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Boron nitride matrices and coatings from boryl borazine molecular precursors

David Cornu, Philippe Miele,* Bérangère Toury, Bernard Bonnetot, Henri Mongeot and Jean Bouix

Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, Université Claude Bernard-Lyon 1, 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France.
E-mail: miele@univ-lyon1.fr

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Thermal treatment of $2,4,6\text{-}[(\mathrm{NHPr^i})_2\mathrm{B}(\mathrm{NPr^i})]_3\mathrm{B}_3\mathrm{N}_3\mathrm{H}_3$ **1** *in vacuo* led to a polyborazine **2** in which the borazine rings are mainly linked by –N–B–N– bridges. Pyrolysis of **2** up to 1400 °C resulted in the formation of high crystallinity hexagonal boron nitride which has been characterised by ESCA, powder X-ray diffraction and FTIR spectroscopy. Precursor **2** has been used to prepare carbon fibres/BN microcomposites by dipping bundles of fibres into a solution of **2** followed by pyrolysis up to 1200 °C. Optical micrographs and SEM analysis have shown that the BN matrices were compact and displayed good adherence properties onto graphite substrates. By contrast, BN coatings obtained from a polymer derived from $\mathrm{B(NHPr^i)_3}$ displayed poor adherence properties. These results are related to the hydrocarbon chain ratio of each preceramic polymer. The effectiveness of the BN protective coatings in preventing oxidation has been measured by isothermal gravimetry in air. As expected, by considering the quality of the coatings, those obtained from **2** showed the most interesting properties.

Introduction

Among high-technological ceramics, boron nitride occupies a unique place owing to its special properties. Its high mechanical strength, its chemical and thermal stability and oxidation resistance have led to demands for fibres, coatings and foams for the preparation of advanced materials.[1] Such specific morphologies which cannot be easily obtained by classical high-temperature powder or CVD preparative methods, have led to a renewed interest for boron nitride molecular precursors and for preceramic polymers derived from them.[2] This technique involves the synthesis of a tailored molecular precursor, its transformation into a polymer, the preparation of the shaped materials followed by an appropriate thermal treatment for conversion into boron nitride. According to the main demanded applications, fibre spinning and oxidation protective coatings of a substrate, the polymeric precursor should be processable. Borazine $\mathrm{H_3B_3N_3H_3}$ and its analogues have been the most studied and successes have been achieved in the elaboration of several preceramic polymers suitable for advanced material fabrication. For example, boron nitride fibres have been obtained from processable polyborazines prepared from 2,4,6-tri(methylamino)borazine alone[3] or with laurylamine,[4] from reaction of 2,4,6-trichloroborazine with $\mathrm{HN(SiMe_3)_2}$,[5] and from dipentylamine-modified polyborazylene.[6] Polyborazines have also proven to be attractive precursors for the production of boron nitride coatings by an impregnation pyrolysis technique. For example, the preparation of C/BN composites from a suitable polyborazylene has been reported.[7] Coatings have also been obtained from reaction of 2,4,6-trichloroborazine with $\mathrm{HN(SiMe_3)_2}$.[8] In our group, we have focused our attention on aminoboranes as far as they lead to polyborazines by condensation reactions.[9] We have previously reported that tris(methylamino)borane $\mathrm{B(NHCH_3)_3}$ is a good BN precursor[10] and can be used as a BN source for fabrication of C/BN microcomposites (h-BN matrices reinforced by carbon fibres) or coatings on carbon with enhanced oxidation resistance properties.[11] In a recent investigation, we have shown that a polymer obtained by heating $\mathrm{B(NHCH_3)_3}$ under argon could be spun into crude polyborazinic fibres which can be subsequently converted into BN tubes.[12]

Expanding upon these results, we have investigated the potentialities of boryl borazine derivatives prepared by reaction between 2,4,6-trichloroborazine and aminoboranes for the preparation of coatings, matrices and fibres. This work was initiated in order to prepare new borazine-backbone polymers displaying multi-atom bridges between the rings. These polymers should exhibit different processing properties compared with classical polyborazine displaying only nitrogen bridges between the rings. The low ceramic yield of these precursors could be balanced by the presence of alkyl groups on the derived polymer that should improve its processing properties according to the conclusions of Sneddon and coworkers.[13]

In the present work, we have studied the thermolysis of the boryl borazine $2,4,6\text{-}[(\mathrm{NHPr^i})_2\mathrm{B}(\mathrm{NPr^i})]_3\mathrm{B}_3\mathrm{N}_3\mathrm{H}_3$ **1** previously described by our group.[14] The thermolysis of **1** *in vacuo* led to the formation of polyborazine **2** in which the borazine rings are mainly connected through N–B–N bridges. Pyrolysis of **2** up to 1400 °C resulted in the quantitative formation of high crystallinity hexagonal boron nitride which has been characterised by ESCA, X-ray powder diffraction and FTIR spectroscopy. Attempts to prepare high-quality boron nitride fibres were unsuccessful but BN/carbon fibre microcomposites were prepared by impregnation pyrolysis. Boron nitride matrices obtained from **2** were compared with those prepared from $\mathrm{B(NHPr^i)_3}$ by means of optical and scanning electron microscopies. Oxidation tests of BN coated graphite samples were conducted using isothermal gravimetry in air at 750 °C.

