

# Borylborazines as new precursors for boron nitride fibres

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## Abstract

A variety of borylborazine-based polymers were successfully converted into boron nitride fibres via the preceramic polymer route. In this procedure, four monomers were polycondensed into highly tractable polymers which could be easily melt-spun into fine-diameter green fibres. These polymeric filaments were then transformed into boron nitride fibres after a well-defined heat-treatment at 1800 °C in a controlled atmosphere. All the resulting ceramic fibres were mechanically tested. In particular, results showed that the promising mechanical properties for two of the polymer-derived fibres were closely related to the structural units of the corresponding preceramic polymers.

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## 1. Introduction

Due to its specific properties, i.e., low density, good resistance towards oxidation up to 850 °C and chemical and structural stability, hexagonal boron nitride (h-BN) is an important ceramic which can be used for high temperature structural applications [1]. However, its use is limited by its inherent brittleness as observed in the non-oxide ceramics. To overcome this problem, the ceramic can be blended by a reinforcing agent such as continuous fibres to give attractive BN/BN composites. Within this goal, our group has recently made very important progresses in the preparation of BN fibres by spinning of preceramic polymer followed by the curing and pyrolysis of the resulting polymer fibres [2,3]. One of the main advantages of this approach is the possibility of using a large variety of precursors, among which borazine-based compounds are the most attrac-

tive. Actually, previous works investigated by Sneddon [4] and Kimura [5] showed that polymers based on the B<sub>3</sub>N<sub>3</sub> borazinic core could present thermoplastic properties and good spinnability. In particular, these works highlighted that the best spinning properties were always found with polymers bearing alkyl-based groups. Recent reinvestigations by our group on this subject exemplified the need of tailoring the polymers structure to improve the processing properties for the melt-spinning operation which is known to be presumably the crucial step [2,6]. Monomers with two kinds of amino groups bearing by the boron atoms have been used to limit the polymer cross-linking and control the nature of the linkages between the borazinic rings within the resulting polyborazines. For example, an ideal designed polymer was prepared starting from 2-[(CH<sub>3</sub>)<sub>2</sub>N]-4,6-(CH<sub>3</sub>NH)<sub>2</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>. It was used to prepare high performance boron nitride fibres with the following mechanical properties: tensile strength,  $\sigma = 1400$  MPa and Young modulus,  $E = 210$  GPa [6a].

With the aim to correlate the polymer structure with the processing properties in mind, we focused

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our attention on the preparation of another kind of polymer-based compounds, i.e., the borylborazine (borazine core surrounded by three aminoboryl groups) [7]. The innovative idea behind this procedure is to tailor the polymeric precursor structure by increasing the distance between two borazinic rings in order to form higher elongated polymer chains as required by Rice et al. [8]. Previous investigations showed that borazine rings mainly connected through N–B–N three-atom bridges could be easily obtained by either thermal polycondensation of a borylborazine [9] or metathesis of a dichloroborazine with an aminoborane [10]. This kind of arrangement provides peculiar and interesting properties like melt-viscosity and elasticity. The resulting polymer has therefore proven to be an attractive candidate for BN fibres [10,11].

The present paper is devoted to the synthesis of borylborazine-based polymers and, in particular, to their use in the preparation of boron nitride fibres by tailoring their structure and composition.

## 2. Results and discussion

In this study, boron nitride fibres were obtained starting from a series of borylborazine model compounds displaying different alkylamino-based groups. Samples **1**, **2** and **3** were synthesised by thermolysis of the following monomers: [(NHMe)<sub>2</sub>B(NMe)]<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> (**A**), [(NHPr<sup>i</sup>)<sub>2</sub>B(NPr<sup>i</sup>)]<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> (**B**) and {(NMe<sub>2</sub>)[(NHPr<sup>i</sup>)<sub>2</sub>B(NPr<sup>i</sup>)]<sub>2</sub>}<sub>3</sub>N<sub>3</sub>H<sub>3</sub> (**C**), respectively. Their molecular structures are illustrated in Fig. 1.

