (19). The high-temperature annealing increases the structural differences observed in the samples treated at 1200°C. The broadest BN crystallites were obtained from polymers I and II while the smallest resulted from polymers III and IV. These differences could be included by the structure of the polymeric precursor (Fig. 1). Polymer I was composed of B_3N_3 rings, which were the basic pattern of *h*-BN, linked directly through BN bonds or combined together in a macrocyclic aromatic arrangement (Fig. 1A) (6, 13, 14). The structure of this polymer was very close to that of boron nitride and led to the more crystallized samples. In polymer II, the small amount of MAB led to few changes compared to the polymer I structure. Therefore this polymer consisted of macrocyclic arrangements bound through $-NCH_3-$ bridges (Fig. 1B). The main difference between polymers I and II resulted only in their physical properties. Polymers III and IV had different structures from those described above. Polymer III was composed of B_3N_3 rings bonded through $-NCH_3-$ bridges (Fig 1B) and direct BN interring bonds (Fig. 1C) with a "two-point" structure (16), while polymer IV was composed essentially of B_3N_3 rings linked through $-NCH_3-$ bridges. The structure of these polymers was not very close to that of BN, which could explain the low crystallite lengths measured in those cases.

TABLE 3
X-Ray Diffraction Data for the Samples after a 1800°C Annealing

	Reflection					
	(002)			(10)		
Sample from	2θ	d(Å)	L_c(Å)	2θ	d(Å)	L_a(Å)
Polymer I	26.59	3.34_9	148.7	41.58	2.16_4	496
Polymer II	26.54	3.38_0	143.2	41.51	2.17	413
Polymer III	26.49	3.36_1	138.0	41.7	2.16_0	362
Polymer IV	26.39	3.37_4	133.3	41.62	2.16_8	369

CONCLUSION

Boron nitride obtained from various borazinic precursors had showed important differences depending on the nature of the borazine involved. These results could be interpreted as a precursor memory of the materials. The best structural organization had been obtained from the polymers involving borazine, $(HBNH)_3$, in their preparation, presumably due to the structural similarities of the macrocyclic arrangement of the polymer with *h*-BN. However, under our experimental conditions, it was not possible to observe the (102) diffraction characteristic of a graphitic structure; this result had been previously described for several carbon fiber precursors.

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