JOURNAL OF Materials CHEMISTRY

Conversion of $B(NHCH_3)_3$ into boron nitride and polyborazine fibres and tubular BN structures derived therefrom

David Cornu,[*a] **Philippe Miele,**[a] **René Faure,**[b] **Bernard Bonnetot,**[a] **Henri Mongeot**[a] **and Jean Bouix**[a]

[a]*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: cornu@univ-lyon1.fr*
[b]*Laboratoire de Chimie Analytique 2, LICAS, Université Claude Bernard—Lyon 1, 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France*

Received 22nd October 1998, Accepted 10th December 1998

The reaction of ammonia with tris(methylamino)borane $B(NHCH_3)_3$ **1** or with a $B(NHCH_3)_3$ derived polyborazine **2** led to completely different processes. Compound **1** reacted spontaneously with NH_3 to give mainly the borazine $(CH_3NH)_3B_3N_3H_3$ and subsequently a BN prepolymer which was not processible. A polymer **2** obtained by heating **1** under argon could be spun into crude polyborazinic fibres. When **2** was heated under ammonia in order to obtain carbon free BN, it was partially dissociated into 1,3,5-trimethyl-2,4,6-tri(amino)borazine $(NH_2)_3B_3N_3(CH_3)_3$ **3**. The borazine **3** was fully characterised by multinuclear NMR spectroscopy, FTIR and mass spectrometry. The structure of **3** has been confirmed by a single crystal X-ray diffraction analysis. An illustration of the formation of **3** was the formation of BN tubes from crude fibres. These results were explained by the TGA curves of the polymer **2** under ammonia or nitrogen.

Introduction

Boron nitride composite materials show potential for use in technological applications by combining the mechanical properties of the composite materials with the intrinsic properties of BN.[1] The polymer route offers technical advantages over chemical vapour deposition and powder processing methods for the formation of forms such as fibres, matrices and foams. Moreover, in the case of polyborazines, there are structural relationships between the polymer and hexagonal boron nitride which should favour the polymer to ceramic conversion. A simple method for the preparation of BN composites consists of the synthesis of a molecular precursor, its polymerization into a processable polymer and finally the conversion of the elaborated product into h-BN. Many types of borazine derivatives have been synthesized and their polymerization led to various polyborazines.[2] Finally, it seems that no satisfactory polymer exists for the most difficult application: the production of good quality BN fibres.[3]

Our attention has been focused on the tris(methylamino)borane $B(NHCH_3)_3$ **1**. This compound can be prepared in high yield by a simple one step reaction involving boron trichloride and methylamine[4] that makes it one of the easiest polyborazine precursors to synthesise. It has been shown that **1** can be used to prepare BN coatings, matrices and Si_3N_4–BN composites.[5] The thermal conversion of **1** into boron nitride is always performed under ammonia in order to limit the residual carbon in the final ceramic. However, no mechanism has been proposed to explain the role of ammonia during the thermal conversion.

In the present work, **1** has been shown to react with ammonia at low temperature to give 2,4,6-tri(methylamino)borazine in a first step prior to formation of the corresponding polyborazine. This polymer was not processible but, as previously described, it could be converted quantitatively to boron nitride by pyrolysis. Another method consisted of polymerizing **1** in an inert atmosphere, a polyborazine **2** was obtained which could be easily spun into several meters of 20–25 μm diameter crude fibres. TGA measurements performed on **2** showed unexpected weight loss. These results have been explained by the partial decomposition of **2** under ammonia. Crude fibres were obtained from polymer **2** and were subsequently converted into boron nitride.

Experimental

Starting materials and instruments

All experiments were performed in an atmosphere of pure argon using standard vacuum-line, Schlenk techniques and an efficient dry box with solvents purified by standard methods.[6] $B(NHCH_3)_3$ was prepared as described in the literature[7] and purified by vacuum distillation. BCl_3 (Alphagaz) and CH_3NH_2 (Fluka) were used as supplied without further purification. ^{11}B, ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 300 spectrometer at 96.28 MHz with $Et_2O \cdot BF_3$ as external reference (positive values downfield) in C_6D_6, and at 300 and 75 MHz in $CDCl_3$, respectively. The ^{15}N NMR spectrum was obtained by gradient HMBC experiment with a Bruker DRX 500 spectrometer. The IR spectra were recorded on a FTIR Nicolet Magna 550 spectrometer as Nujol mulls between CsI plates in a hermetic cell or as KBr pellets. Size exclusion chromatography (SEC) analysis was performed in CH_2Cl_2 using a Gilson 118 UV detector at 240 nm and Waters styragel columns. A B70 Setaram apparatus was used for TGA measurements. The DSC analyses were performed on a TA8000 Mettler–Toledo apparatus. Mass spectrometry (EI) and elemental analyses were obtained from the Service Central d'Analyses du CNRS.