Experimental

Reagents and instruments

All experiments were performed under an atmosphere of pure argon and anhydrous conditions using standard vacuum-line, Schlenk techniques and an efficient dry box with solvents purified by standard methods. 2,4,6-[(NHPr^i)$_2$B(NPr^i)]$_{3.0}$B$_3$N$_3$H$_3$ **1** was prepared by reaction of 2,4,6-trichloroborazine with tris(isopropylamino)borane as previously reported[14] and used without further purification. 2,4,6-Trichloroborazine[15] and tris(isopropylamino)borane[9,16] were prepared as described in the literature and purified by vacuum sublimation and distillation respectively. Boron trichloride, used for tris(isopropylamino)borane and 2,4,6-trichloroborazine syntheses, and high-purity ammonia used as reducing atmosphere were purchased from Alphagaz. High-modulus P55 carbon fibres were supplied by Union Carbide and graphite (LCL 2188) was provided from Carbone Lorraine. ^{11}B NMR spectra were recorded on Brüker AM300 and DRX500 spectrometers at 96.28 and 160.461 MHz (high resolution) respectively, with Et$_2$O·BF$_3$ as an external reference (positive values downfield) in toluene and/or C$_6$D$_6$ solutions. ^{1}H and ^{13}C spectra were obtained at 300 and 75 MHz, respectively, in CDCl$_3$. The IR spectra were obtained on an FTIR Nicolet Magna 550 spectrometer as Nujol mulls between CsI plates in a hermetic cell. Size exclusion chromatography (SEC) analysis was performed in CH$_2$Cl$_2$ using a Gilson 118 UV detector at 240 nm and waters styragel columns. A calibration curve was generated from the chromatograms of 2,4,6-trimethylaminoborazine and polyborazines derived from it. Thermogravimetric analysis was performed on a TG 92 Setaram instrument. DSC analysis was performed on a TA8000 Mettler-Toledo apparatus. Analytical data were obtained from the Service Central de Microanalyses du C.N.R.S, and by ESCA analysis for BN.

Thermal polymerization of 2,4,6-[(NHPr^i)$_2$B(NPr^i)]$_3$B$_3$N$_3$H$_3$ 1: preparation of polyborazine 2 and its ceramic conversion

4.24 g (6.74 mmol) of **1** were heated *in vacuo* (10^{-4} mm Hg) at 40 °C for 4 h, then at 60 °C for 2 h and finally at 80 °C for 3 h. The volatiles were condensed under cooling with liquid nitrogen and identified as pure tris(isopropylamino)borane (0.58 g, 3.14 mmol) by FTIR and ^{1}H NMR spectra. Finally, the polyborazine **2** was collected (3.66 g) and analysed by FTIR, multinuclear NMR spectroscopy and elemental analysis. Polyborazine **2** is a white granular solid which is soluble in a variety of solvents such as toluene, dichloromethane, benzene and chloroform; size exclusion chromatography (SEC)/UV analyses gives a value $M_w = 1100$. Thermogravimetric analysis of **2** (530 mg) was performed at 2 °C min^{-1} up to 1400 °C in a stream of NH$_3$–N$_2$ (1 : 1) 2 h h^{-1} up to 500 °C or N$_2$ (between 500 and 1400 °C). Weight loss: in the range 50–250 °C, ≈50% wt; in the range 250–600 °C, ≈24% wt; in the range 600–1000 °C, ≈1% wt. No significant weight loss was observed in the range 1000–1400 °C. The remaining solid was identified as boron nitride (137 mg). Bulk pyrolysis of **2** (1.79 g) was carried out under NH$_3$ up to 600 °C then under N$_2$ up to 1200 °C following the ceramic conversion procedure described for the elaboration of composites. BN Yield: 0.48 g.

