

# Alkylaminoborazine-based precursors for the preparation of boron nitride fibers by the polymer-derived ceramics (PDCs) route

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## Abstract

Various borazine-based polymeric precursors can be prepared from tris(alkylamino)boranes and B-tri(chloro)borazine. Their chemical structures are described and compared in this review, along with their melt-spinnability. After polymer-to-ceramic conversion, the mechanical performances of the ensuing BN fibers are analyzed in relation with the structure of the corresponding thermoplastic polymers. The most promising results were obtained with B-tri(methylamino)borazine, which appears, at the present time, as the best candidate for a potential industrialization of the process. However, promising results were also obtained with borylborazines. This comparative study clearly emphasizes that the synthesis of tailored polyborazines is one of the key point for the preparation of high-performance BN fibers.

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## 1. Introduction

Boron nitride is an old commercial ceramic material of great importance for advanced technological applications. Similarly to carbon, different polymorphic forms of BN can be prepared, namely hexagonal (h-BN), cubic (c-BN), rhomboedral (r-BN) or würtzite (w-BN) boron nitride. The hexagonal polymorph is composed of sheets of hexagons, on the summits of which are alternatively placed boron and nitrogen atoms. All atoms are linked by covalent bonds within the sheets (*a*-axis) whereas two subsequent layers are linked by Van der Waals-type bonds (*c*-axis). The sheets are stacked up in such a way that hexagons of two consecutive layers are below each other and, along the *c*-axis, boron atoms alternate nitrogen atoms (Fig. 1). The anisotropic structure of h-BN provides unique mechanical, electrical, optical and thermal properties. The most relevant are the following:<sup>1</sup>

- Low coefficient of thermal extension (CTE), lower in *a* than in *c* direction

- Great resistance towards thermal shocks between 25 °C and 2000 °C (under nitrogen)
- Strong resistivity of  $3 \cdot 10^7 \Omega \text{ cm}$  in *a* direction and  $3 \cdot 10^9 \Omega \text{ cm}$  in *c* direction
- Great resistance towards oxidation upon 900 °C
- High tensile strength and Young's modulus in the *a* direction

As expected, these properties are highly dependent on the chemical purity, crystallinity and microstructural ordering of the samples and, thus, on their preparation method.

BN powders can be prepared by classical high-temperature route, involving cheap reagents like boric acid and urea (e.g.).<sup>2</sup> Most of the BN articles commercially available are made by hot-pressing of BN powders or by chemical vapor deposition (CVD) growth technique.

Among BN shaped materials, continuous thin fibers are of particular scientific and technologic importance, due to their potential application as fibrous reinforcements within composite materials, in replacement of carbon fibers for uses at high temperature in aggressive environment. Numerous works have been devoted to the preparation of BN fibers. Historically, Economy et al. were the first to achieve BN fibers in

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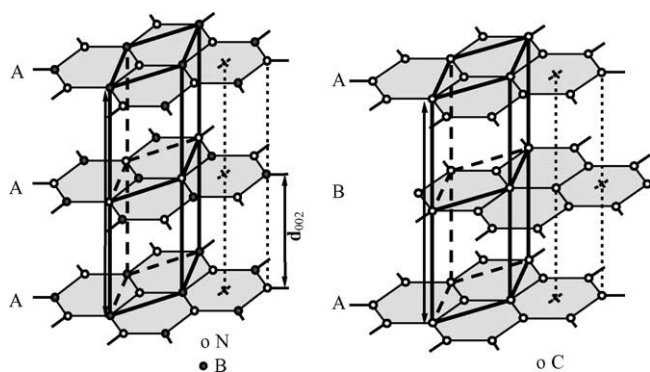


Fig. 1. Comparative crystallographic structure of h-BN and carbon graphite.

the 60s.<sup>3</sup> Their technique was based on the thermal nitridation of  $B_2O_3$  fibers by ammonia, followed by heat treatment at higher temperature under nitrogen. Although this technique allowed the fabrication of fibers with interesting mechanical properties (tensile strength,  $\sigma$ , of 1.3 GPa and Young's modulus,  $E$ , of 70 GPa), it presented some technological and purity inconveniences. First, control of the nitridation process was rather difficult and green fibers always contained residual oxide phases, which led to a decrease in their mechanical properties during ageing.

This conclusion clearly emphasized the need for a more versatile method for BN fibers preparation, namely the preceramic polymer route. The conversion of inorganic polymers into non-oxide ceramics was initially proposed by Lappert et al.<sup>4</sup> and Chantrell and Popper<sup>5</sup> in the 60s, and later developed by Yajima et al.<sup>6</sup> and Verbeek and co-workers<sup>7</sup> for the preparation of Si-based ceramic fibers in the 70s. This chemical approach was reviewed elsewhere.<sup>8</sup> It consists in the synthesis of a molecular precursor, its transformation into a preceramic polymer, which should be soluble and/or melt-processable, and finally the thermal and chemical conversion of the shaped crude product into ceramics like for instance ceramic fibers (Fig. 2).

Numerous studies were devoted to the synthesis of molecular and/or polymeric BN precursors in the past three decades. These works stimulated two reviews depicting 20 years of progress in the field of boron–nitrogen chemistry.<sup>1,9</sup> Among boron- and nitrogen-containing molecular compounds, borazine,  $H_3B_3N_3H_3$ , and its derivatives like the B-tri(alkylamino)borazines,  $[(RR')N]_3B_3N_3R''_3$ , are of particular interest (Fig. 3). Indeed, the borazinic core consists in a six-member ring, which is the basis of the structure of h-BN.

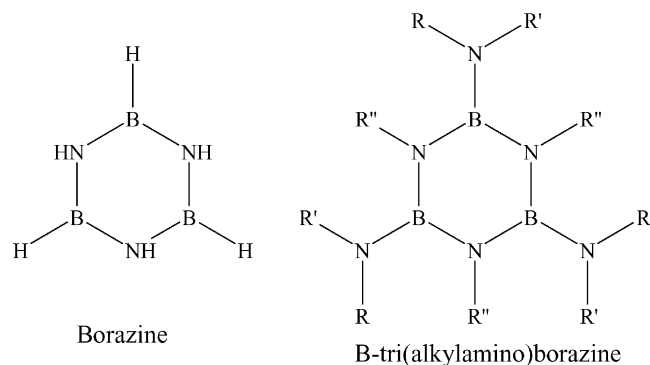


Fig. 3. Comparative structures of borazine and B-tri(alkylamino)borazine.