Reaction of 1 with ammonia

6.05 g of **1** were stirred under an ammonia flow for 30 min at room temperature then for 4 h at 50 °C and finally for 2 h at 100 °C. The reaction was monitored using ^{1}H NMR spectroscopy: a sample was withdrawn from the mixture before each temperature rise. Finally, 3.24 g of a whitish residue were obtained and analysed by FTIR and ^{1}H NMR spectroscopy, showing that **1** had been completely converted to $(CH_3NH)_3B_3N_3H_3$, along with a small amount of polyborazine. The volatiles evolved during the reaction were trapped at −10 °C and identified as pure CH_3NH_2 by its gas FTIR spectrum. $(CH_3NH)_3B_3N_3H_3$ was also prepared as described in the literature[8] and characterised by ^1H NMR spectroscopy. Pyrolysis at 1200 °C of 2.5 g of the whitish residue consisting mainly of $(CH_3NH)_3B_3N_3H_3$ under an ammonia flow (10 ml min^{-1}) yielded 1.1 g of a solid characterized as boron nitride.

^1H NMR ($CDCl_3$): $B(NHCH_3)_3$: δ 1.54 (m, N*H*, 3H), 2.42 (m, C*H*, 9H); final product containing mainly $(CH_3NH)_3B_3N_3H_3$: δ 1.80 (m, N*H* amino), 2.16 (br s, NH_2), 2.22 (br s, N*H* bridge), 2.57 (br s, CH_3 amino), 2.64 (br s, CH_3 bridge), 2.80 (m, N*H* borazine ring), 3.06 (m, N*H* borazine ring); $(CH_3NH)_3B_3N_3H_3$: δ 1.80 (m, N*H* amino, 3H), 2.57 (m, CH_3 amino, 9H), 2.80 (s, N*H* borazine ring, 3H). FTIR data for the product containing mainly $(CH_3NH)_3B_3N_3H_3$ (cm^{-1}): 3517 m, 3440s (ν_{NH}); 2964w, 2924w, 2854w (ν_{CH}); 1617 m (NH_2 bending); 1454 m, 1408s ($\nu_{BN\ ring}$ and CH_3 bending); 1263 (ν_{CN}); 1102; 1018; 705 (BN out-of-plane bending). Elemental analysis for BN. Calc.: B, 43.6; N 56.4. Found: B, 40.5; N, 58.0; C, 0.4; H, 0.8%.

Thermal polymerization of 1: preparation of polyborazine 2

13.03 g of **1** were heated for 21 h up to 180 °C (at a linear heating rate) then for 76 h at 180 °C and finally for 20 h at 198 °C. During the experiments, the mixture was stirred and an argon flow transported the methylamine produced into water. The resulting methylamine solution was titrated with HCl (0.2 M). The total amount of CH_3NH_2 formed was 67.36 mmol, indicating a degree of polymerization of 72%. The polyborazine **2** was a light brown powder which was soluble in CH_2Cl_2 and according to preliminary size exclusion chromatography (SEC)/UV experiments had $M_w = 900$ and slowly hydrolyses when exposed to air at room temperature. Polyborazine **2** was analysed by FTIR, multinuclear NMR spectroscopy and elemental analysis. The DSC analyses were performed on a 15.0 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 ($T_g = 73$ °C). Thermogravimetric analyses of **2** were performed under nitrogen or a gaseous mixture of ammonia (95%) and nitrogen (5%). Polyborazine fibres were drawn on a graphite spool at 150 °C by using a classical extruding process set in a glove box. The spool is carefully transferred to the furnace. Owing to the sensitivity of the polyborazine **2** towards water, these two steps were performed under a nitrogen atmosphere.

FTIR data for **2** (cm^{-1}): 3460 (ν_{NH}); 2955, 2923, 2839 (ν_{CH}); 1482 ($\nu_{BN} + CH_3$ bending); 1354 ($\nu_{BN\ exocyclic}$); 1186, 1068, 709 (BN out of plane deformation). ^{11}B NMR data for **2** (C_6D_6): δ 27.2 (*B*NHCH$_3$), 30.1 [*B*N(CH$_3$)]. Elemental analysis for **2**. Found: B, 19.2; N, 37.0; C, 34.5; H, 9.3%.