FTIR data for **2** (cm^{-1}): 3431 (ν_{NH}), 2960, 2929, 2861 (ν_{CH}), 1496 ($\nu_{BN\ amino}$), 1465 ($\nu_{BN\ ring}$), 1380 ($\nu_{BN\ exocyclic}$), 1258 (ν_{CN}), 1190, 1120, 700 (BN out of plane deformation), 803 ($\nu_{B(borazine)-N(aminoboryl)}$). NMR data for **2**: ^{13}C (CDCl$_3$): δ 44.51 (*C*H bridge), 42.01, 41.82 (*C*H amino), 26.71, 26.64 (*C*H$_3$ amino), 25.18, 25.13 (*C*H$_3$ bridge). ^{1}H (CDCl$_3$): δ 3.35 (m, C*H* bridge, N*H* borazine, C*H* amino; *ca.* 4H), 2.10 (d, N*H* amino, $J_{HNCH} = 10.2$ Hz, *ca.* 1H), 1.15 (d, CH_3 bridge, $J_{HCCH} = 6.66$ Hz), 1.05 (d, CH_3 amino, $J_{HCCH} = 6.19$ Hz) total integration of CH$_3$: *ca.* 16H. ^{11}B (C$_6$D$_6$) 298 K: δ 26.5 (br, *B*-borazine), 23.8 (br, *B*-aminoboryl). 348 K: 26.6 (*B*-borazine), 24.0 (*B*-bridge), 22.4 (*B*-aminoboryl). Elemental analysis for **2**. Found: C, 51.9; H, 11.9; B, 11.2; N, 25.0%.

Data for BN obtained at 1400 °C: FTIR (cm^{-1}): 3400 vw (ν_{NH}), 1390 s, 793 m (ν_{BN}). Ceramic yield: Calc. from elemental analysis of **2**, 25.7%. Found: 25.9%. Elemental analysis. Calc.: B, 43.6; N, 56.4. Found: B, 43.4; N, 56.2%. XRPD: *d*/Å (2*θ*/°) 3.38 (26.30), 2.17 (41.52), 2.09 (43.14), 1.68 (54.61), 1.25 (75.80).

Data for BN obtained at 1200 °C: Ceramic yield: Calc. from elemental analysis of **2**, 25.7%. Found: 26.8%. FTIR and XRPD spectra of the ceramic indicate the presence of turbostratic boron nitride.

Preparation of polyborazine 3

0.90 g of **2** was heated for 7 h at 150 °C yielding the polyborazine **3** (0.76 g) and B(NHPr^i)$_3$ (0.14 g, 0.76 mmol). Polyborazine **3** is a light brown solid which is soluble in benzene and dichloromethane and was analysed by ^{11}B NMR spectroscopy. The DSC analyses of **3** were performed on a 13.7 mg sample between −10 and 170 °C using a heating rate of 10 °C min^{-1}. Two scans were performed to determine the T_g value ($T_g = 57$ °C).

^{11}B NMR data for **3** (C$_6$D$_6$) 293 K: δ 26.4 (broad, *B*-borazine), 23.9 (*B*-aminoboryl). 348 K: 26.5 (br, *B*-borazine), 24.0 (*B*-bridge), 22.3 (shoulder, *B*-aminoboryl).

Composites and coatings preparation by an impregnation pyrolysis technique

The impregnations were carried out in a glovebox. Before impregnation, the graphite samples were heated to 1200 °C under nitrogen to remove moisture. For impregnation of graphite, crude B(NHPr^i)$_3$ was used and solutions were prepared by dissolving oligomer **2**, which is solid, in the minimal volume of toluene yielding a viscous oil. Bundles of fibres or cubic graphite samples (1 g) of edge *ca.* 8 mm were dipped into the precursor solution for coating and drained to evacuate the excess liquid. The samples, disposed in a quartz boat, were transferred from the glovebox to the furnace under a nitrogen atmosphere owing to the sensitivity of B(NHPr^i)$_3$ and oligomer **2** toward moisture. The pyrolysis was performed under a 0.1 L min^{-1} NH$_3$ flow up to 600 °C (heating rate 50 °C h^{-1}) then under a nitrogen stream up to 1200 °C (heating rate 100 °C h^{-1}). The samples were then allowed to cool to room temperature. The samples were analysed by optical or scanning electron microscopy. The oxidation resistance of the BN coated samples was estimated by isothermal TGA under air. The coated samples were first heated under vacuum (10^{-3} Pa) up to the test temperature, then under air flow while the weight loss was recorded.

Results and discussion

Thermolysis of 2,4,6-[(NHPr^i)$_2$B(NPr^i)]$_3$B$_3$N$_3$H$_3$ 1: formation of BN oligomeric precursors 2 and 3

Owing to its structure, thermolysis of **1** should resemble either those of alkylaminoboranes, involving the elimination of Pr^{i}NH$_2$ between two bis(isopropylamino)boryl groups,[16] or those of other borazines;[4,10,17] in the latter case, the alkylaminoboryl group would act as an amino reactant leading to the liberation of tris(isopropylamino)borane.