Two different strategies were investigated for the preparation of BN fibers. The borazinic ring may be either a part of the polymer backbone or be pendant to the polymer backbone. The latter was reviewed elsewhere<sup>9</sup> but, according to our knowledge, this kind of polymer has never been used for fiber preparation. It is interesting to notice that in addition to these two kinds of polymer, Seyferth and Rees produced BN fibers from linear polymers obtained by reaction of decaborane with diamines,  $[-B_{10}H_{12}\text{-diamine-}]_n$ .<sup>10</sup> Short green fibers were obtained from a dimethylformamide solution and their pyrolysis under ammonia up to 1000 °C gave BN fibers.

More suitable for large batch productions are the polymers derived from borazine,  $H_3B_3N_3H_3$ , namely the polyborazylenes. They were extensively studied in reason of their excellent ceramic yield, which is related to the absence of carbon-based groups in their structure. They were thermally synthesized via dehydrogenation reactions. The major encountered problem was that these polymers were thermoset and could not be melt-processed into shaped green articles, and particularly into polymer fibers. A possibility to overcome that drawback is to dissolve polyborazylenes into liquid borazine.<sup>11</sup> The resulting solution could exhibit a viscosity consistent with a spinning operation at 70 °C. The as-spun fibers were converted into BN fibers at 1250 °C under ammonia. Unfortunately, only few BN fibers of 3  $\mu\text{m}$  in diameter were prepared and they displayed many defects preventing their handling. An alternative route to overcome the thermoset behavior of polyborazylenes was proposed by Sneddon et al.<sup>12</sup> It consisted in the linkage of dipentylamino groups to the polyborazylene backbone, yielding the so-called “second-generation polyborazylene” polymers. Their rheological properties were appropriate for a melt-spinning step and flexible, uniform and defect-free crude fibers were prepared. A thermal treatment under ammonia up to 1000 °C led to the formation of amorphous BN fibers of  $\sim 30 \mu\text{m}$  in

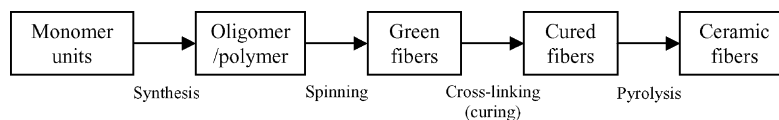


Fig. 2. General procedure for the preparation of ceramic fibers by the PDCs route.

diameter. Their low mechanical performances ( $\sigma$  of 180 MPa and  $E$  of 14 GPa) should be related both to an inappropriate melt-spinning apparatus and to the final pyrolysis temperature, which is too low to afford a complete crystallization of the fibers. Nevertheless, it appears clearly that the presence of carbon-based groups within the polymer notably increases its melt-processability.

Beside polyborazylene derivatives, the polyborazines are the most promising polymeric precursors. The term polyborazine refers to all polymers containing borazinic rings,  $B_3N_3$ , which are not prepared from borazine,  $H_3B_3N_3H_3$ . Paine and co-workers prepared polyborazines by reaction of B-tri(chloro)borazine with disilazane-based reactants.<sup>13</sup> Their dissolution in liquid ammonia could yield to a solution exhibiting spinnability.<sup>13</sup> BN fibers of 5–50  $\mu\text{m}$  in diameter were obtained after pyrolysis up to 1650 °C. Paciorek et al. prepared thermoplastic polymers from B-tri(amino)-*N*-tri(alkylsilyl)borazines.<sup>14</sup> Green fibers were melt-spun from some polymers and subsequently converted into amorphous BN fibers by thermal treatment under ammonia up to 1000 °C. Kimura and Kubo also established that polyborazines, prepared by thermolysis of a mixture of laurylamine and B-tri(methylamino)borazine, exhibited melt-spinnability.<sup>15</sup> Crude fibers were prepared and then converted by an appropriate thermal treatment into BN fibers with following characteristics: diameter, 10  $\mu\text{m}$ ; tensile strength, 980 MPa and Young's modulus, 78 GPa. All these works highlight the importance of the presence of alkylamino groups in polyborazines to provide required properties for melt-spinning.

In conclusion, one of the most promising methods for the preparation of BN fibers is to use thermoplastic polyborazines derived from B-tri(alkylamino)borazines. Since 1998, our group has reinvestigated the B-tri(alkylamino)borazine chemistry in order to prepare polyborazines tailored for the preparation of BN fibers by melt-spinning. In the present paper, these different routes are reviewed and comparatively studied in terms of the structural differences between the polymers and of the mechanical performances of the resulting BN fibers.

## 2. Experimental

It is important to notice that all boron-nitrogen derivatives presented therein are moisture-sensitive. Therefore, all ex-

periments were performed under atmosphere of pure argon using standard vacuum line and Schlenk techniques. Polymer green fibers have been prepared on a lab-scale melt-spinning apparatus set up in a glove-box. In a typical experiment, polymer was molten within a heater block until an appropriate viscosity was obtained. It was subsequently pressed by a piston through a spinneret having a single 0.2 mm diameter capillary. The polymer fiber emerging from the capillary as an endless filament was stretched and collected on a rotating spool. The green fibers were then converted into ceramic fibers by an appropriate curing and pyrolysis process, under ammonia then nitrogen up to 1800 °C (see, ref. 16). The polymer-to-ceramic conversion under ammonia allows to cure green fibers and to remove all the carbon-containing groups.