Structures of polyborazines **1** and **2** were previously discussed [11]. According to the structure of the starting molecular precursors, they present B<sub>3</sub>N<sub>3</sub> rings linked

through either direct BN inter-ring bonds (minor reaction pathway) or three-atom bridges (major reaction pathway). The simultaneous occurrence of these two polycondensation mechanisms (Fig. 2) was recently confirmed by solid state <sup>15</sup>N CP MAS NMR spectroscopy [12]. Based on these NMR data, Fig. 3 proposes an ideal structure for polymers **1** and **2**.

Sample **3** was prepared starting from {(NMe<sub>2</sub>)[(NHPr<sup>i</sup>)<sub>2</sub>B(NPr<sup>i</sup>)]<sub>2</sub>}<sub>3</sub>N<sub>3</sub>H<sub>3</sub>. Although, in a previous study [6a], we showed a possible condensation of the poorly reactive –NMe<sub>2</sub> group by thermal treatment, it is shown in the present paper that the dimethylamino groups are retained within the polymer since no trace of dimethylamine was detected during the polycondensation by gas chromatography coupled with a mass spectrometry. This is also supported by the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the polymer which present the signals corresponding to this group. As a consequence, the two mechanisms previously proposed also occur simultaneously during the polycondensation. In this context, it is clear that the presence of diamino groups bearing by one boron atom inhibits extensive tri-dimensional cross-linking reactions and leads to a “two-point” polymer (referring to the description given by Paine and co-workers [13]).

Polymer **4** was prepared by metathesis reaction of a dichloroborazine derivative (NMe<sub>2</sub>)Cl<sub>2</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> with an aminoborane B(NHMe)<sub>3</sub> (Fig. 4).

Structure of polymer **4** was already described [10]. We also demonstrated that the use of a starting functionalised borazine leads to a “two-point” polymer since the =B–NMe<sub>2</sub> group would not react at room temperature and, therefore, would not participate in the initial ring condensation chemistry. Consequently, the resulting polymer only presents N–B–N bridges between the rings

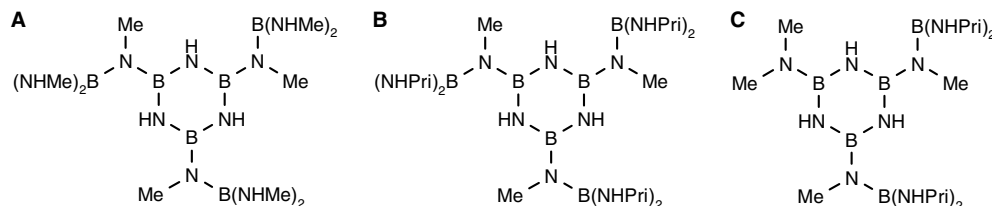


Fig. 1. Starting precursors: **A**, [(NHMe)<sub>2</sub>B(NMe)]<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>; **B**, [(NHPr<sup>i</sup>)<sub>2</sub>B(NPr<sup>i</sup>)]<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub> and **C**, (NMe<sub>2</sub>)[(NHPr<sup>i</sup>)<sub>2</sub>B(NPr<sup>i</sup>)]<sub>2</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>.

