Complete characterisation of BN fibres obtained from a new polyborylborazine

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Abstract

A new polymer was prepared at room temperature from a di-chloroborazine and a reactive aminoborane. It displays borazine rings unambiguously linked through three atoms N–B–N bridges. This connecting mode was evidence by ^{15}N solid state NMR. This polyborazine was processed into a continuous polymer fibre of about 21 μm diameter, which was subsequently heat-treated under NH_3/N_2 up to 1800 °C for conversion into BN fibres. The achievement of hexagonal boron nitride was confirmed by X-ray diffraction and Raman spectroscopy. Tensile tests were carried out on the ceramic fibres. The average tensile strength is about 1000 MPa and the Young's modulus is close to 200 GPa. Structural characterisation of the BN fibres was undertaken by polarised light and transmission electronic microscopies.
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1. Introduction

Achievement of high performance hexagonal boron nitride (h-BN) fibres can be considered as a technological challenge since they are needed for the preparation of BN/BN composites with good mechanical characteristics.[1] Taking advantage of the unique set of properties of h-BN,[2] these structural materials could be used in high technological field, at high temperature in oxidative atmosphere, for instance. Moreover, preparation of BN shaped materials, especially fibres, need appropriate method for a good processibility. As evidenced by numerous studies reported in the literature,[3,4] the preceramic polymer route is the most suitable one for the preparation of BN fibres. Actually, a polymer can be proceeded into crude fibre by melt-spinning before its conversion into ceramic. These previous works have also emphasised the need of tailored polymer for the above mentioned crucial step. For example, Sneddon and coworkers[3b] has developed an interesting alternative concerning the preparation of a "second-generation" polymer with dipentylamino pendant groups which limit its reticulation and afford itself good processing properties. In much in the same way, our group has recently demonstrated clear relationships between: (a) the structure of B-alkylamino-substituted borazines, (b) that of the polymers derived therefrom, (c) the melt-spinning behaviour of the latter and (d) the final fibres properties. Indeed, a good processibility is linked to a good polymer alignment in the green fibre and consequently to high mechanical properties of the ensuing BN fibre.[5] It appears that a better comprehension of the polymer structure depends on a better knowledge of the polymerisation mechanisms. In this context, inspiriting by the work of Paine and co-workers[6] and Paciorek et al.,[7] we have investigated the preparation of a new type of polymer by co-condensation reactions at room temperature. By this way, the polymer architecture is better described in relation with the unambiguous reaction mechanism.

The present paper reports the synthesis and the characterisation of a "two points" polymer (referring to the description given by Paine and coworkers[6b]), the achievement of high performances BN fibres therefrom and the complete structural characterisation of these fibres.

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2. Experimental

2.1. Synthesis

All experiments were performed under argon atmosphere and anhydrous conditions using standard vacuum-line, Schlenk techniques and an efficient dry box with solvents purified by standard methods.

2,4-di(chloro)-6-(dimethylamino)borazine[8] ($Cl_2[(CH_3)_2N]B_3N_3H_3$) (**1**) (4.6 g, 24.2 mmol) in toluene (100 ml) were slowly added at $-10\,^\circ C$ under stirring to a solution of tri(methylamino)borane[9] ($B(NHCH_3)_3$) (**2**) (2.6 g, 24.2 mmol) and Et_3N (15 ml). After the addition, the mixture was stirred for 1 h at $-10\,^\circ C$ and then for 24 h at room temperature. The residue was filtered off and the filtrate was evaporated yielding a yellow powder. To compact the product, the powder was heated at $150\,^\circ C$ for 15 min. Polymer **3** (5.2 g) was collected as a yellow granular solid.

2.2. Characterisation

X-ray pattern was performed with a Philips PW 3710/3020 X-ray diffractometer ($\lambda = 1.54\,\text{Å}$). Scanning electron micrographs (SEMs) were obtained with a Hitachi S800 microscope. Raman spectrum was carried out at 784 nm with a Kaiser Optical Systems Raman microscope. Transmission Electron Micrograph (TEM) was recorded with a Topcon EMB-002B microscope (diffraction pattern was obtained on a 0.5 μm selected area).