As a base-line study for the understanding of the mechanism of thermal polymerization, a sample of **1** was heated *in vacuo* and a distillate was separated from the residue. The thermolysis was monitored by ^{1}H, ^{13}C NMR and FTIR spectroscopies. The distillates at each stage were found to be pure B(NHPr^i)$_3$, their NMR and IR spectra being the same as previously reported.[16] This result clearly indicates that **1** behaves as a tris(alkylamino)borazine and consequently two possible mechanisms have to be considered for such condensation reaction:[17–19] the formation of direct boron–nitrogen bonds between the rings and their linkage through amino bridges. Therefore, the thermolysis of **1** should lead either to a biphenyl type oligomer (a) and/or to an oligomer displaying three atom bridges

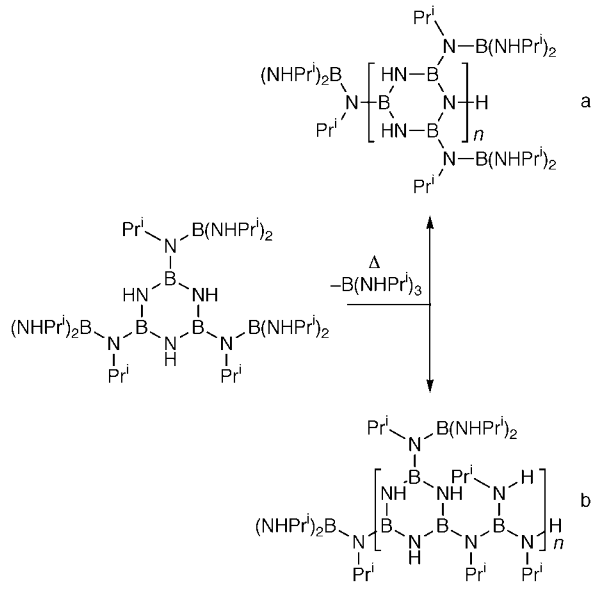

Fig. 1 Possible mechanisms for the condensation reaction of 2,4,6-[(NHPr^i)$_2$B(NPr^i)]$_3$B$_3$N$_3$H$_3$ **1**.

between the rings (b) (Fig. 1). Compared to **1**, the ^{1}H NMR spectra of the oligomers displayed an overlapping of the CH and NH borazine signals and a gradual increase in intensity of this contribution relative to the signals of the protons of the NH amino groups, confirming that polycondensation took place. Heating **1** yielded **2** which contains oligomeric species according to its SEC chromatogram. The molecular weight distribution average for **2** ($M_w = 1100$ g mol^{-1}) mirrored its low molecular weight component and indicated that it contains mainly the dimer (Fig. 1, $n = 2$), a low proportion of trimer (Fig. 1, $n = 3$) and probably traces of **1** in accordance with the amount of B(NHPr^i)$_3$ collected. Variable temperature high-resolution ^{11}B NMR spectroscopy has been performed for compound **2**. The spectrum of **2** at 348 K is well resolved and displays three signals (Fig. 2). By comparison with the 293 K spectrum, the low field signal sharpens without significant change in the chemical shift whereas the other signal splits into two peaks. The signal at δ 26.6 corresponds to the boron atoms of the borazine rings. The broadness and the asymmetry of this peak could be interpreted by considering the existence of inequivalent boron atoms depending on their bridging or terminal substituents. Two other signals appear in the aminoborane region, (δ 22–24), even though the ^{1}H NMR spectrum of **2** clearly indicates the absence of B(NHPr^i)$_3$. The peak at δ 24.0, shifted to low field compared to the isopropylaminoboryl resonance in **1** (δ 22.6),[14] is attributed to isopropylaminoboryl bridges; a comparable effect has been reported for [(NHPr^i)$_2$B]$_2$NPr^i in which the magnetic environment of the boron atoms is intermediate between those observed in the corresponding alkylaminoborane and borazine.[16] The weak higher field signal at δ 22.4 is assigned to boron atoms of terminal aminoboryl groups in accord with the value found for these groups in **1**.[14] In order to confirm this interpretation, we have prepared a high-molecular weight polyborazine **3** by heating a sample of **2** up to 150 °C. The chromatogram of **3** did not show an individual peak of monomer **1** but did show an envelope with significantly larger molecular weight average ($M_w = 9600$) indicating its polymeric nature in accordance with its glass transition temperature ($T_g = 57$ °C). The ^{11}B NMR spectrum of **3** at 348 K was similar to those observed for **2** and showed three featureless resonances (δ 26.5, 24.0, 22.3) attributed to borazine boron atoms, to boron atoms of the isopropylaminoboryl bridges and to terminal isopropylaminoboryl groups, respectively. For oligomer **2** and polymer **3**, the broadness of the signals precludes any determination of the integration ratio. However, the relative intensity of the boryl-bridge peak (δ 24.0) compared to the terminal isopropylaminoboryl peak (δ 22.3) is consistent with the formation of an oligomer with a high proportion of bridging boryl groups (Fig. 1, oligomer b) even if the formation of direct boron–nitrogen bonds between the rings may occur as quoted above.[18,19] The steric hindrance of the highly encumbered –N(Pr^i)B(NHPr^i)$_2$ groups should limit the extent of this phenomenon.