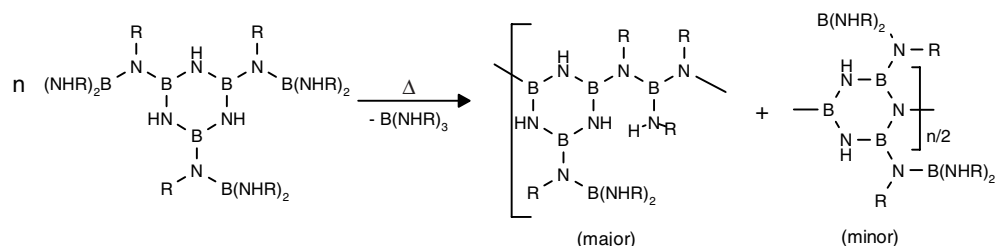
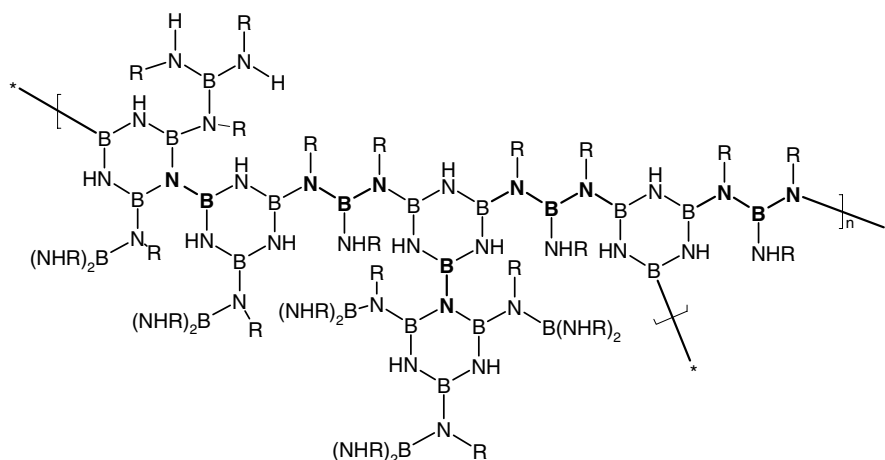
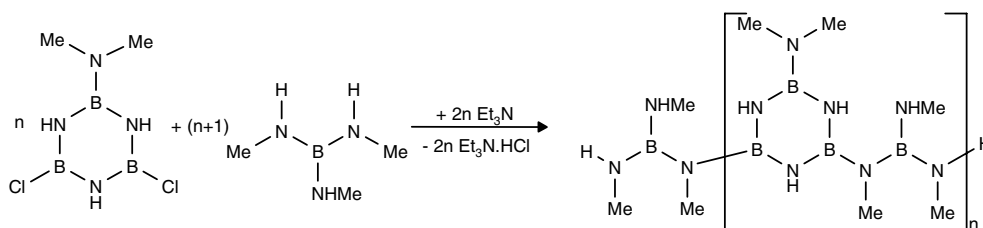


Fig. 2. Two reaction modes during the thermolysis of compounds **A** and **B**.

Fig. 3. Ideal structure proposed for polymers **1** and **2** exclusively based on NMR results.Fig. 4. Reaction scheme for the preparation of polymer **4**.

[10]; this exclusive mechanism was also confirmed by solid state  $^{15}\text{N}$  CP MAS NMR analyses [12].

Table 1 summarises the main characteristics of polymers **1**, **2**, **3** and **4**. DSC and TG analyses allow to measure the glass transition temperature ( $T_g$ ) and the ceramic yield (at 1000 °C in a  $\text{NH}_3$  atmosphere) for each polymer, respectively. Moreover, the polycondensation degree was estimated as the ratio between the evolved  $\text{B}(\text{NHR})_3$  (mol.) and the starting monomer (mol.).

A good *ad equation* between the theoretical (calculated from the polycondensation degree) and the experimental ceramic yield for the three polymers **1**, **2** and **3** is observed. For polymer **4**, the higher difference between both values most probably results from the volatiliza-

tion of a part of the low-molecular weight oligomeric species at low temperature. The ceramic yield obtained at 1000 °C is obviously higher for polymers **1** and **4** in relation with the nature of the pendant alkyl groups (methyl instead of isopropyl). Furthermore, for all polymers, polycondensation degree, glass transition and spinning temperatures are closely related; these three parameters obviously increase in the same way.