3. Results and discussion

3.1. Polymer synthesis

Synthesis of the borylborazine-based polymer was performed at room temperature by co-condensation of 2,4-Cl_2-6-$[(CH_3)_2N]B_3N_3H_3$ (**1**)[8] and $B(NHCH_3)_3$ (**2**)[9] in a 1:1 molar ratio, in presence of a tertiary amine to remove the hydrogen chloride formed. The amount of triethylamine hydrochloride collected was exactly that expected for a 100% recovery. Equation (1) illustrates the reaction scheme.

The tris(methylamino) borane **2** presents a high reactivity at room temperature and can act as a particular amine.[10] Consequently, borylamino groups of **2** are exchanged with chlorine atoms of **1** leading to polyborazine **3** in which borazine rings are linked through borylamino ($-N(CH_3)B(NHCH_3)N(CH_3)-$) bridges. Although the dimethylamino group is a weakly B-bonded blocking group it would not react at room temperature and not participate in the initial ring condensation chemistry.[6b] Hence, use of this functional borazine allows a "two points"[6b] polymerisation reaction without competitive attack at the blocked boron site. After filtration of the by-product, a yellow powder is isolated by vacuum evaporation.

3.2. Polymer characterisation

The infrared spectrum exhibits a typical absorption of borazine ring at 695 cm^{-1}.[11] The ν(B–Cl) band, at ∼740 cm^{-1} is replaced by a band at 809 cm^{-1} attributed to the B–N extracyclic vibration.[10] Elemental analyses[12] of **3** are consistent with the formula $B_1N_{1.6}C_{1.5}H_{3.5}$ while a N/B ratio of 1.7 was expected. The total absence of chlorine atoms in **3** is emphasised by the latter analyse in which no chlorine is detected. Thus, the terminating borazine groups can be reasonably assumed to be mainly borylamino groups $-N(CH_3)B(NHCH_3)_2$ and few $-N(CH_3)_2$ groups related to the probably low proportion of 2,4-$[(CH_3)_2N]_2$-6-$(Cl)B_3N_3H_3$ in the starting borazine.

The obtained polymer was fully characterised by NMR technique. The ^{15}N CP MAS spectrum shows signals of overlapping peaks ranging from -280 to -360 ppm. Using results from a previous study[13] both peaks exhibiting an IRCP[1] behaviour, at -311 and -348 ppm can be assigned to $B_2N\underline{H}$ and B$\underline{N}$(H)Me sites, respectively. The others peaks at -326 and -340 ppm could be assigned to non-protonated nitrogen groups: $B_2\underline{N}$Me and B$\underline{N}$Me$_2$ sites, respectively, in good agreement with the expected structure of polymer **3** (Fig. 1).

3.3. Polymer processing—fibres mechanical characterisation

The above as-prepared polymer is suitable for processing by melt-spinning using a lab-scale apparatus set up in a glove box under nitrogen following a procedure previously described.[14] It presents rheological and thermal properties tailored for its extrusion in the molten state. The green fibre is continuously stretched by rotating onto a spool. Kilometres of a continuous and flexible fibre was obtained at 90 $^\circ C$ from **3**. This spinning temperature is lower than those previously found.[5a,5b] An important difference is observed in the low glass-transition temperature, $T_g = 20\,^\circ C$ compares to others polymers prepared thermally.[5a,5b] This low value mirrors probably a low degree of reticulation of the network in relation with the "two-points" proposed structure. The spinnability of the extruded polymer is very good. Two winding rates could be applied without problem to obtain a continuous fibre: 35 and 100 m min^{-1} for run 1 and run 2 respectively (see Table 1).

As shown in Fig. 2, the crude fibres are smooth, uniform and free of defects.