## 3. Discussion

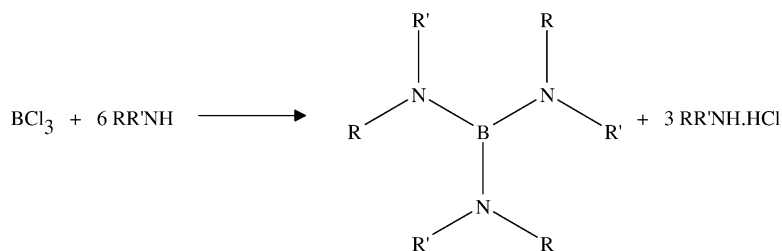
### 3.1. Tris(alkylamino)boranes

The tris(alkylamino)boranes can be prepared in high yield through a simple reaction involving boron trichloride and an excess of the corresponding alkylamine (Scheme 1).<sup>17,18</sup>

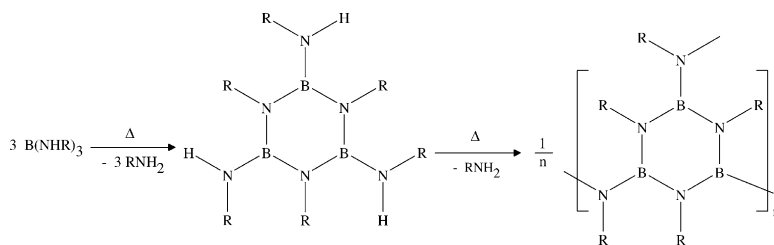
It is also well-known that the thermolysis of tris(monoalkylamino)boranes,  $B(NHR)_3$ , under reduced pressure or inert atmosphere, led to the formation of B-(alkylamino)-*N*-(alkyl)borazines,  $[R(H)N]_3B_3N_3R_3$ , and finally to the corresponding polyborazines (Scheme 2).<sup>17,18</sup> The transformation of tris(alkylamino)boranes into polyborazines can therefore be conducted through a simple one-spot reaction. The key step of this process is the elimination of alkylamines and the formation of alkylamino bridges,  $-B-N(R)-B-$ , between two boron atoms (Scheme 3).

The main feature of borazines and polyborazines derived from tris(monoalkylamino)boranes is that their borazinic nitrogen atoms are bonded to alkyl groups.

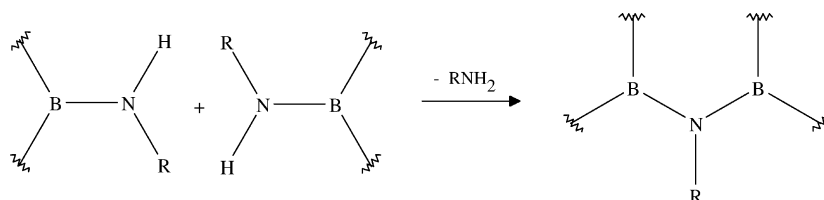
Among these compounds, tris(methylamino)borane,  $B(NHCH_3)_3$ , seems the most promising for the preparation of BN fibers because it offers the best ceramic yield within this series. This derivative was moreover used for the fabrication of BN matrices, coatings and  $Si_3N_4$ -BN composites.<sup>19</sup> Direct heating of  $B(NHCH_3)_3$  under argon flow and mechanical stirring, up to 180 °C, led to the formation of the thermoplastic polyborazine **1**<sup>20</sup> (Scheme 4). Size exclusion chromatogra-



Scheme 1.



Scheme 2.



Scheme 3.

phy analysis gave  $M_w$  value of  $\sim 900$  and DSC analysis gave a glass transition temperature,  $T_g$ , of  $73^\circ\text{C}$ .<sup>20</sup>

Continuous green fibers were easily melt-spun from **1** at  $150^\circ\text{C}$  using classical spinning conditions described in the experimental part. Polymer-to-ceramic conversion was conducted under ammonia up to  $650^\circ\text{C}$  then under nitrogen up to  $1800^\circ\text{C}$ . SEM images of the final product showed that most of the fibers were split during the thermal treatment and only thin BN skin remained. Some retained their initial aspects forming BN tubes (Fig. 4).<sup>20</sup> These observations indicated a difference in behavior between the core and the surface of the fibers during the heating step.

Thermogravimetric (TG) analyses of **1** were performed under ammonia and/or nitrogen in order to explain the formation of BN tubes. It appeared that ammonia decomposed polymer **1** into the B-amino-*N*-methylborazine **2**,  $(\text{NH}_2)_3\text{B}_3\text{N}_3(\text{CH}_3)_3$ , via transamination reactions (Scheme 5).<sup>20,21</sup>

It was observed that, at low temperature, polycondensation of **2** mainly occurred giving the thermoset polyborazine **3**, which is composed of  $\text{B}_3\text{N}_3$  rings mainly linked through  $\text{-B-N(H)-B-}$  bridges. In contrast, at higher temperature, **2** was