Due to the presence of  $=\text{N}-\text{R}$  ( $\text{R} = \text{Me}$  or  $\text{Pr}^i$ ) units, all polymers displayed suitable rheological properties for spinning experiments. As a result, polymer fibres could be obtained by melt-extrusion through a spinneret and subsequent stretching by a spool. The spinning temperature for each polymer is reported in Table 1. From a

Table 1  
Main characteristics of polymers **1**, **2**, **3** and **4**

	Polymer <b>1</b>	Polymer <b>2</b>	Polymer <b>3</b>	Polymer <b>4</b>
Starting precursors	$[(\text{NHMe})_2\text{B}(\text{NMe})]_3-$ $\text{B}_3\text{N}_3\text{H}_3$	$[(\text{NHPr}^i)_2\text{B}(\text{NPr}^i)]_3-$ $\text{B}_3\text{N}_3\text{H}_3$	$(\text{NMe}_2)[(\text{NHPr}^i)_2\text{B}-$ $(\text{NPr}^i)]_2\text{B}_3\text{N}_3\text{H}_3$	$\text{Cl}_2(\text{NMe}_2)\text{B}_3\text{N}_3\text{H}_3 +$ $\text{B}(\text{NHMe})_3$
Polycondensation conditions	150 °C/1.5 h	150 °C/9 h	150 °C/30 h	-10 °C/1 h RT/24 h
Polycondensation degree	1.3	1.4	1.1	0.9 <sup>a</sup>
Theoretical ceramic yield	46.6	30.9	32.5	54.5
Ceramic yield <sup>b</sup> (%)	47	31	33	48
$T_g$ (°C)	55	60	40	20
Spinning temperature (°C)	140	150	110	90

<sup>a</sup> Estimated from the starting reagents.

<sup>b</sup> Under  $\text{NH}_3$  up to 1000 °C.

general point of view, we noticed that the difference between the spinning temperature and the glass transition temperature is lower for the low cross-linked polymers (**3** and **4**) than for the higher cross-linked ones (**1** and **2**). Polymer **3** could be easily extruded at 110 °C, this low spinning temperature is in good agreement with its low  $T_g$  [6a]. The green fibres obtained from polymer **3** are regular in diameter (16–18  $\mu\text{m}$ ), smooth and without surface defects (Figs. 5(a) and (b)). The as-prepared green fibres were then converted into ceramic fibres by an appropriate chemical and thermal treatment (in an ammonia atmosphere up to 1000 °C then in a nitrogen atmosphere up to 1800 °C). The **3**-derived preceramic fibres obtained after heat treatment in a  $\text{NH}_3$  atmosphere at 1000 °C are also free of defects and of flexible form (Fig. 5(c)). The average diameter drop to about on-half the original average value (9  $\mu\text{m}$ ) in good agreement with the weight loss and density change which occur up to 1000 °C.

After the whole polymer-to-ceramic conversion, the fibres were white in colour, homogeneous, with a final diameter of 8  $\mu\text{m}$  which means that there is a very small volume change between 1000 °C (preceramic fibres) and 1800 °C (ceramic fibres). Nevertheless, the ceramic fibres became thin and of brittle form due to the crystallisation process which occur at high temperature from 1400 to 1800 °C. Fig. 6 presents micrographs of BN ceramic fi-

bres obtained from polymer **3**. In particular, Fig. 6(b) shows that the fibre was fluted on the surface along the fibre axis while the high magnification image obtained on the fibre cross-section (Fig. 6(c)) shows a coarse-grained micro-texture due to the well-defined BN crystallites. These features highlighted a high degree of crystallisation of the ceramic material.

In contrast, the polymer **1** presented a poor extrusion ability resulting in numerous filament breakings as well as a poor stretching ability. This feature was related to the important chemical structure inhomogeneity of this polymer due to a faster polymerisation process [11]. Indeed, the presence of  $-\text{B}(\text{NHMe})$  pendant groups results in an increasing of the monomer reactivity and then in a very fast condensation of the monomeric units.

Achievement of boron nitride was supported by FTIR, X-ray diffraction and Raman spectroscopy analyses since the spectra and XRD pattern all present the expected signals for this ceramic.

Table 2 reports the diameter and the mechanical properties measured on the different fibres samples **1.1**, **2.1**, **3.1** and **4.1**, respectively, obtained from polymers **1**, **2**, **3** and **4**.