Reaction of 2 with ammonia

2.10 g of **2** were heated for 44 h at 80 °C under an ammonia flow. A volatile compound (0.8 g) sublimed and formed colourless crystal plates. The gas formed during the reaction was trapped at −10 °C and identified as pure methylamine by FTIR spectroscopy. The polyborazinic residue (0.74 g) was partially soluble in CH_2Cl_2. The sublimed crystals were identified as pure $(NH_2)_3B_3N_3(CH_3)_3$ **3**. Elemental analysis for **3**. Found: C, 21.49; H, 8.84. Calc. for $C_3H_{15}B_3N_6$: C, 21.50; H, 8.96%. NMR data for **3**: ^{11}B (C_6D_6): δ 26.02; ^{13}C ($CDCl_3$): δ 29.71; ^1H (CD_2Cl_2): δ 2.19 (s, N*H*, 2H), 2.54 (s, C*H*, 3H); ^{15}N (C_6D_6): δ 34 (d, *N*H$_2$, $^1J_{NH} = 79.3$ Hz); 57 (d, *N*CH$_3$, $^2J_{NCH} = 1.2$ Hz). Mass spectrometry (EI): *m/z* 168 $[\mathbf{3}]^+$ (66%), 167 $[\mathbf{3}-H]^+$ (100%), 153 $[\mathbf{3}-CH_3]^+$ (12%).

X-Ray crystallographic study of $(NH_2)_3B_3N_3(CH_3)_3$ 3

A flat crystal of **3** (0.80 × 0.40 × 0.05 mm) was covered with a film of paratone in order to conduct X-ray experiments in an ambient medium over a period of some hours. Single crystal diffraction data were collected using a Nonius KappaCCD diffractometer. The structure was solved by direct methods using MAXUS[9a] and refined on F^2 with all the data by means of SHELXL-93.[9b] All the hydrogen atoms were located from ΔF syntheses. Details of the data collection and structure refinement can be found in Table 1.

Table 1 Crystal structure determination of $(NH_2)_3B_3N_3(CH_3)_3$ **3**

Formula	$C_3H_{15}B_3N_6$
Molecular weight	167.6
Temperature/K	295
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	7.992(2)
b/Å	9.275(1)
c/Å	12.987(3)
β/°	106.36(3)
V/Å^3	923.7(3)
D_c/g cm^{-3}	1.205
μ(Mo-Kα)/mm^{-1}	0.08
Z	4
Reflections collected	2008
Reflections observed [$I > 2\sigma(I)$]	507
Goodness of fit	1.15
R,R_w	0.054, 0.095

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/133. See http://www.rsc.org/suppdata/jm/1999/757/ for crystallographic files in cif format.

Results and discussion

Reaction of $B(NHCH_3)_3$ 1 with ammonia

The conversion of $B(NHPr^i)_3$ into boron nitride has been previously studied.[10] Tris(isopropylamino)borane reacts spontaneously with ammonia at room temperature leading to the formation of 2,4,6-tri(isopropylamino)borazine and subsequently to a polymer in which the borazine rings are linked through NH bridges. This reaction occurred at room temperature because of the high reactivity of the $NHPr^i$ groups towards ammonia.

A different behaviour was observed for $B(NHCH_3)_3$ which reacts more slowly with ammonia. First, **1** was stirred for 30 min at room temperature and then for 4 h at 50 °C under a NH_3 flow. The ^1H NMR spectrum of the residue was complex but a broad signal corresponding to NH_2 groups at δ 2.16 was clearly present. This observation was confirmed by the FTIR spectrum which displayed a band at 1617 cm^{-1} characteristic of a NH_2 bending mode.[11] Methylamino groups of **1** were substituted by NH_2 groups during the reaction which led to the elimination of methylamine. The mechanism was similar to that described[10] for $B(NHPr^i)_3$ (Fig. 1). The absence of a signal corresponding to N*H* borazine groups in the ^1H NMR spectrum showed that no cyclisation reaction had occurred at this temperature. Consequently, the main products were partly amino substituted tris(methylamino)borane.

After 2 h at 100 °C, the final product was identified as mainly 2,4,6-tri(methylamino)borazine (Fig. 2) according to its multinuclear NMR spectra. The observation of a broad

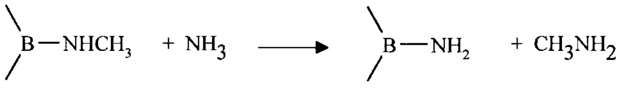

Fig. 1 Reaction of a methylamino group with ammonia.