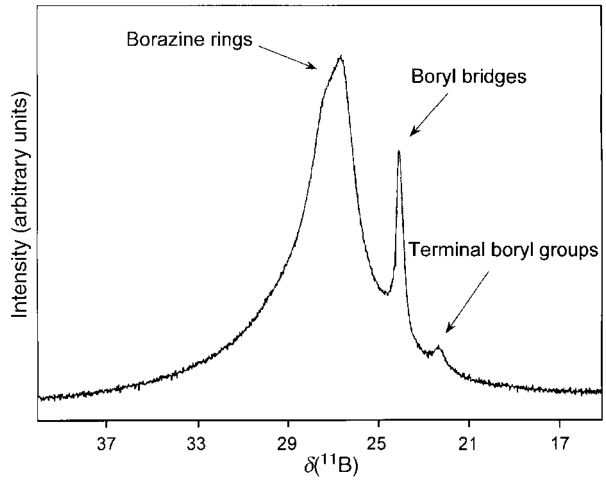

Fig. 2 High resolution ^{11}B NMR spectrum of oligomer **2** (348 K).

As a preliminary investigation of the pyrolysis chemistry of oligomers derived from **1**, a thermogravimetric analysis of **2** up to 1400 °C was performed under NH$_3$–N$_2$. The resulting TGA curve resembles those previously reported for polyborazines[16,20] and showed that the oligomer undergoes a two-stage major weight loss. The light grey residue was identified as boron nitride with low carbon content. As for the amminolysis of B(NHPr^i)$_3$, the rapid first stage is presumably the consequence of the replacement of isopropylamino groups by ammonia[16] whereas the other stages probably result from decomposition reactions subsequently followed by the ceramic conversion into fused-ring structures. The IR spectrum of the residue shows absorbances at 793 and 1390 cm^{-1} that are characteristic of BN.[1,21] However, a very weak vibration at *ca.* 3400 cm^{-1} suggests the presence of residual NH groups and shows that the thermolysis was not rigorously complete. ESCA analysis yields a nearly ideal B/N ratio of 1.007. The X-ray powder diffraction pattern displays sharp lines with resolved (004) and (103) reflections at 2θ *ca.* 54 and 76°, respectively. A measured spacing of 3.38 Å for the (002) reflection corresponds very well with the reported value for hexagonal boron nitride (3.33 Å).[1,22] A higher value (3.5–3.6 Å) was observed for most turbostratic modifications[1,23] which indicates a small turbostratic disorder for this boron nitride sample. A 25.9% ceramic yield comparable with the theoretical value was measured. This low ceramic yield is due to the choice of the tris(isopropylamino)borane as a model reactant; however, the alkylaminoboranes have been demonstrated to be good BN precursors despite their low ceramic yield.[10,11,16] Thus, we have obtained h-BN with a degree of crystallinity as high as those of BN ceramics prepared at the same temperature from classical polyborazines.[1,24,25] This demonstrates that the oligomer **2**, and more generally, polyborazines derived from **1** are good precursors of bulk boron nitride. With the aim of preparing boron nitride coatings on carbon, boron nitride bulk samples were prepared by pyrolysis of **2** following the same procedure as those described in the Experimental section for composite elaboration, *i.e.* under NH$_3$ then N$_2$ up to 1200 °C. As expected, and owing to the variation of properties of boron nitride on the pyrolysis temperature,[1,26] we obtained a more disordered turbostratic h-BN at 1200 °C. The X-ray powder diffraction spectrum of this material showed classical broad peaks including the unresolved (002) reflection at 2θ *ca.* 24° and the (100) and (101) reflections as a doublet at 2θ *ca.* 43°. Consistent with the XRPD measurements, the FTIR spectrum displayed a broad absorption centred at *ca.* 1390 cm^{-1} and a sharp medium band at *ca.* 800 cm^{-1}. Residual NH groups were evidenced by a weak absorption around 3420 cm^{-1}.

Fabrication of BN/carbon fibre microcomposites from $B(NHPr^i)_3$ and 2

Tris(isopropylamino)borane $B(NHPr^i)_3$ has been already used as boron nitride source for coatings, matrices and Si_3N_4–BN composites.[27] However, since **1** can be considered as a derivative of $B(NHPr^i)_3$, we have reinvestigated the properties of coatings and matrices prepared from the latter for comparison with those obtained from **2**.