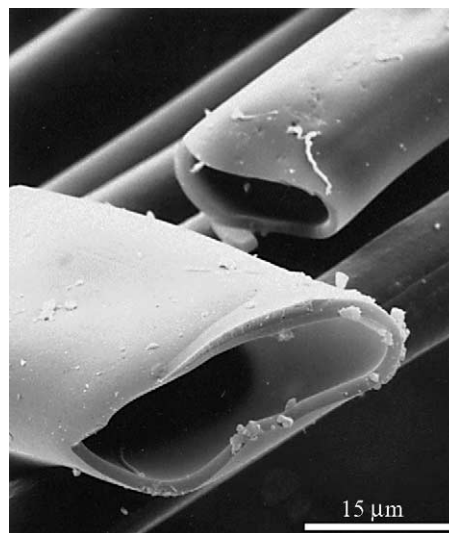
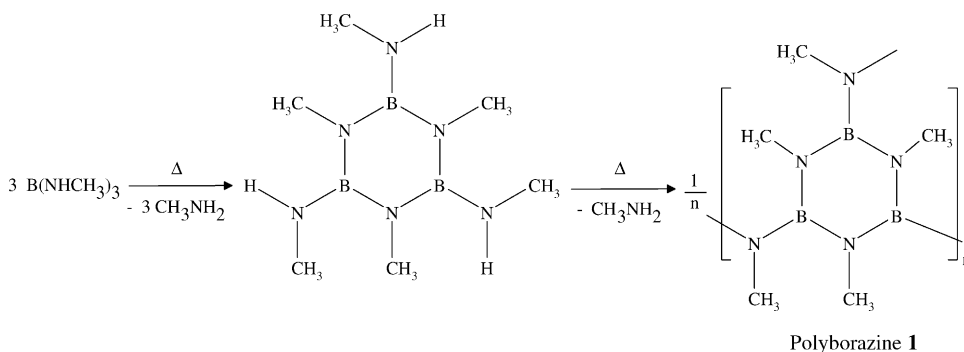
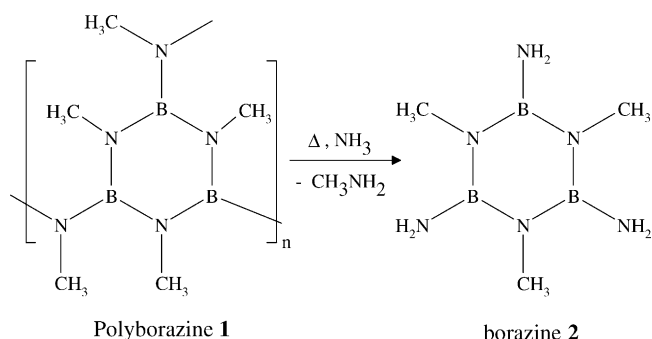


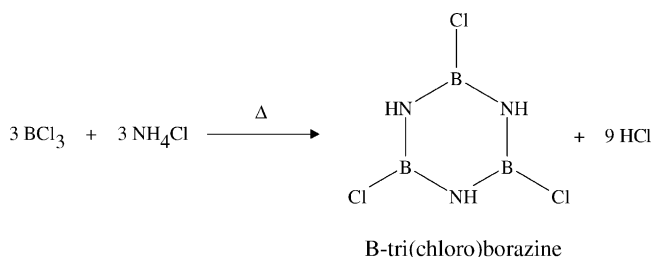
Fig. 4. SEM image of BN tubes resulting from the heating of polymer **1** fibers.



Scheme 4.



Scheme 5.

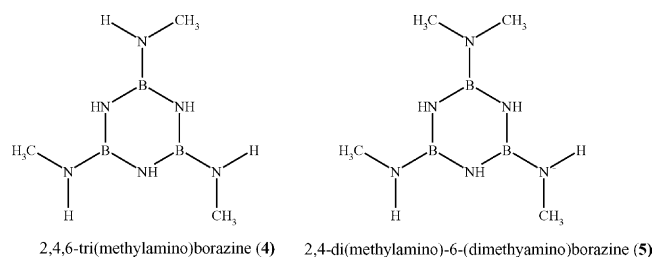


Scheme 6.

rather sublimed.<sup>20</sup> Moreover, **3** gave boron nitride in high yield when heated up to 1800 °C.

These results tend to support the following mechanism for the formation of BN tubes: during the first stage of the pyrolysis process, i.e., the curing step, the temperature was low and the surface of the fibers was in contact with an excess of ammonia. Polyborazine **1** was decomposed by the latter into borazine **2**, which mainly yielded thermoset polyborazine **3** onto the surface of the fibers. These were therefore cured and the so-formed skin could support a further increase in temperature. At higher temperature, the core of the fibers reacted with ammonia giving **2**, which then sublimed.

Due to the thickness of their skins, the BN tubes could not be handled, showing that aminoborane-derived polyborazines are not suited for the production of high-performance BN reinforcing agents. This conclusion should be related to the presence of alkyl groups bonded to the nitrogen borazinic atoms within the polymeric precursors, which appears to be

Fig. 5. Comparative structures of borazine **4** and **5**.

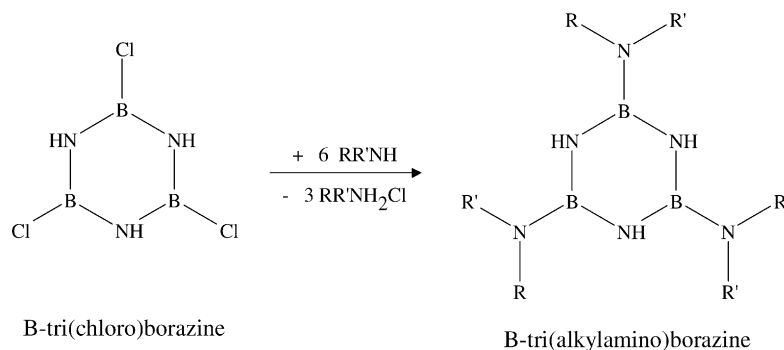
crippling for the polymer-to-ceramic conversion step of BN fibers preparation. Consequently, attention was focused on polyborazines containing hydrogen bonded to the borazinic nitrogen atoms.

### 3.2. B-tri(alkylamino)borazines

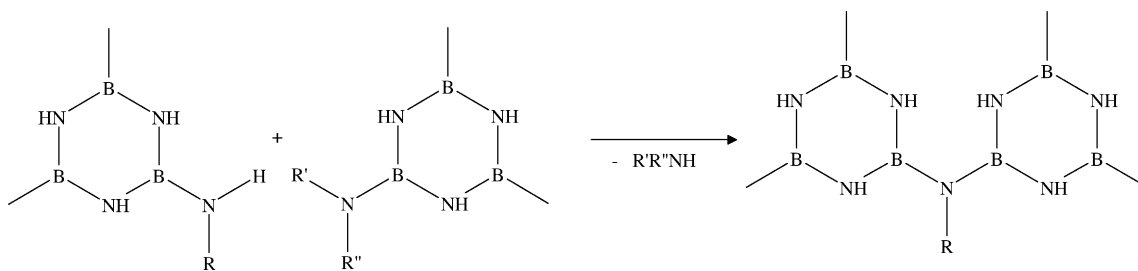
One convenient route for the preparation of B-tri(alkylamino)borazines, (RR'N)<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>, exhibiting hydrogen atoms bonded to the borazinic nitrogen atoms is the substitution reaction of chlorine atoms of B-tri(chloro)borazine (TCB), Cl<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>. The latter is well-known from the 50s and can be easily prepared from boron trichloride and ammonium chloride (Scheme 6).<sup>22</sup>