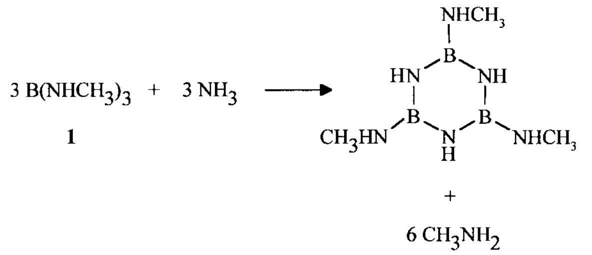

Fig. 2 Reaction of **1** with ammonia: formation of 2,4,6-tri(methylamino)borazine.

and weak singlet corresponding to NH groups at δ 3.09 in the ^{1}H NMR spectrum showed also the presence of a small quantity of polyborazinic oligomers. Moreover, the borazine rings of the oligomers appeared as linked through two types of bridges: NH and NCH_3 bridges. A weak signal at δ 2.22 was attributed to N*H* bridges between the borazine rings according to the value reported for the N*H* bridging group of $[(CH_3)_3N_3B_3(CH_3)_2]_2NH$.[12] The chemical shift value for the NCH_3 bridge between borazine rings is in the range δ 2.64[7]–2.78.[2] Therefore, the singlet observed at δ 2.64 indicated that the borazine rings were also linked through NCH_3 bridges. The presence of two types of bridges is in good agreement with previously reported results on the polymerization of 2,4,6-tri(alkylamino)borazines.[13]

2,4,6-Tri(methylamino)borazine based polymers are known to produce boron nitride in high yields.[14] An ammonia treatment starting at low temperature leads to a quantitative conversion of **1** to boron nitride *via* the formation of polyborazines. The fact that in these polyborazines the cyclic nitrogen atoms are bound to hydrogen atoms and not to alkyl groups is of prime importance as will be demonstrated below.

Preparation of polymer 2 and its reaction with ammonia

The preparation of BN composite materials requires the synthesis of processing polymers.[15] Classical polyborazines have been obtained by thermolysis of 2,4,6-tri(alkylamino)borazines and consist of borazine rings, B_3N_3, linked by direct BN bonds and through nitrogen bridges,[13] these structures were considered as incompatible with good processing properties.[15]

We have obtained a polymer **2** by thermolysis of **1** up to 198 °C according to a published method:[5] deamination reactions led to the formation of the 1,3,5-trimethyl-2,4,6-tri(methylamino)borazine $(NHCH_3)_3B_3N_3(CH_3)_3$ which was subsequently converted into a polymer **2** containing borazine rings linked through NCH_3 bridges[7] (Fig. 3). Its ^{11}B NMR spectrum exhibited two broad signals corresponding to boron atoms bound to methylamino groups (δ 27.2) and to methylamino bridges (δ 30.1). These values are consistent with those reported by Narula *et al.* for $[(CH_3)_3N_3B_3(CH_3)_2]N(CH_3)$.[12] When heating under ammonia at 80 °C, the polymer **2** was partly decomposed into a volatile borazine **3** and methylamine leading to the formation of a small amount of polyborazinic residue. Compound **3** was identified as 1,3,5-trimethyl-2,4,6-tri(amino)borazine (Fig. 4).

The TGA curves [Fig. 5(a) and (b)] differed when **2** was heated under an NH_3–N_2 flow or under an N_2 flow. Narula *et al.*[12] reported a similar behaviour for a linear polyborazine composed of $(CH_3)B_3N_3(CH_3)_3$ rings bound through $N(CH_3)$ bridges, but no explanation was given. For TGA performed under a nitrogen flow, the weight loss was 44% and the black residue was characterised as BN containing a large amount of carbon (28%). By contrast, when the TGA was performed under a mixture of ammonia and nitrogen, the weight loss was 83% and the BN residue was light grey with low carbon content (0.7%). The weight loss was greater than the theoretical value (56%) showing the loss of boron species during the experiment. The very important difference in weight loss between these two experiments must be attributed to the effect of ammonia which decomposed the polymer into methylamine and 1,3,5-trimethyl-2,4,6-tri(amino)borazine **3**.