The composites were prepared by using an impregnation pyrolysis technique. Carbon fibres were impregnated by dipping into either $B(NHPr^i)_3$ or a solution of oligomer **2** and submitted to a thermal treatment. To allow the draining of the excess of the solution before the pyrolysis, the impregnated fibres were placed on graphite holders. For wetting the samples, the precursor must be a liquid with an appropriate viscosity in order to allow infiltration into the interstices between fibres. However, a compromise has to be found between the volatility, the wetting properties and the ceramic yield of the precursor. For these reasons, $B(NHPr^i)_3$, which is volatile, was treated by ammonia at room temperature before being pyrolysed. As previously reported, $B(NHPr^i)_3$ is very stable with respect to autopolymerisation but reacts spontaneously with ammonia at room temperature leading to 2,4,6-tri(isopropylamino)borazine and subsequently to a polyborazine with rings connected through NH bridges.[16] Thus, the precursor becomes less volatile and the ceramic yield is increased compared to $B(NHPr^i)_3$. 2,4,6-$[(NHPr^i)_2B(NPr^i)]_3B_3N_3H_3$ **1**, which is a viscous non-volatile liquid, could be used in this process but the oligomer **2** was preferred because of its higher ceramic yield. Furthermore, the use of a solution of **2** in toluene avoided precursor shrinkage during pyrolysis.

An optical micrograph of a transverse section of a microcomposite prepared from $B(NHPr^i)_3$ is shown in Fig. 3. Besides the carbon fibres, boron nitride is observed but does not form a dense matrix. The fibres are separated from the matrix and not totally embedded indicating a lack of adherence of the BN matrix on the carbon fibres. This result is similar to that we have previously reported and could be related to the low carbon content of the polyborazine derived from $B(NHPr^i)_3$ which limits its carbon wetting properties.[27]

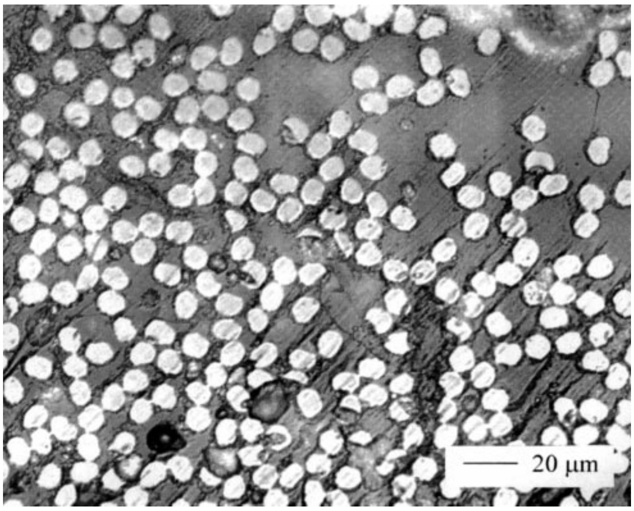

Fig. 4 Optical micrograph of a cross section of a BN coated carbon fibre bundle; the BN coating is obtained from **2**.

When complete, the amminolysis of $B(NHPr^i)_3$ has been shown to lead to a carbon free precursor giving BN coatings which do not adhere to the substrate. This behaviour is different from that observed for tris(methylamino)borane $B(NHCH_3)_3$. This compound readily undergoes classical cyclisation and polycondensation reactions but reacts more slowly with ammonia.[10] This reaction yields a 2,4,6-tri(methylamino)borazine based polymer displaying NH and NCH_3 bridges between borazine rings[12] which is retained on a carbon surface during pyrolysis.[11]

On the other hand, Fig. 4 shows clearly that precursor oligomer **2** has thoroughly wetted each carbon filament and has not been stripped during pyrolysis. The carbon fibres are distributed in a dense matrix and Fig. 5 shows that the matrix adopts the exact shape of the bundle. Although the conversion of the precursor **2** into boron nitride implies evolution of isopropylamine as in the case of tris(isopropylamino)borane ceramic conversion, the obtained matrices display good adherence properties and are comparable to those prepared from $B(NHCH_3)_3$.[11] This means that polyborazines with high carbon ratios interact readily with carbon fibres leading to adherent BN matrices on fibres. On the other hand, composites or coatings obtained from low carbon containing polyborazine exhibit poor interface adherence and will require hot-pressing techniques to infiltrate the precursor into the carbon fibre bundles.[7]