From a general point of view, the as-prepared fibres report good mechanical properties excepted for fibres **1.1** (for whose the poor  $\sigma$  is related to the large diameter). These promising properties could be ascribed to

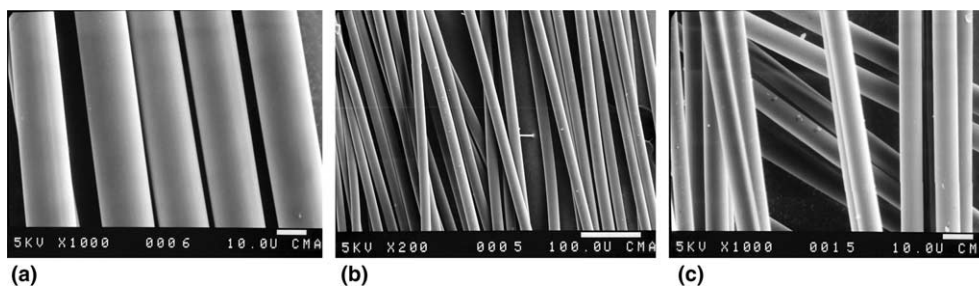


Fig. 5. SEM images of (a, b) green fibres and (c) preceramic fibres heated at 1000 °C.

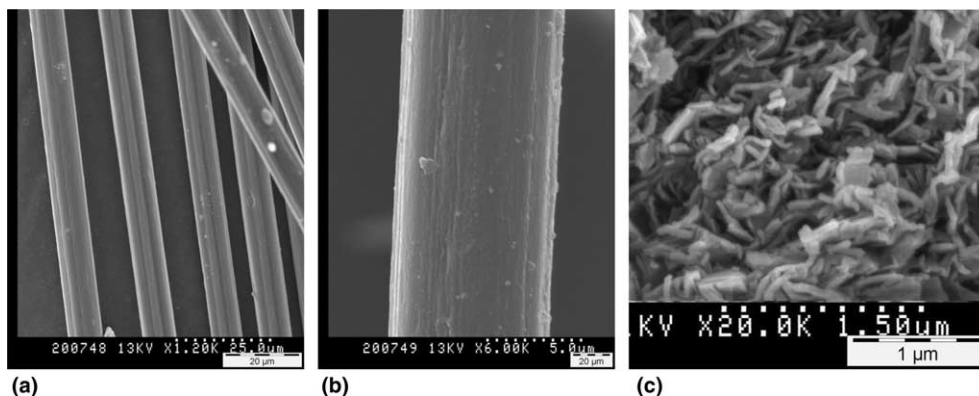


Fig. 6. SEM images of ceramic fibres heated at 1800 °C.

Table 2  
Diameter and mechanical properties measured on the four fibre samples

	Fibres 1.1	Fibres 2.1	Fibres 3.1	Fibres 4.1
Used polymer	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Green fibre diameter ( $\mu\text{m}$ )	~40	30	18	20
Ceramic fibre diameter ( $\mu\text{m}$ )	24.3	10.5	8	9.3
Tensile strength, $\sigma$ (MPa)	170	1130	560	1020
Young's modulus, $E$ (GPa)	30	170	140	190
Strain, $\varepsilon$ (%)	0.54	0.66	0.38	0.50

the nature of the used polymers (presence of flexible three-atom bridges and carbon-based groups within the polymer [4]) which increases their melt-spinnability. These observations showed the close relationship between mechanical properties, diameter and melt-spinnability.

Although these values are not as high as those measured on BN fibres prepared from alkylaminoborazine-based polymers [6a,14], the first attempts reported here showed the potentiality of these borylborazine-based polymers as candidates tailored for the preparation of BN fibres.

### 3. Experimental

#### 3.1. General

All experiments were performed in an argon atmosphere and anhydrous conditions using standard vacuum-line, Schlenk technique and efficient dry-box. All the solvents were used after distillation by standard methods.

