Journal of Organometallic Chemistry 657 (2002) 91–97

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Pyrolysis of poly[2,4,6-tri(methylamino)borazine] and its conversion into BN fibers

S. Bernard *, D. Cornu, P. Miele *, H. Vincent, J. Bouix

Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, Université Lyon 1, 43, boulevard du 11 novembre 1918, bâtiment Berthollet, F-69622
Villeurbanne Cedex, France

Received 3 September 2001; accepted 23 April 2002

Abstract

The pyrolysis process of poly[2,4,6-tri(methylamino)borazine]-based fibers has been studied in detail. The condensation of polymer leads to infusible fibers with a three-dimensional polymeric network from 70 to 400 °C. A polymer–mineral transition occurs since 400 to give amorphous hydrogenated fibers at 1000 °C. The chemical conversion process is complete at 1400 °C and the BN fibers crystallize up to 1800 °C. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: PolyMAB; BN fibers; Cross-link; Polymer–mineral transition; Ceramization; Crystallization

1. Introduction

Hexagonal boron nitride (*h*-BN) is known as anisotropic material with interesting thermal and electric properties, good resistance to oxydation and high mechanical properties [1]. This ceramic is predominantly produced via powder-metallurgical process. Difficulties inherent to this traditional powder-based technique for manufacturing complex forms of *h*-BN (fibers-reinforced composites, nanocomposites and coatings) can be overcome by the use of preceramic polymers [2–4]. They offer several important advantages such as a low impurity level, homogeneous element distribution and flexible forming methods.

There are two majors polymeric precursors for the fabrication of boron nitride fibers: polyborazylenes and polyborazines. Concerning the former, Sneddon and coworkers [5] have studied the conversion process of polyborazylene into boron nitride ceramic and shown that a spinnable oligomer can be obtained by linking dipentylamino groups to the polymer backbone. BN fibers with poor mechanical properties were produced [6]. For the latter, Kimura et al. have prepared BN fibers with high mechanical properties from a mixture of tri(methylamino)borazine and laurylamine [7].

Following a similar approach, a particularly useful family of preceramic borazine-based polymers, polyalkylaminoborazines, was investigated as precursors of BN fibers in our laboratory [8,9]. In this paper, a poly[2,4,6-tri(methylamino)borazine] (PolyMAB) schematically illustrated in Fig. 1 is prepared by thermal condensation of 2,4,6-tri(methylamino)borazine (MAB) as it was detailed in Section 3.

The polymer is spun by conventional melt-spinning technique into crude fibers which are pyrolyzed under specific conditions into BN fibers. The fiber diameter reduces by half after the pyrolysis process up to 1800 °C as shown in Fig. 2.

Up to now, the mechanisms which govern both the fabrication of the ceramic fibers and the evolution of their behavior during pyrolysis annealing are not well-established. In this study, the conversion of polyborazine fibers into ceramic fibers is studied by TGA, GC–MS, FTIR and XRD analysis to provide an understanding of the obtaining of carbon-free boron nitride fibers.

---

* Corresponding authors

E-mail addresses: sbernard@univ-lyon1.fr (S. Bernard), miele@univ-lyon1.fr (P. Miele).

PII: S0022-328X(02)01543-7

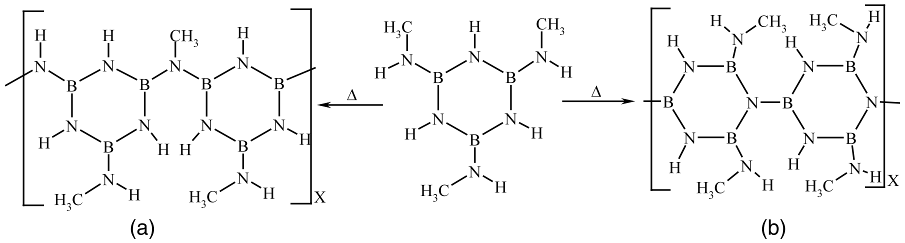


Fig. 1. Thermal condensation of 2,4,6-tri(methylamino)borazine into two possible models of polymer.