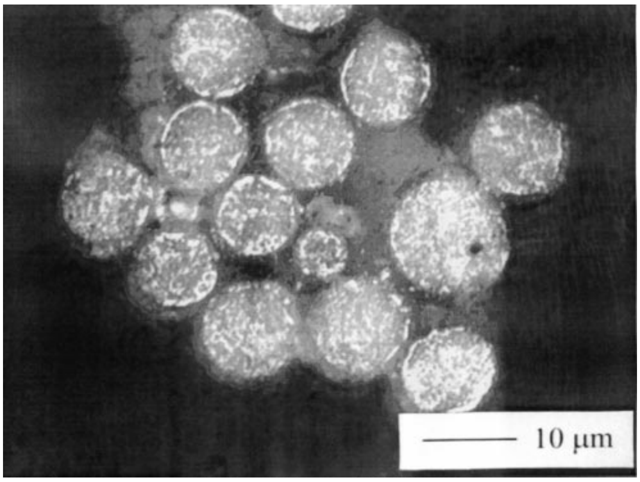

Fig. 3 Optical micrograph of a cross section of a BN coated carbon fibre bundle; the BN coating is obtained from $B(NHPr^i)_3$.

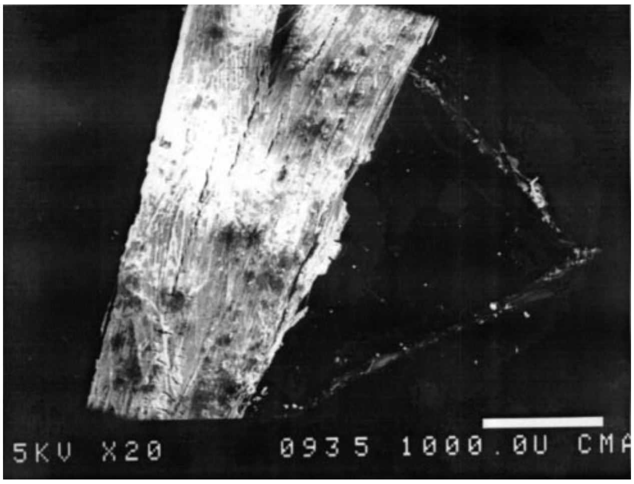

Fig. 5 SEM image of the C/BN microcomposite obtained from **2**.

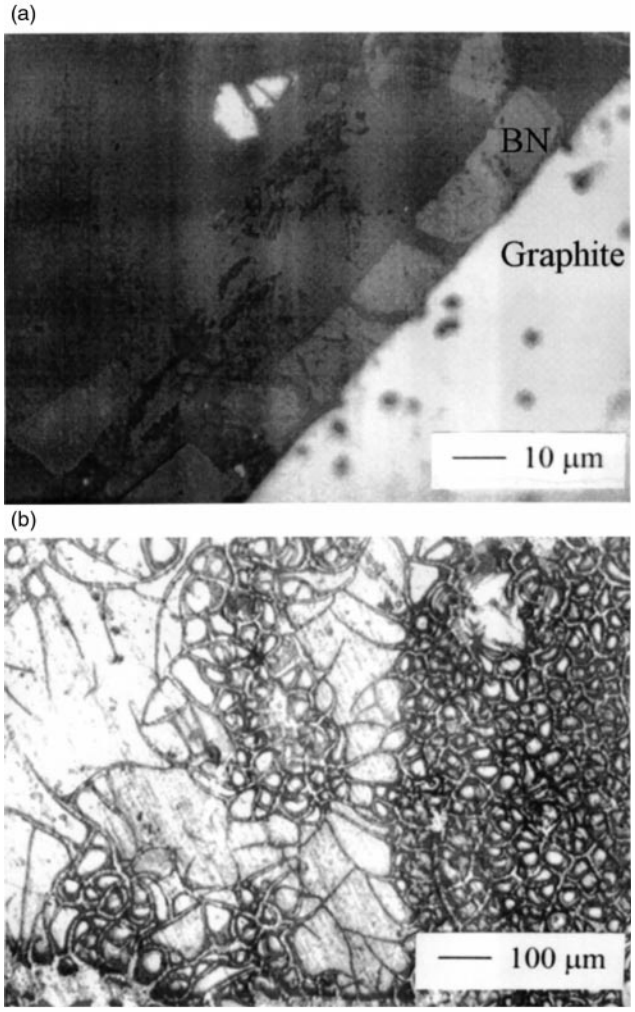

Fig. 6 Optical micrographs of a cross section (a) and a front view (b) of a BN coated graphite sample; the BN coating is obtained from $B(NHPr^i)_3$.

Fabrication of BN coatings on graphite substrates

Following a procedure similar to those described for the preparation of matrices, cubes of graphite have been impregnated with $B(NHPr^i)_3$ or a solution of oligomer **2**.