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[1] Inversion Recovery Cross Polarisation, this sequence was used in order to distinguish the nitrogen sites according to their degree of protonation and differentiate NH groups from non-protonated N groups. The signals of protonated nitrogen sites that present a more intense $^{15}N-^1H$ dipolar coupling, are indeed expected to invert, with increasing inversion time, more rapidly than non protonated nitrogen atoms showing longer inversion time values.
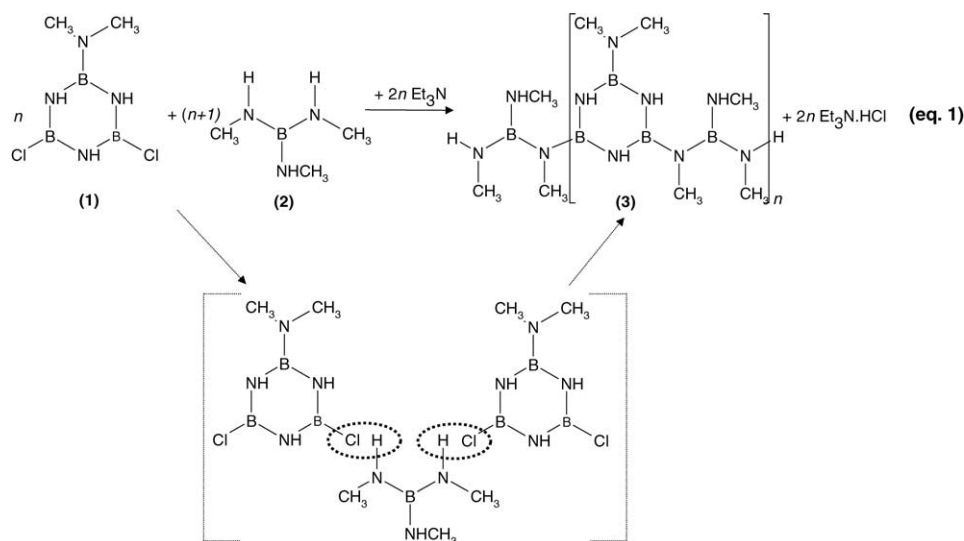
Fig. 1. Condensation reactions leading to polymer **3**.

Table 1
Melt-spinning parameters and mechanical characterisation of the obtained fibres

	Extrusion rate (mm min^{-1})	Winding rate (m min^{-1})	ϕ crude fibres (μm)	ϕ BN fibres (μm)	σ (MPa)	E (GPa)
Run 1	1	35	30	10	855	150
Run 2	1	100	23	9	1020	190

The post-spun polymer is cured under an ammonia atmosphere by gradual heating up to 650 °C. This first range of temperature, determined thanks to the TGA curve, corresponds to the curing process: meaning transamination and condensation pathways. The latter analysis performed on the bulk polymer under ammoniac gives a yield of 52% at 1000 °C. The TGA carried out on the green fibres leads to the same value. The heat treatment is followed under ammonia up to 650° to remove the totality of the carbon contaminants and then under nitrogen up to 1800 °C for the boron nitride crystallisation step. At the end of this program, fibres are white, lightly flexible and still around the spool. SEM images presented in Fig. 3 show fibres of ∼10 μm in diameter with a remained circular section and striated lengthwise without surface defects, as it has been previously reported by our group for poly(alkylamino)borazine-derived fibres.[5a] The fibre cross-section displays a grainy texture with numerous cavities which seem to be randomly distributed.
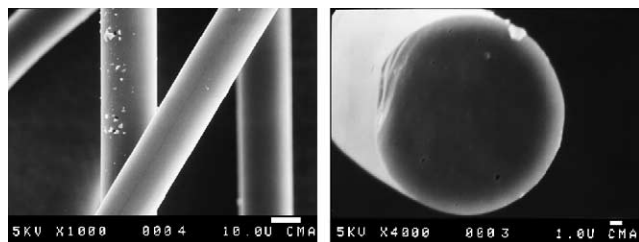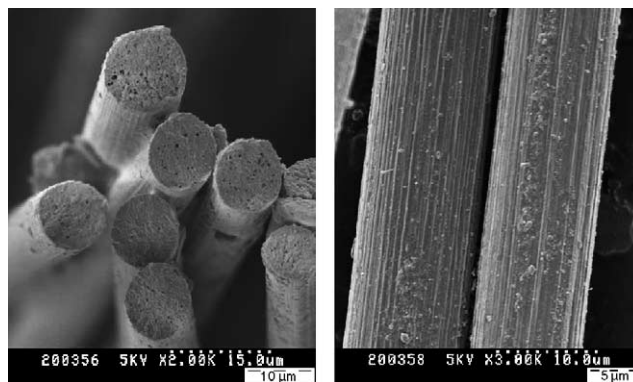

Fig. 3. Scanning electronic micrographs of BN fibres treated at 1800 °C.

Ceramic fibres were characterised mechanically and the measured properties[2] are presented in Table 1 function of the winding rate. Despite the presence of defects, fibres obtained in both runs display relatively good mechanical properties with tensile strength (σ) slightly above 1000 MPa and elastic modulus (E) around 200 GPa for the best run. These values should be significantly improved since the mechanical properties and specially σ are very dependant on the local defects in the fibres. Actually, during the mechanical tests several filaments have shown a σ up to 1600 MPa.