Chlorine atoms can be substituted with amino groups through the direct reaction of an excess of primary or secondary amines with TCB (Scheme 7).<sup>23</sup>

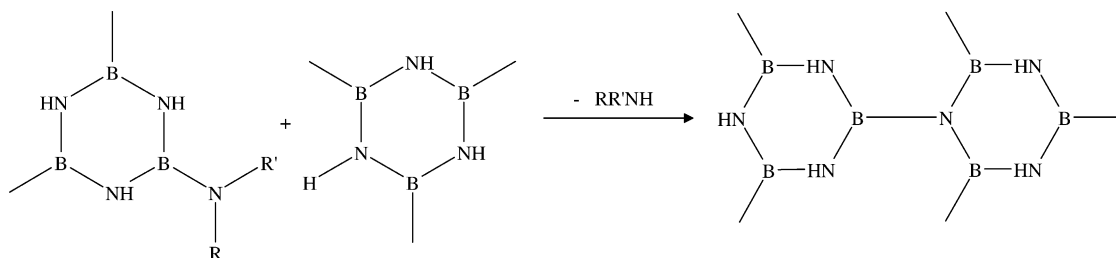
As mentioned above, the results obtained with polyborazylens tend to support that the precursors must contain carbon-based groups in order to exhibit melt-spinnability. Among B-tri(alkylamino)borazines, those pertaining methyl groups seem the most appropriate due to their higher ceramic yields. Within this series, two different borazines emerged as potential candidates for high-performance BN fibers preparation: 2,4,6-tri(methylamino)borazine [CH<sub>3</sub>(H)N]<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> (**4**) and 2,4-di(methylamino)-6-(dimethylamino)borazine [CH<sub>3</sub>(H)N]<sub>2</sub>[(CH<sub>3</sub>)<sub>2</sub>N]B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> (**5**) (Fig. 5). The polycondensation reactions of B-(alkylamino)borazines are well-documented. When heated under inert atmosphere or under vacuum, they can undergo condensation or rearrangement reactions. First, condensation reactions can occur be-



Scheme 7.



Scheme 8.



Scheme 9.

tween two amino groups pertaining to two different borazines. The mechanism is similar to that depicted for tris(alkylamino)borane (Scheme 3) and leads to the formation of alkylamino bridges between two rings (Scheme 8).<sup>24</sup>

More recently, Paciorek et al. reinvestigated the behavior of B-(alkylamino)borazines during heating and showed the existence of three competitive mechanisms.<sup>21,25</sup> Beside the formation of alkylamino bridges (depicted above), direct inter-cyclic bonds can be formed (Scheme 9).

Beside these two condensation mechanisms, intra-cyclic rearrangements can be envisaged when borazines contain secondary amino substituents (Scheme 10).

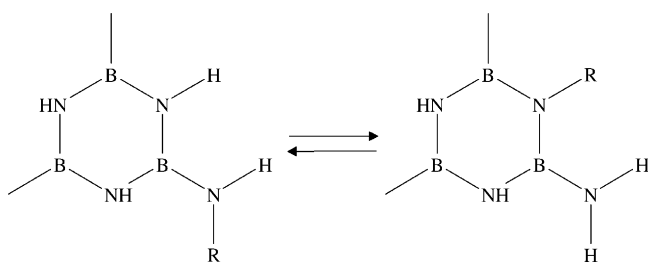
These reactions led to the formation of amino groups, which can undergo condensation reactions and formed either amino bridges,  $-B-N(H)-B-$ , or direct inter-cyclic bonds with elimination of ammonia.

The thermolysis under argon of borazines **4** and **5** up to  $\sim 180^\circ\text{C}$  yielded polymers **6** and **7**, respectively. Polymers **6** and **7** both exhibited glass transition temperatures in the range  $65\text{--}90^\circ\text{C}$ , depending on the experimental conditions.<sup>26–28</sup>

The structure of polyborazines **6** and **7** can be discussed according to the possible polycondensation mechanisms depicted above.<sup>16,26,29</sup> Gas chromatography analy-

ses performed during the thermolysis of borazine **4** showed that methylamine is the main gas evolved and only traces of ammonia were detected. In contrast, both methylamine and dimethylamine evolved during the thermolysis of **5**, the latter being the main one eliminated. Traces of ammonia were also detected. The preferential elimination of dimethylamine during the heating of **5** is consistent with the relative lability of the corresponding amines. It is also interesting to note that, during heating of both **4** and **5**, amines are mainly eliminated above  $130^\circ\text{C}$  and that the proportion of ammonia in the mixture increased with the temperature up to  $180^\circ\text{C}$ . Therefore, both polycondensation pathways, namely formation of amino bridges and direct inter-cyclic bonds, can be envisaged for the formation of **6** and **7**. Moreover, the increasing amount of evolved ammonia tends to support that the intra-cyclic rearrangement is favored at higher temperature. Liquid-state  $^{13}\text{C}$  NMR investigations tend to support that the amount of  $B-N(\text{CH}_3)-B$  bridges is lower in polyborazine **7** than in **6**.<sup>26</sup> However, solid state  $^{15}\text{N}$  NMR analyses are in progress in order to obtain more information concerning the structure of **6** and **7**.<sup>30</sup> Indeed, borazinic nitrogen atoms exhibit different electronic environments whether they are bonded to hydrogen atoms, other borazinic rings or methyl groups.