2. Results and discussion

2.1. *Characterization of polyMAB-based fibers pyrolysis process*

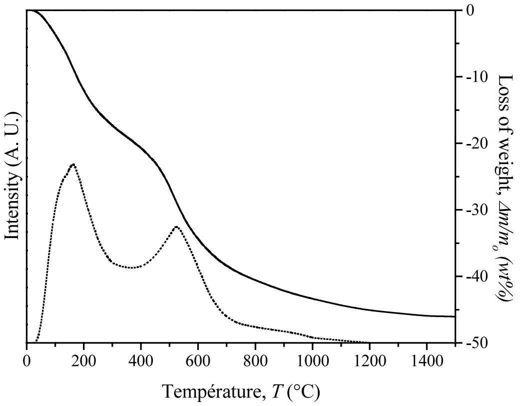
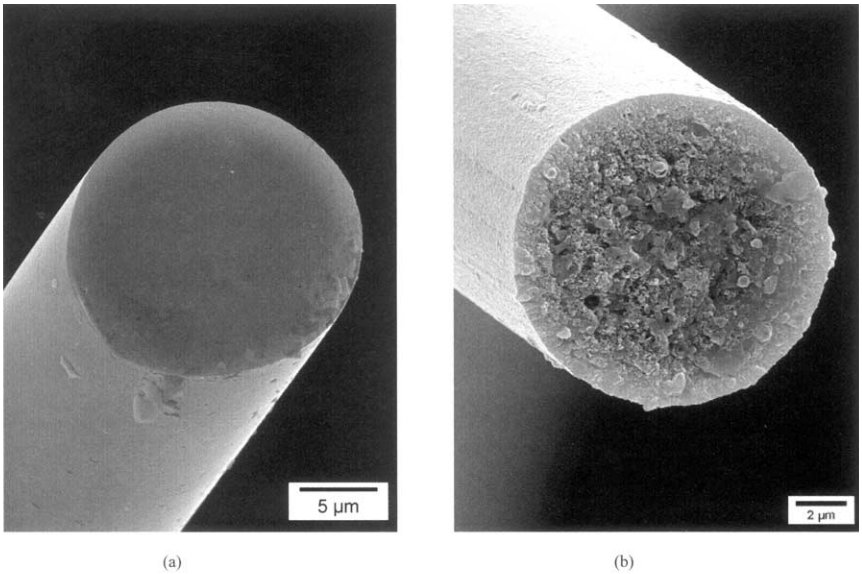


Fig. 3. TG and CH_3NH_2 elimination curves for polyMAB (heating rate: 0.8 °C min^{-1} under an NH_3–N_2 mixture up to 1000 °C and in a pure nitrogen flow from 1000 to 1500 °C).

The thermogravimetric (TG) and concomitant methylamine (CH_3NH_2) evolution curves during the pyrolysis of polyMAB-based fibers are shown in Fig. 3. The thermal behavior of polyMAB is characterized by a continuous weight loss over the entire temperature range 30–1400 °C. The thermogram shows that the thermal degradation is particularly important during two ranges of temperature, from 70 to 400 °C and between 400 and 1000 °C. The first weight loss up to 400 °C is about 20 wt.% and the elemental analysis results are in agreement with the TG interpretations although the data are approximate. The analytical composition of the residue derived from the data at 400 °C summarized in Table 1 is about $C_{0.30}N_{1.41}BH_{2.38}$ at 400 °C. The total loss at 400 °C is thus about $C_{0.41}N_{0.12}H_{0.72}$ with respect to the starting polyMAB. These results show that the weight loss up to 400 °C corresponds to an important and main evolution of carbon contaminants: a carbon loss of about 60 at.% occurs up to 400 °C, in contrast to only a 23 at.% of hydrogen loss and a 8 at.% nitrogen loss. The second important weight loss is about 23 wt.% whereas the total weight loss is close to 43 wt.% at 1000 °C. At this temperature, samples are typically found to correspond to the analytical formula $C_{0.09}N_{1.06}BH_{0.25}$ which can be associated to a total loss of $C_{0.21}N_{0.35}H_{2.13}$ between 400 and 1000 °C. The carbon evolution is



(a) (b)

Fig. 2. Typical SEM images of polymer fibers (a) and BN fibers (b) cross-section prepared from polyMAB.