Fig. 2. Scanning electronic micrographs of green polymeric fibres.

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[2] Tensile tests 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.[14] Young' modulus was evaluated from the strength strain curves.

As we have previously reported,[5b] at the given extrusion rate, increasing the winding rate, lowers the fibre diameter and increases the values of σ and E.

3.4. Structural characterisation of the fibres

Analyses by X-ray diffraction and Raman spectroscopy were performed on the sample derived from run **2**. Data obtained from these analyses are reported in Table 2.

Both graphs present signals characteristic of well crystalline h-BN. The XRD pattern clearly shows three well resolved diffraction peaks corresponding to d spacing at 3.30, 2.17 and 1.67 Å that can be indexed as the $(0\,0\,2)$, $(1\,0)$ and $(0\,0\,4)$ reflections, respectively, associated with crystallised BN.[15] The calculation of the ratio between intensities of the $(0\,0\,2)$ peak, relative to the c axis and the $(1\,0)$ peaks, characteristic of the a axis (i.e. $R_{(0\,0\,2)/(1\,0)}$) gives information about the position of the crystallites with respect to the fibre axis.[16] In that case, the ratio of 38.5 evidences a preferential orientation of the crystallites in a direction parallel to the fibre axis, following the $(0\,0\,2)$ crystallographic axis. From the Raman spectrum, conclusions are similar concerning the high crystallinity of the ceramic with only the expected signal at 1368 cm^{-1} characteristic of the B−N bond.[17]
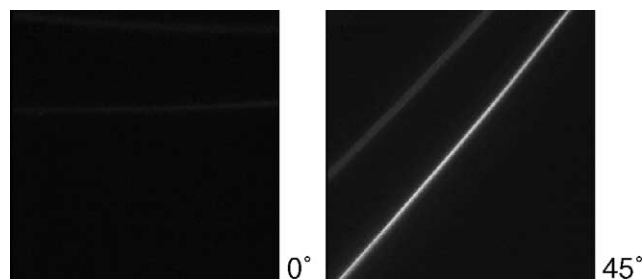

Fig. 4. Polarised light micrographs of BN fibres.

These features were supported by further analyses with polarised light microscopy (PLM) on the BN fibres. Actually, as graphite, h-BN is a uniaxial crystal with the optical axis along the $[0\,0\,1]$ direction. Hence, this method provides information about layer orientation, which is averaged at the micron scale.[18] Pictures obtained on the fibres are presented in Fig. 4.