Continuous green fibers were melt-spun from **6** and **7**. Both crude fibers were flexible and free of defects as shown in Fig. 6. They were successfully converted into high-performance BN fibers by heat treatment under ammonia then nitrogen. Fig. 7 shows comparative SEM images of the ensuing ceramic fibers. BN fibers obtained from polyborazine **7** exhibit fluting on their surface. This can be related to the lower ceramic yield of **7**, involving a stronger shrinkage during the polymer-to-ceramic conversion step. Moreover, **7**-derived BN fibers display a more granular texture than that of **6**-derived fibers. This can be related to their higher degree



Scheme 10.

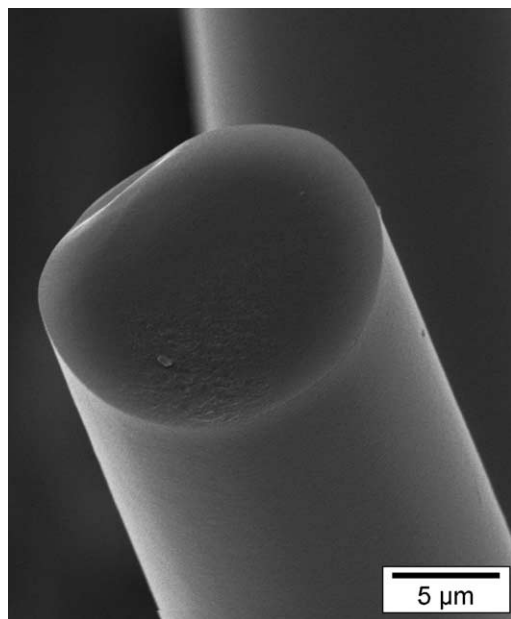


Fig. 6. Typical SEM image of a green fiber obtained from polyborazine **6**.

of crystallization. Therefore, their mechanical properties are different. Indeed, we showed that the crystallization step, as the ultimate step of the polymer-to-ceramic conversion process, was necessary to increase the mechanical properties of the fibers.<sup>28</sup> **6**-derived fibers reached their maximal tensile strength,  $\sigma$ , at 1800 °C. For instance, values as high as 2.0 GPa in tensile strength and 400 GPa in Young's modulus were measured.<sup>31</sup> Above 2000 °C, a strong decrease in  $\sigma$  was generally observed and related to a concomitant increase in the degree of crystallization. In contrast, **7**-derived fibers exhibited maximal values in tensile strength (1.3 GPa)

at 1600 °C. Above this temperature,  $\sigma$  decreased due to a higher degree of crystallization. All these conclusions should be related to noticeable differences in structure between these two polymers. The structure of **7** is probably closer to that of h-BN than **6**, leading to a crystallization process shifted to the lower temperature. This tends to support our assumption concerning the structure of **7**, which should exhibit more direct inter-cyclic BN bonds than that of **6**. Along with a higher degree of crystallization, the main drawback of **7**-derived fibers is their lower failure strain,  $\epsilon$ , than that of **6**-derived fibers. They exhibit therefore a higher toughness and should be handled with more care. As a consequence, we are now focusing our attention on the B-tri(methylamino)borazine **6** for a potential industrialization of the BN fibers preparation process.

### 3.3. Borylborazines

Wynne and Rice suggested an ideal polymer structure tailored for the melt-spinning process.<sup>8</sup> It consists in a linear backbone composed of rings linked through multi-atom bridges. The rings should prevent reversion reactions and the bridges should afford sufficient flexibility during the spinning step. Therefore, much attention is focused on the preparation of boron- and nitrogen-containing polymers exhibiting such structure. To our knowledge, Clément and Proux described the first example of polyborazines having multi-atom bridges between the rings. They were prepared by transamination reactions of borazines (Scheme 11).<sup>32</sup>

The main drawback of these polymers is that their multi-atom bridges were mainly made of carbon, which should lead to a drastic decrease in their ceramic yield. The key point of this study was to replace alkyl-diamines by tris(alkylamino)boranes, B(NHR)<sub>3</sub>. The main

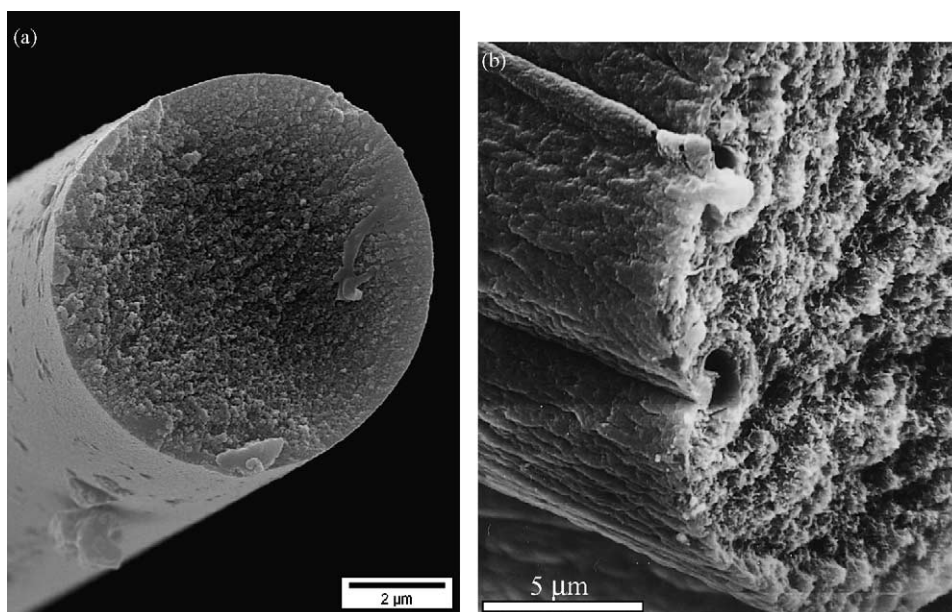
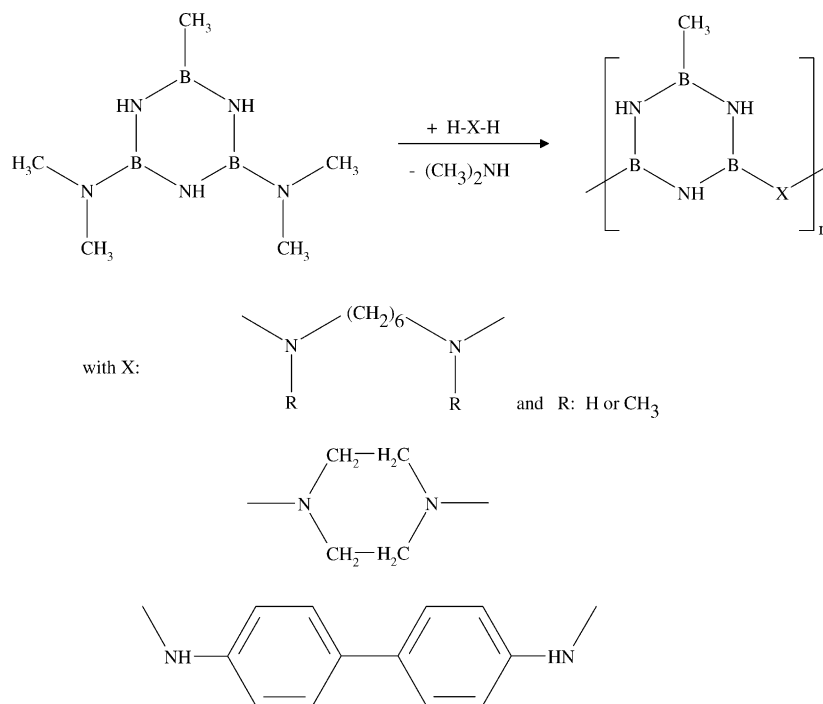