Table 1
Carbon, nitrogen, hydrogen and boron content (wt.%) of polyMAB and pyrolyzed polyMAB-based fibers up to 1500 °C

Elemental content (wt.%)	Carbon	Nitrogen	Hydrogen	Boron
PolyMAB	19.4	49	7	24.6
Resulting fibers at 400 °C	10	54	6.5	29.5
Resulting fibers at 1000 °C	3.8	55	1	40.2
Resulting fibers at 1500 °C	0	54.3	0	45.7

about 70 at.% whereas the nitrogen and hydrogen losses increase up to almost 25 and 90 at.%, respectively. At this stage, the resulting fibers contain nitrogen and hydrogen excess. The remaining nitrogen and hydrogen atoms are then evolved between 1000 and 1500 °C. The total weight loss is about 46 wt.% at 1500 °C which give a pyrolysis yield of 54%. At this stage, the white fibers are typically found to contain boron and nitrogen weight percents, respectively, of 54.3 and 45.7% demonstrating that the stoichiometry of the resulting ceramic is approaching that of *h*-BN. During the TG analysis, the main gaseous specie observed by GC–MS is CH_3NH_2. The gas evolution from polyMAB-based fibers characterized by a continuous loss from 30 to 1100 °C is divided in two distinct steps corresponding to two main weight losses (Fig. 3). While the CH_3NH_2 loss is important from 20 to 400 °C as shown the CH_3NH_2 release curve, it seems that others products are evolved above 400 °C as attest the elemental analysis results. These data evidenced that the hydrogen and nitrogen losses increased in the second stage compared with the first one while the carbon contaminant loss is practically constant. To complete these analysis and data, we have obtained the FTIR spectra of the polymer and its solid pyrolysis products as a function of temperature.

2.2. FTIR study up to 400 °C

The changes in FTIR spectra of fibers during the heat-treatment up to 400 °C are shown in Fig. 4. The FTIR spectrum of polyMAB-based fibers (Fig. 4(a)) exhibits a characteristic sharp band at 3430 cm^{-1} assigned to the stretching of N–H and characteristic C–H stretching observed in the 2900 cm^{-1} region. Additional signals at around 1460, 1120 and 730 cm^{-1} are, respectively, characteristic of the borazine B–N stretching coupling with CH_3 deformation in methylamino groups ($-NHCH_3$), C–N stretching coupling with the NH deformation and B–N ring deformation. After the first important weight loss, the FTIR spectrum at 400 °C (Fig. 4(b)) displays absorptions characteristic of the initial polyMAB-based fibers. It was observed by GC–MS analysis that the first weight loss of the polyMAB is related to the important CH_3NH_2 loss with the temperature increase. This fact is also supported by the IR spectra of the condensate at 400 °C. Indeed, during the heat treatment, no significant changes in the position of the peaks are observed but the decrease in intensity of the N–H, C–H and C–N relative to the intensity of the BN ring absorption is clearly visible. Moreover, a band with a very low intensity appears at ~ 3210 cm^{-1} and can be assigned to the stretching vibration of NH_2 groups. Unfortunately, we could not identify the nature of the reactions associated with CH_3NH_2 evolving from polyMAB and NH_2 groups appearance. Nevertheless, it is probable that the CH_3NH_2 release occurs via the formation of intermacromolecular processes as shown in Scheme 1 [7,10]. The presence of NH_2 groups means that the borazine rings are not fully preserved as the structural unit of the resulting material. The NH_2 groups are certainly formed from intramacromolecular mechanisms with borazine ring openings presented in Scheme 2 and postulated by Paciorek [10], Toeniskoetter [11], Rye [12] and Kimura [13]. However, the reader should not conclude that the structures depicted in Schemes 1 and 2 are necessarily formed during pyrolysis of the polyMAB-based fibers.