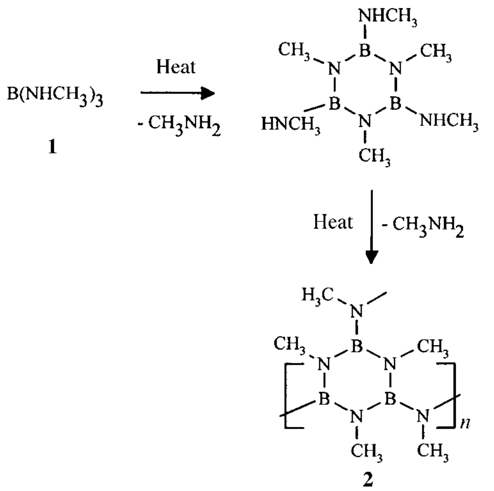

Fig. 3 Thermal behaviour of **1** under argon: formation of polyborazine **2**.

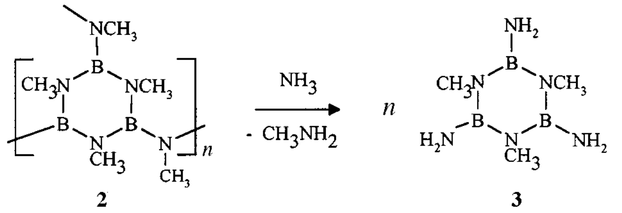

Fig. 4 Reaction of **2** with NH_3: formation of $(NH_2)_3B_3N_3(CH_3)_3$ **3**.

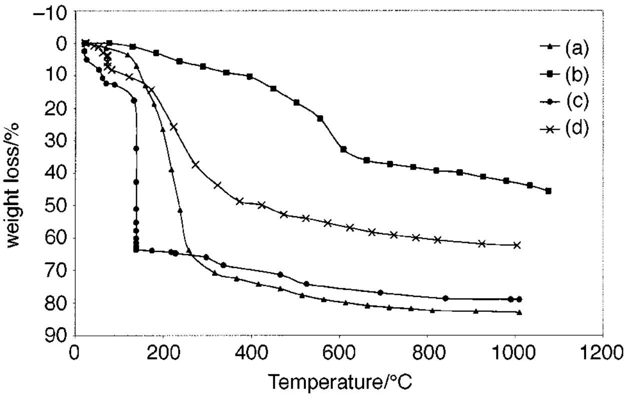

Fig. 5 Thermogravimetric analyses of **2** (heating rate 2 °C min^{-1}): (a) under a NH_3 (95%)/N_2 (5%) flow; (b) under a N_2 flow; (c) under a NH_3 (95%)/N_2 (5%) flow, plateau temperature 130 °C for 12 h; (d) under a NH_3 (95%)/N_2 (5%) flow, plateau temperature 75 °C for 12 h.

The high volatility of the borazine **3** which sublimes to some extent during the ammonia treatment of the polyborazine **2** explains the rapid weight loss before 300 °C. Paciorek *et al.*[13] described the thermal degradation of **3** and showed that it can undergo polymerization reactions in a closed system. Thus, the same polymerization reactions probably took place to a limited extend under our conditions. The TGA curves indicate that *ca.* 70% of **3** sublimed and 30% underwent polymerization reactions. Thermogravimetric analyses in which the temperature rise was interrupted by steady temperature plateaux [Fig. 5(c) and (d)] were also performed to determine if the polymerization of **3** mainly took place at low or at high temperature. When the temperature of the plateau was 130 °C, the weight loss (78%) was nearly identical to those observed in the dynamic analyses. However, when the temperature of the plateau was 75 °C, the weight loss was lower (only 62%). This result clearly points to formation of the polymer mainly taking place at low temperature (below 130 °C) and that the borazine **3** sublimed at higher temperature.

This polymer degradation was only observed when the borazine nitrogen atoms were bound to methyl groups. Polyborazine **2** did not lead to the formation of boron nitride with low carbon content or high yield.

Characterisation of the 1,3,5-trimethyl-2,4,6-tri(amino)borazine 3

Compound **3** was obtained as a sublimate during the decomposition of **2** under ammonia. This borazine could also be prepared by reaction of ammonia with 1,3,5-trimethyl-2,4,6-trichloroborazine[13,16] and was characterized by its FTIR and multinuclear NMR spectra, elemental analysis and mass spectrometry. The IR spectrum is consistent with the spectrum reported by Toeniskoetter and Hall.[16] The structure of **3** was unambiguously determined by NMR techniques. It is interesting that the ^{15}N NMR measurement allowed the determination of the NH coupling constant values ($^1J_{NH} = 79.3$, $^2J_{NCH} = 1.2$ Hz). These values are not significantly different from those reported[17] for $C_6H_5NH_2$ ($^1J_{NH} = 78$ Hz) and $N(CH_3)_3$ ($^2J_{NCH} = 0.85$ Hz).