Fig. 7. SEM images of the BN fibers obtained from (a) polyborazine **6** and (b) polyborazine **7**.



Scheme 11.

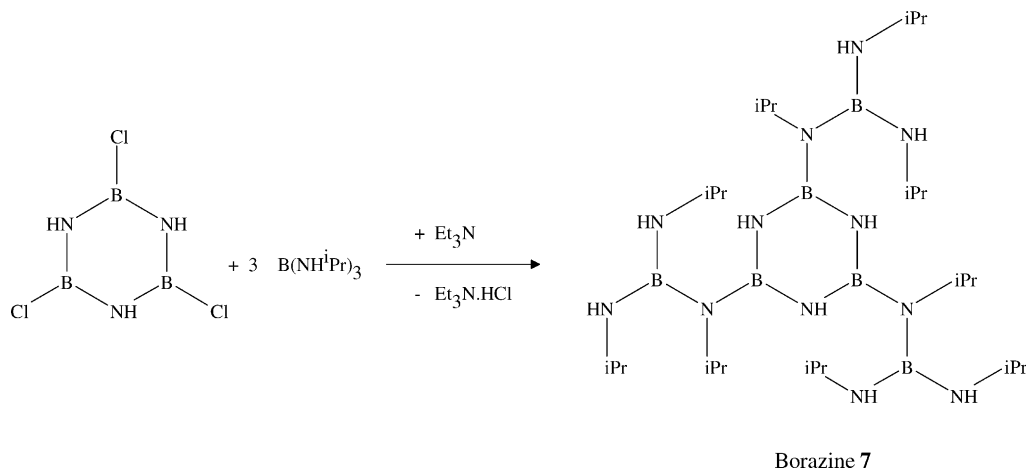
advantage of the latter is that they are made around a –N–B–N– backbone. We have first demonstrated that the reaction of B-tri(chloro)borazine with B(NH*i*Pr)<sub>3</sub> led to the formation of the corresponding borylborazine, B-tri[bis(isopropylamino)boryl(isopropyl)amino]borazine **7** (Scheme 12).<sup>33</sup>

This derivative underwent polycondensation reactions upon thermolysis in vacuum. B(NH*i*Pr)<sub>3</sub> was detected as the only compound evolved during the experiment. Polyborazine **8** containing both direct inter-ring bonds and three-atom bridges was obtained (Scheme 13). According to <sup>11</sup>B and <sup>1</sup>H NMR results, **8** mainly contained three-atom bridges.<sup>34</sup>

BN matrices and oxidation-protective coatings were successfully prepared from this polymer.<sup>34</sup> A good ceramic

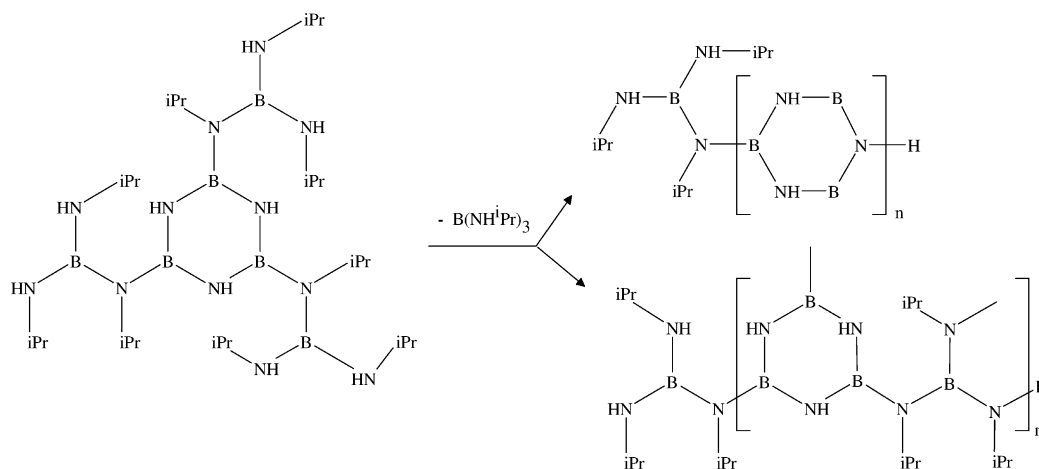
yield is a key point for the preparation of BN fibers in order to reduce the shrinkage of green fibers during curing and pyrolysis. Borylborazine **9** was therefore prepared from B(NHCH<sub>3</sub>)<sub>3</sub> and subsequently heated in vacuum up to 150 °C. It is interesting to notice that **9** was always obtained mixed with its oligomers, due to the high reactivity of B(NHCH<sub>3</sub>)<sub>3</sub>. The latter was detected as the unique product evolved during heating of **9** and NMR investigations showed that the resulting polyborazine **10** mainly contained three-atom bridges between the rings (Scheme 14).<sup>35,36</sup>

Polyborazine **8** with a glass transition temperature of 60 °C was successfully melt-spun into continuous low-diameter green fibers. In contrast, polyborazine **10** with a glass transition temperature of 55 °C was difficultly melt-spun into



Scheme 12.