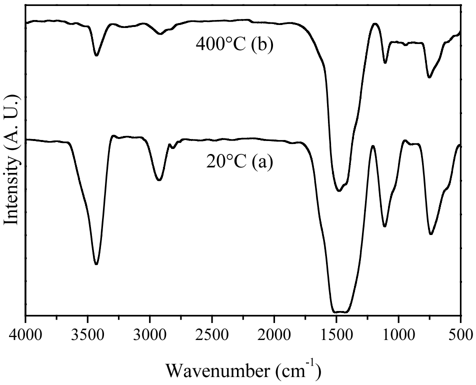
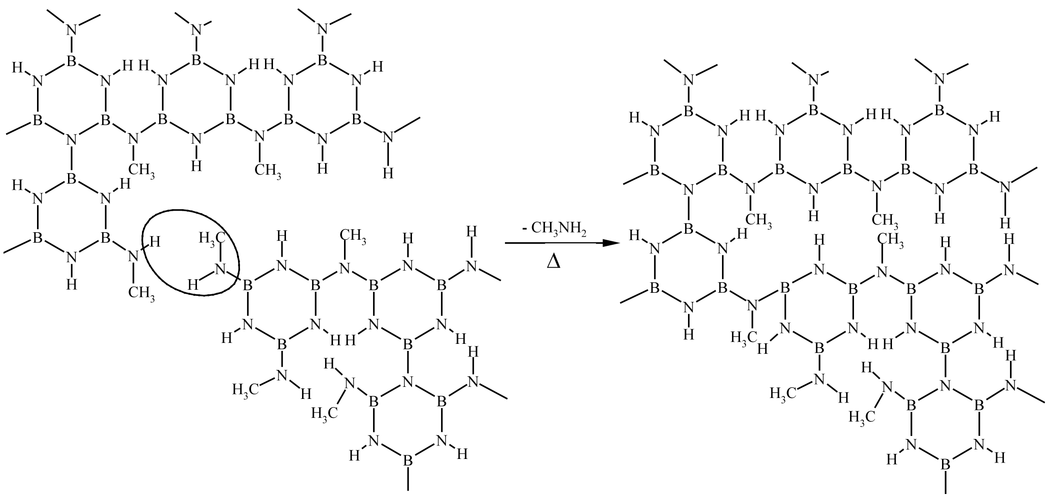


Fig. 4. FTIR spectra of polyMAB-based fibers at 20 °C (a) and 400 °C (b).

As shown in Scheme 1, the $-NHCH_3$ groups pertaining to two borazine rings react together with subsequent elimination of CH_3NH_2. This develops $-N(CH_3)$-bridged-bonds between macromolecules in the resulting fibers. There exists also a possibility of direct B–N linkage establishment when the $-NHCH_3$ groups react with hydrogen atoms of the ring nitrogen atom by a similar mechanism. The intermacromolecular process as shown in Scheme 1 in the low temperature step ($<$ 400 °C) due to the considerable CH_3NH_2 loss therefore creates gradually a three-dimensional polymeric network.

In Scheme 2, the initial step results from a breaking of rings B–N bond followed by B–N bond rotation and ring closure with subsequent hydrogen atom shift from the ring nitrogen to amino nitrogen. The amount of $-NH_2$ groups increases with the increasing borazine ring openings. The consolidation of borazinic rings occurred