Since **3** was obtained as crystals, the structure of this compound was analysed by X-ray diffraction techniques. ORTEP drawings of the molecular structure of $(NH_2)_3B_3N_3(CH_3)_3$ are shown in Fig. 6.

Details of the data collection and structure refinement can be found in Table 1 and relevant bond lengths and angles are given in Table 2. The determination confirmed the structure deduced on the basis of the spectroscopic analysis. It consists of a borazine ring where the boron atoms bear amino groups whereas the nitrogen atoms are bonded to methyl groups. As expected, the borazine ring is almost planar and the endo-ring B–N bond distances are typical of the partial delocalization of the nitrogen lone pair around the $(BN)_3$ ring. The endo-ring distances are between 1.418(4) and 1.439(4) Å, falling in the range of the distances found in other borazine rings.[12,18–21] The B–N–B ring angles [av. 121.8(3) °] are greater than N–B–N ring angles [av. 118.1(3) °]. Similar findings have been reported for $(HBNH)_3$,[18] $(Me_2NBNH)_3$[19] and $(ClBNH)_3$.[20] However, it is interesting that B–N–B ring angles are more open in **3** than in the above species, whilst N–B–N angles are more compressed. This phenomenon is presumably due to the simultaneous presence of methyl substitutents (σ electron donors when attached to nitrogen) and amino substituents (π donors when attached to sp^2 boron) on the borazine ring. The exo-ring B–N bond lengths [av. 1.421(4) Å] are identical within experimental error to the endo-ring B–N bond lengths [av. 1.427(5) Å], which indicates a bond order of greater than unity. Further, the exo-ring distances are comparable to the distances found for analogous bonds in $(Me_2NBNH)_3$[19] and $B(NMe_2)_3$,[22] where likewise the boron atoms are surrounded by three nitrogen atoms. In addition, a slight deviation of the position of the exo nitrogen atoms from the mean least-squares plane calculated for the borazine ring is observed. These observations are consistent with the existence of some degree of π interaction between exo nitrogen atoms and the borazine ring boron atoms. Nevertheless, the accuracy of the determination, particularly for hydrogen atoms, did not allow for confirmation of the expected trigonal planar geometry of the exo-nitrogen atoms. The N–C bond distances are normal for single bond distances [av. 1.467(4) Å] and can be compared with distances in already described N-methyl substituted borazines.[12]

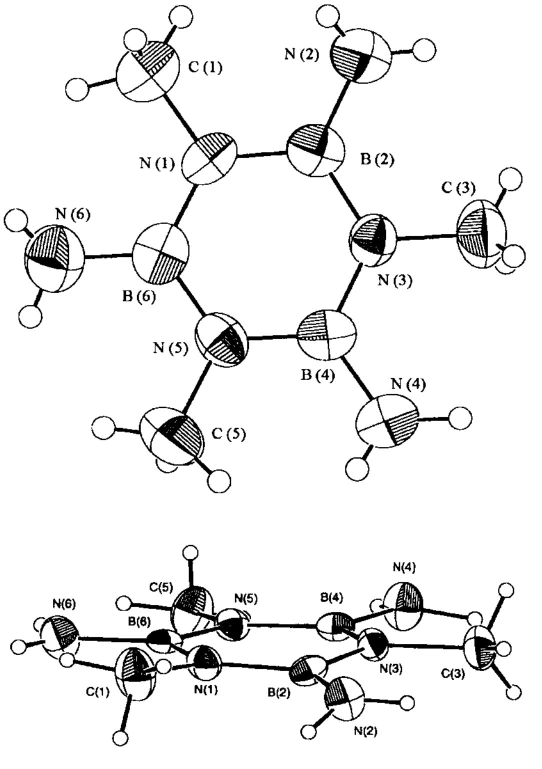

Fig. 6 ORTEP drawings of molecular structure and atomic numbering scheme for $(NH_2)_3B_3N_3(CH_3)_3$ **3**.