Light intensity is not very high but there is, alternatively a straight minimum (extinction) and a straight maximum in the light intensity for positions separated by 45°. This observation is in good accordance with XRD results and confirms that crystallites of BN are well
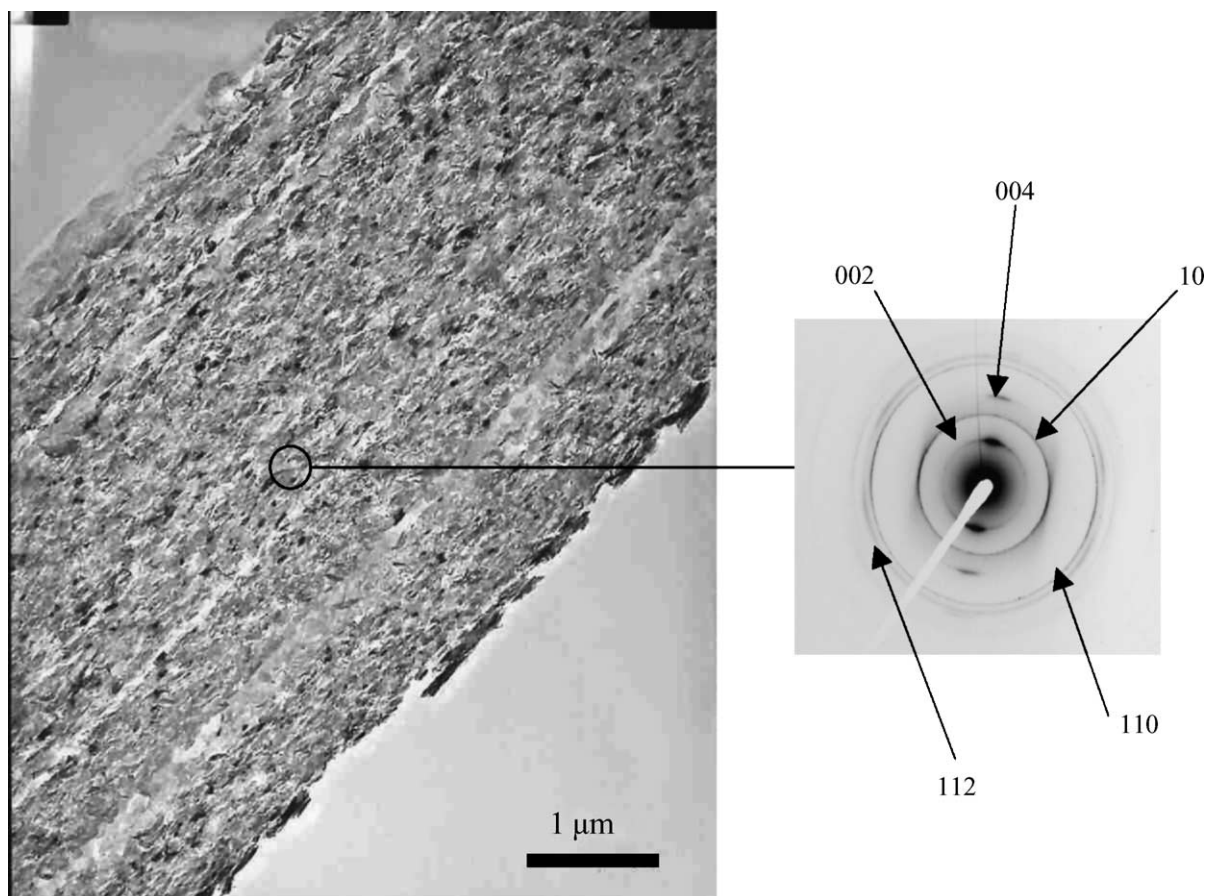

Fig. 5. TEM picture and selected area diffraction pattern performed on the BN fibre.

Table 2
Data obtained from the XRD pattern of the BN fibres

	(0 0 2)			(1 0)			$R\,(h, k, l)$
	$2\theta\,(^\circ)$	d (nm)	I (%)	$2\theta\,(^\circ)$	d (nm)	I (%)	(0 0 2)/(1 0)
BN fibres	26.99	3.30	100	41.60	2.17	2.6	35.8
Polycrystalline BN[15]	26.76	3.33	100	42.16	2.14	15	6.7

oriented in the fibre through a direction parallel to the fibre axis.

To conclude definitively, a BN fibre has been analysed by transmission electronic microscopy. The TEM micrograph and the corresponding selected area diffraction pattern are given in Fig. 5.

The SAD pattern is characteristic of crystallised hexagonal boron nitride,[19] we can clearly see five well defined and fine diffraction rings relative to the (0 0 2), (1 0), (0 0 4), (1 1 0) and (1 1 2) planes. Furthermore, the (0 0 2) semi-circulars (discontinuities in the diffraction ring) are very thin meaning that the BN crystallites constituent of the fibres are oriented.[19]

From the whole results, we can say, first, it is fundamental to well crystallise the ceramic to obtain fibres with high tensile strength. Actually, previous work[14] reports that tensile strength of pyrolysed fibres that are still amorphous can be evaluated above 200 MPa. Second, it unambiguously appears that BN crystallites preferably oriented through an axis parallel to the fibre axis results in the achievement of fibres with high mechanical properties.

4. Conclusion

This innovative study shows first the possibility for preparation at room temperature of a new borazine-based polymer by an original approach allowing a good control of the polymer structure and second the production of high performance boron nitride fibres from this new polymeric precursor.

The low cross-linked polyborazine synthesised here displays flexible borylamino bonds between the rings. These kind of linkage mode was unambiguously evidence by high resolution ^{15}N solid state NMR. Next, to the best of our knowledge, it is the first time, that a poly(borylamino)borazine prepared by a soft route presents well appropriate rheological properties for melt-spinning and especially for the achievement of boron nitride fibres with tensile strength upon 1000 MPa.

From a structural characterisation point of view, we have clearly confirmed that the good mechanical properties are correlated: (1) to well crystallise ceramic and (2) to a preferential orientation of the BN crystallites through a direction parallel to the fibre axis. This last feature was evidenced by several characterisations techniques (XRD, optical microscopy and SAD pattern).

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