#### 3.2. Preparation of polymers 1, 2, 3 and 4

Syntheses and characterisations of polymers **1**, **2** and **4** were already reported in previous papers [9,10]. Polymer **3** was prepared by polycondensation of  $(\text{NMe}_2)[(\text{NHPr}^i)_2\text{B}(\text{NPr}^i)]_2\text{B}_3\text{N}_3\text{H}_3$ . The latter was synthesised by reaction of two eq. of  $\text{B}(\text{NHPr}^i)_3$  with one eq. of  $(\text{NMe}_2)\text{Cl}_2\text{B}_3\text{N}_3\text{H}_3$  in toluene in presence of a tertiary amine. The polycondensation of this monomer was conducted in vacuo under mechanical stirring. A sample of 10.0 g (20.4 mmol) of monomer was slowly heated up to 150 °C during 30 h leading to 6.0 g of a yellow vitreous solid. The volatiles evolved during the process were trapped in liquid nitrogen and characterised as pure tris(isopropylamino)borane (4 g – 21.6 mmol) by  $^1\text{H}$  and  $^{11}\text{B}$  liquid NMR. No trace of dimethylamine was detected. Characterisation of polymer **3**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  (ppm) = 1.05 (s,  $(\text{H})(\text{B})\text{N}[(\text{CH})(\text{CH}_3)_2]$ ), 1.23 (m,  $\text{B}_2\text{N}[(\text{CH})(\text{CH}_3)_2]$ ), 1.80 (m,  $\text{NH}$  amino), 2.16 (m,  $\text{NH}$  amino), 2.56 (s,  $\text{BN}(\text{CH}_3)_2$ ), 3.46 (m,  $\text{NH}$  boraz +  $(\text{H})(\text{B})\text{N}[(\text{CH})(\text{CH}_3)_2]$  +  $\text{B}_2\text{N}[(\text{CH})(\text{CH}_3)_2]$ );

$^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  (ppm) = 25.3 ( $\text{B}_2\text{N}[(\text{CH})(\text{CH}_3)_2]$ ), 27.1 ( $(\text{H})(\text{B})\text{N}[(\text{CH})(\text{CH}_3)_2]$ ), 37.1 ( $\text{BN}(\text{CH}_3)_2$ ), 42.7 ( $(\text{H})(\text{B})\text{N}[(\text{CH})(\text{CH}_3)_2]$ ), 45.6 ( $\text{B}_2\text{N}[(\text{CH})(\text{CH}_3)_2]$ );  $^{11}\text{B}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  (ppm) = 27.9 ( $\text{N}_2\text{BN}(\text{B})(\text{C})$ ), 25.5 (as,  $\text{N}_2\text{BN}(\text{CH}_3)_2$  +  $B$ -bridge), 23.0 ( $B$ -aminoboryl); DSC:  $T_g = 40$  °C; TGA: 33% (up to 1000 °C under  $\text{NH}_3$ ).

#### 3.3. Fibres preparation

Polymer green fibres have been prepared on a lab-scale melt-spinning apparatus set up in a glove-box filled under nitrogen using previously published procedure [2].

After the processing, the green fibres were heated in a tubular silica furnace up to 1000 °C under  $\text{NH}_3$  (25 °C  $\text{h}^{-1}$ ) and then placed in a graphite furnace for a high temperature treatment (1800 °C) under  $\text{N}_2$  (100 °C  $\text{h}^{-1}$ ).

#### 3.4. Mechanical characterisation

Tensile properties were determined from failure tests performed on 50 filaments with a gauge length of 10 mm by using the statistical approach of Weibull as previously described [6a,15].

### 4. Conclusion

In this paper, we reported results of an entire study devoted to borylborazine-based polymers. Four different polymers prepared either by thermal or chemical route from different starting precursors could be successfully converted into BN fibres. We are able to control the polymer structure, depending on the polycondensation mode and the monomer type. It is clear that the high melt-spinnability which is directly linked to an appropriate extrusion and stretchability of the polymer, is provided by both the presence of flexible three-atom bridges and carbon-based groups within the polymer.

Further works are in progress to optimize the polymers characteristics (in terms of polycondensation degree, ceramic yield and nature of the pendant groups) in order to increase the mechanical properties of the derived fibres.

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