Table 2 Selected body lengths (Å) and angles (°) for $C_3H_{15}N_6B_3$ **3** (standard deviations in parentheses)

N(1)–B(2)	1.429(5)	N(5)–B(4)	1.423(5)
N(3)–B(2)	1.439(4)	N(5)–B(6)	1.422(4)
N(3)–B(4)	1.418(4)	N(1)–B(6)	1.429(5)
B–NH_2 (av.)	1.421(4)	N–CH_3 (av.)	1.467(4)
N(1)–B(2)–N(3)	117.4(3)	B(4)–N(5)–B(6)	121.8(3)
B(2)–N(3)–B(4)	121.6(3)	N(5)–B(6)–N(1)	118.2(4)
N(3)–B(4)–N(5)	118.7(3)	B(6)–N(1)–B(2)	122.0(3)
N(1)–B(2)–N(2)	121.1(3)	N(3)–B(2)–N(2)	121.5(4)
N(1)–B(6)–N(6)	119.9(4)	N(5)–B(6)–N(6)	122.0(4)
N(3)–B(4)–N(4)	119.7(4)	N(5)–B(4)–N(4)	121.5(3)

BN tubes from melt spinning polymer 2

Crude fibres of polymer **2** of diameter 20–25 µm have been melt drawn at 150 °C (Fig. 7). Several meters of monofilaments could be easily wound on a graphite spool and subsequently ceramised.

Gradual heating was performed in ammonia up to 650 °C

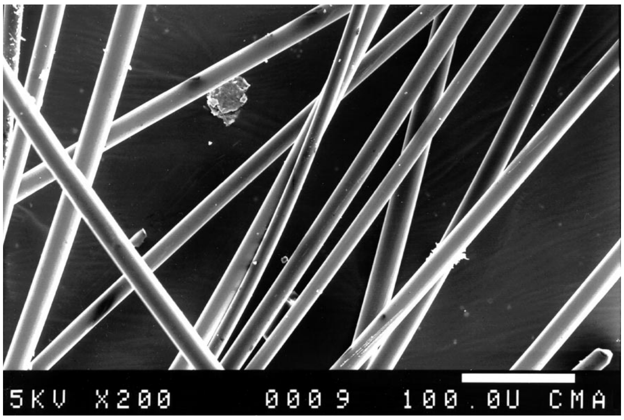

Fig. 7 SEM image of crude fibres of polymer **2**.

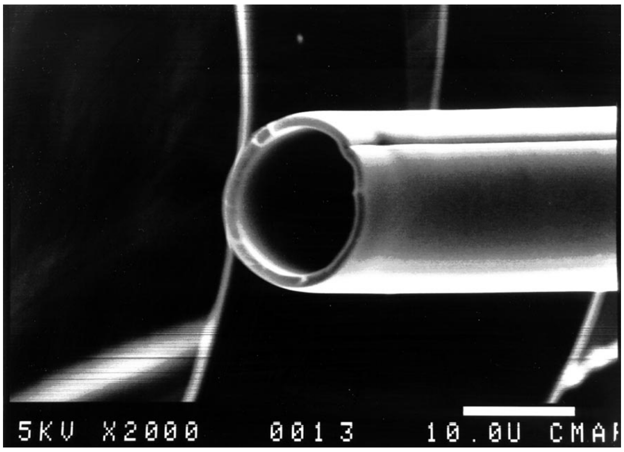

Fig. 8 SEM image of BN tubular forms obtained by the pyrolysis under ammonia of **2** crude fibres.

(heating rate 25 °C h^{-1}) and in nitrogen up to 1200 °C (heating rate 100 °C h^{-1}). After the thermal treatment, the regular polymeric fibres exhibited a very important change in appearance. Most of them were split and a thin BN skin remained. Some retained the fibre aspect but SEM images showed that they were empty (Fig. 8). The tubes were too fragile for any determination of mechanical properties. The tubes were powdered, analysed by FTIR and powder X-ray diffraction techniques and identified as boron nitride. The effect of ammonia, as described above, suggested that the thermal treatment of crude fibres led to the decomposition of the polymer and to the formation of a low quantity of residue. The tubular forms obtained indicate a different behaviour between the surface and the core of the fibres. On the basis of this observation, we suggest the following mechanism: at the beginning of the pyrolysis, the temperature is low and the surface is in contact with a large amount of NH_3. According to the TGA results previously described, the sublimation of **3** is limited under these conditions and its polymerization is predominant. Therefore, the first step of the pyrolysis leads to the formation of a solid skin of reticulated polyborazine which is not decomposed by ammonia. At higher temperatures, the cores of the fibres react with ammonia leading to the formation of the borazine **3** which then sublimes.

Conclusions

The thermal treatment of **1** under ammonia at low temperature resulted in the formation of 2,4,6-tri(methylamino)borazine and of the corresponding polyborazine and the use of ammonia during the first steps of the thermal ceramic conversion of **1** is necessary to obtain carbon free BN in good yields.