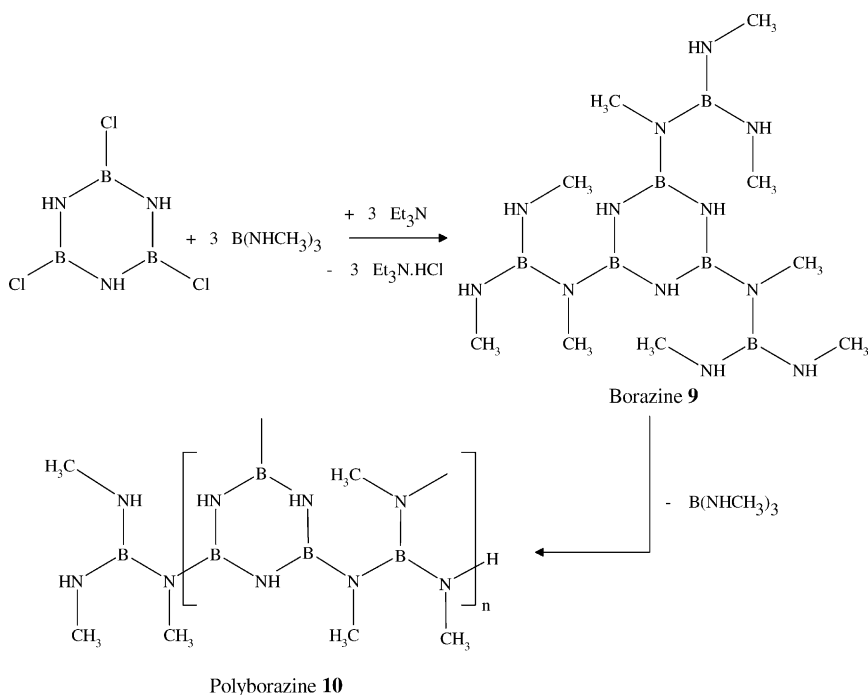
Possible inter-ring linkages in Polyborazine **8**

Scheme 13.

several meters of large-diameter green fibers. The poor melt-spinnability of **10** can be related to the higher reactivity of the corresponding di(methylamino)boryl(methyl)amino groups, which should result in a more three-dimensional structure for **10**. Both green fibers were subsequently converted into BN fibers under ammonia up to 1000 °C then nitrogen up to 1800 °C. Polymer **8**-based fibers had tensile strength of 890 MPa and Young's modulus of 140 GPa whereas values of 170 MPa and 30 GPa, respectively, were measured for **10**-based fibers.<sup>35,36</sup> This result is of particular interest because it showed that mechanical performances of BN fibers are more

related to the structure of their polymeric precursor than to its ceramic yield.

SEM image of a **8**-based fiber is shown in Fig. 8 and fluting can be observed on the surface along the fiber axis. Moreover, the cross-section exhibits a coarse-grain texture with numerous cavities. These observations should be related to the low ceramic yield of **8** and, therefore, to an important shrinkage during the polymer-to-ceramic conversion step. However, when fibers with comparable mechanical properties were obtained,  $T_g$  of **8**-based polymer was significantly lower than that of B-tri(alkylamino)borazine-based polymers, and so the



Scheme 14.

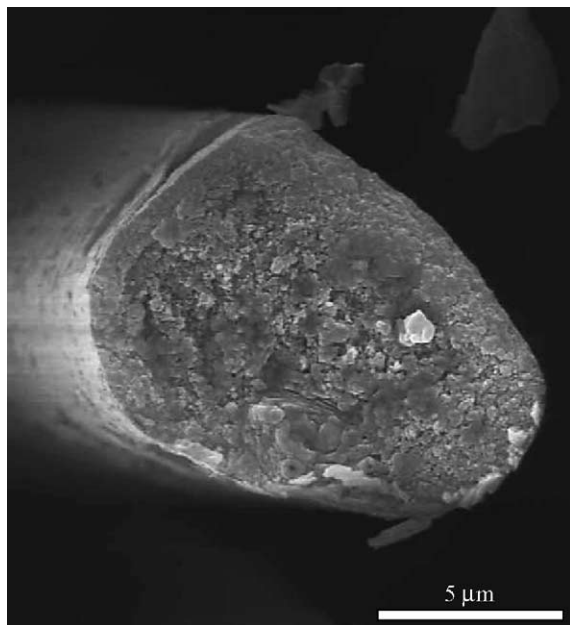


Fig. 8. SEM images of a BN fiber obtained from polymer **8**.

melt-spinning temperatures. Therefore, in order to improve the mechanical properties of **8**-derived fibers, some works are in progress with the aim of preparing **8**-like polymers having  $T_g$  comparable to these of **6**.

#### 4. Conclusion

Various borazine-based polymeric precursors were described and compared in terms of chemical structure and performance of the BN fibers they led to. The most promising results were obtained with B-tri(methylamino)borazine **4**, which appears, at the present time, as the best candidate for a potential industrialization of the process. However, an interesting alternative is the borylborazine route. Although the mechanical performances of their ensuing fibers are lower than these obtained with **4**, this study shows that the ceramic yield of the precursor, which was universally considered as a key point, must be counterbalanced with its chemical structure. Therefore, the synthesis of tailored polymeric precursors and a technical optimization of the melt-spinning and pyrolysis steps are seen as the key points for preparing, in a close future, BN fibers exhibiting mechanical performances required for uses in CMCs as reinforcing agents.

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