Fig. 6 shows a cross section (a) and a front view (b) of a graphite sample coated with BN prepared from $B(NHPr^i)_3$. Consistent with the results described above for the elaboration of matrices, the coating of *ca.* 10 μm thickness is not homogeneous and does not adhere to the substrate [Fig. 6(a)]. The fragments observed on the cross section probably correspond to the variable area BN plates evidenced on the surface micrograph [Fig. 6(b)]. The utilisation of precursor **2** led to a homogeneous coating (10–20 μm thick) on the entire surface of the graphite cube (Fig. 7). This observation corroborates the results obtained with carbon fibres demonstrating that polyborazine **2** is suitable for preparing adherent and homogeneous BN coatings on graphite substrates.

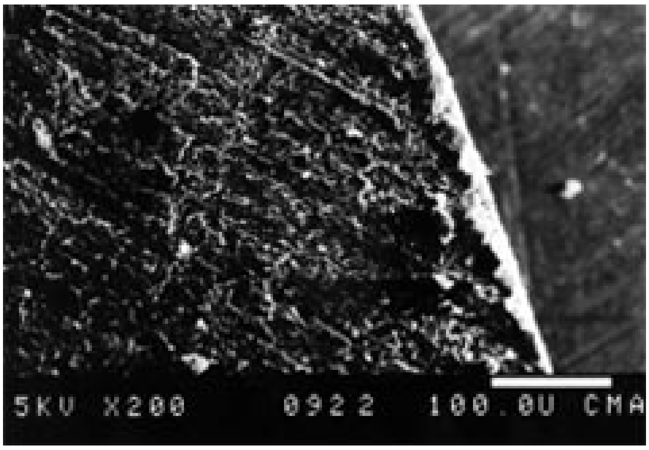

Fig. 7 SEM image of a cross section of a BN coated graphite sample; the BN coating is obtained from **2**.

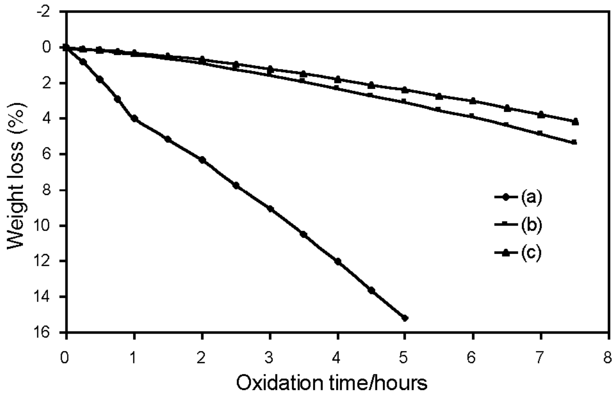

Fig. 8 Isothermal oxidation weight loss (750 °C, air) of uncoated graphite (a), $B(NHPr^i)_3$-derived BN coated graphite (b) and **2**-derived BN coated graphite (c).

Since the mass of the BN coating is negligible compared to the mass of the substrate, the oxidation resistance of similar coated and uncoated samples can be compared by isothermal TGA at 750 °C (Fig. 8). After 5 h, a 15% weight loss was observed for an uncoated substrate whereas the weight loss was only 2 and 3% for samples coated from $B(NHPr^i)_3$ and oligomer **2**, respectively. These results confirm the efficiency of BN coatings in reducing air oxidation of carbon samples, both precursors providing good properties despite the presence of defects in the case of $B(NHPr^i)_3$. However, the small difference between the two curves could be related to the quality of the coatings and consequently to the carbon content of the precursor as discussed above. These results are consistent with those previously reported on similar types of graphite samples protected by a thin BN coating prepared from $B(NHCH_3)_3$[11] and on BN/C composites with 50 wt% BN.[7]

Conclusion

Heating 2,4,6-$[(NHPr^i)_2B(NPr^i)]_3B_3N_3H_3$ **1** *in vacuo* led to a new polymer **2** in which the borazine rings are mainly connected through –N–B–N– bridges. This polymer has been used to prepare adherent boron nitride coatings on graphite substrates whereas those obtained from the carbon free polymer derived from $B(NHPr^i)_3$ exhibited poor interface adherence. These results show that the adherence of boron nitride coatings on graphite substrates depends on the carbon wetting properties of the preceramic polymer, the lowering of the hydrocarbon chains ratio drastically reducing the wetting properties. Thus, while the ceramic yield of a precursor has to be considered, the adjustment of its alkyl chain content is of crucial importance for the preparation of boron nitride coatings on a graphite substrate. The other goal of our work was to obtain a spinnable precursor for the production of fibres; preliminary attempts were made to prepare boron nitride fibres from a boryl borazine based polymer comparable to **2**. Although crude fibres could be spun, the resulting boron nitride fibres displayed poor properties. Work is in progress to improve the rheological properties of this kind of polyborazine.

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