$B(NHCH_3)_3$ **1** could be thermally converted under argon into polyborazine **2**. This polymer presented interesting spinnable properties and could be drawn into crude fibres. However, the pyrolysis under ammonia, required to eliminate the carbon moieties during the ceramisation, led to the partial decomposition of the polymer into the borazine **3**. This phenomenon is presumably due to the presence of methyl groups bound to the borazinic nitrogen atoms. The ceramic yields observed for **2** were low and the pyrolysis under ammonia of crude fibres led to the formation of tubular BN structures.

Acknowledgements

We thank AEROSPATIALE for supporting this work. We gratefully acknowledge J. M. Létoffé for the DSC analyses and B. Fenet for the ^{15}N NMR measurements.

References

1 R. T. Paine and C. K. Narula, *Chem. Rev.*, 1990, **90**, 73.
2 R. T. Paine and L. G. Sneddon, *Chemtech*, 1994, **7**, 29.
3 T. Wideman and L. G. Sneddon, *Chem. Mater.*, 1996, **8**, 3.
4 D. W. Aubrey and M. F. Lappert, *J. Chem. Soc.*, 1959, 2927.
5 B. Bonnetot, F. Guilhon, J. C. Viala and H. Mongeot, *Chem. Mater.*, 1995, **7**, 299. C. Doche, F. Guilhon, B. Bonnetot, F. Thevenot and H. Mongeot, *J. Mater. Sci. Lett.*, 1995, **14**, 847.
6 D. D. Perrin, W. L. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, London, 1966.
7 B. Bonnetot, B. Frange, F. Guilhon and H. Mongeot, *Main Group Met. Chem.*, 1994, **17**, 583.
8 K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, 1959, **81**, 3561.
9 (*a*) S. Mackay, C. J. Gilmore, C. Edwards, A. Henderson and N. Stewart, *Comprehensive Crystallography Software*, University of Glasgow, Scotland, 1997; (*b*) G. M. Sheldrick, SHELXL -93, University of Göttingen, Germany, 1993.
10 F. Guilhon, B. Bonnetot, D. Cornu and H. Mongeot, *Polyhedron*, 1996, **15**, 851.
11 A. Meller and R. Schlegel, *Monatsch. Chem.*, 1964, **95**, 382.
12 C. K. Narula, D. A. Lindquist, M.-M. Fan, T. T. Borek, E. N. Duesler, A. K. Datye, R. Schaeffer and R. T. Paine, *Chem. Mater.*, 1990, **2**, 377.
13 K. J. L. Paciorek, D. H. Harris and R. H. Kratzer, *J. Polym. Sci.: Polym. Chem. Ed.*, 1986, **24**, 173.
14 Y. Kimura and Y. Kubo, *Polym. Prepr.*, 1993, **34**, 337.
15 K. J. Wynne and R. W. Rice, *Annu. Rev. Mater. Sci.*, 1984, **14**, 297.
16 R. H. Toeniskoetter and F. R. Hall, *Inorg. Chem.*, 1963, **2**, 29.
17 G. J. Martin, M. L. Martin and J.-P. Govesnard, *^{15}N NMR Spectroscopy*, Springer-Verlag, Berlin, 1981.
18 R. Boese, A. H. Maulitz and P. Stellberg, *Chem. Ber.*, 1994, **127**, 1887.
19 H. Hess and B. Reiser, *Z. Anorg. Allg. Chem.*, 1971, **381**, 91.
20 D. L. Coursen and J. L. Hoard, *J. Am. Chem. Soc.*, 1952, **74**, 1742.
21 W. Harshbarger, G. H. Lee, R. F. Porter and S. H. Baver, *J. Am. Chem. Soc.*, 1969, **91**, 551; P. J. Fazen, E. E. Remsen, J. S. Beck, P. J. Caroll, A. R. McGhie and L. G. Sneddon, *Chem. Mater.*, 1995, **7**, 1942; U. Müller, *Acta Crystallogr., Sect. B*, 1971, **27**, 1997; J. G. Haasnoot, G. C. Verschoor, C. Romers and W. L. Groeneveld, *Acta Crystallogr., Sect. B*, 1972, **28**, 2070; M. F. Welker, I. Manners, M. Parvez and H. R. Allcock, *J. Chem. Soc., Chem. Commun.*, 1989, 871.
22 A. H. Clark and G. A. Anderson, *Chem. Commun.*, 1969, 1082.

Paper 8/08213H