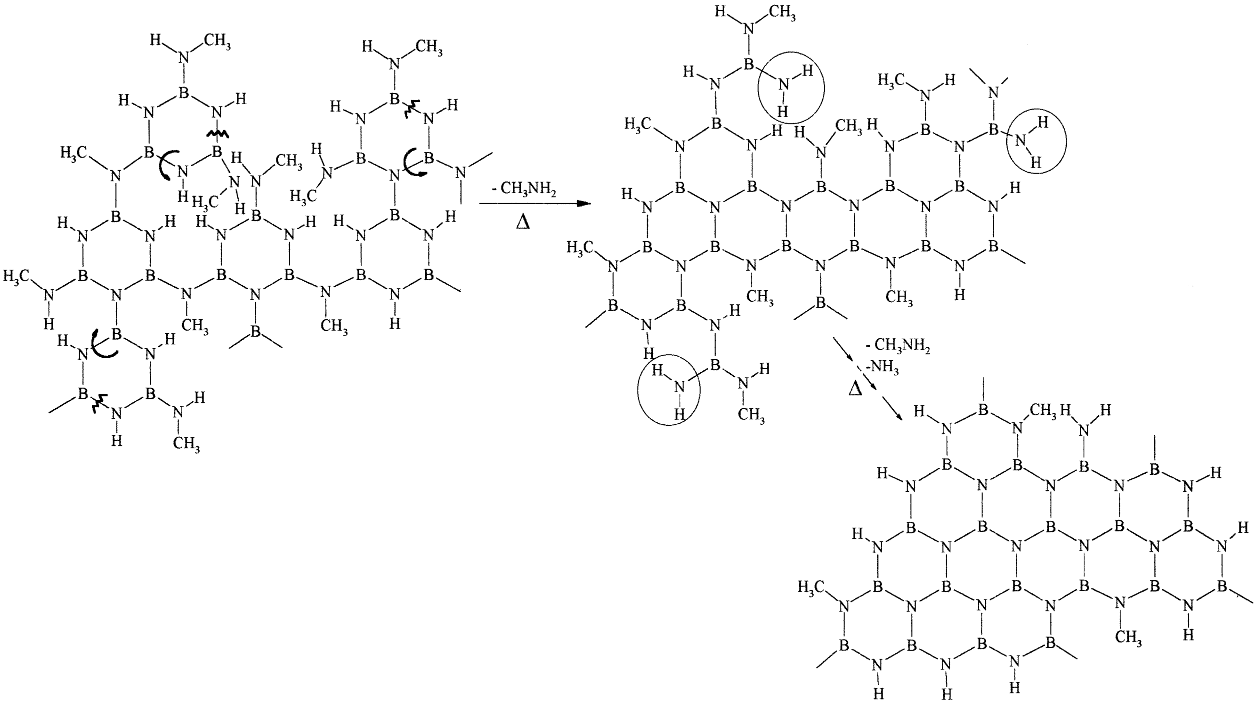


Scheme 1. Evolution of CH_3NH_2 via the formation of intermacromolecular bonds.

with CH_3NH_2 evolution by transfer of a hydrogen atom to the $-NHCH_3$ groups. The transfer of a second hydrogen atom to the $-NH_2$ groups formed would then permit loss of NH_3 molecules. However, the borazine ring opening process seems minor up to 400 °C as shown by the low intensity of the $-NH_2$ band compared with B–N and N–H stretching bands at 1460 cm^{-1} (Fig. 4(b)). The first stage can be described as a dominating further condensation of the polyMAB with branching (Scheme 1) and the resulting solid at 400 °C may be consequently considered as a thermally cross-linked polymer fiber.

2.3. FTIR study from 400 to 1000 °C

Fig. 5 shows FTIR spectra of fibers corresponding to the second important weight loss. Further heating up to 1000 °C results in a gradual decrease of N–H (3430 cm^{-1}), C–H (2920–2840 cm^{-1}) and C–N (1120 cm^{-1}) stretching absorptions. However, the intensity of the absorption band assigned to the stretching vibration of $-NH_2$ groups at 3210 cm^{-1} increases at 500 °C (Fig. 5(a)) compared with the spectrum at 400 °C (Fig. 4(b)) and it is particularly significant in the FTIR spectrum corresponding to a treatment up to 800 °C (not



Scheme 2. Borazine ring opening process with formation of NH_2 groups.

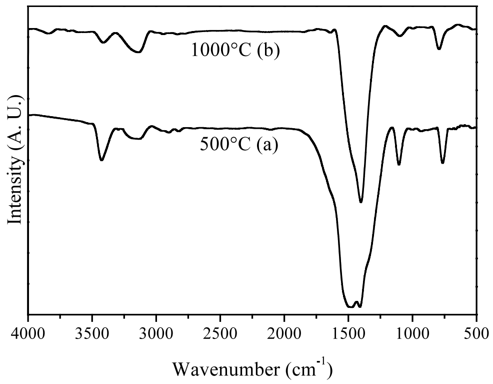


Fig. 5. FTIR spectra of polyMAB-based fibers at 500 (a) and 1000 °C (b).

produced) and 1000 °C (Fig. 5(b)). The $-NH_2$ groups proportion increases from 400 to 800 °C then becomes stable up to 1000 °C while the amount of $-NHCH_3$ groups decreases continuously since 400 °C. This means that a considerable amount of intramacromolecular rearrangements by borazine ring opening processes occurred (Scheme 2) whereas, in the same time, CH_3NH_2 always evolved due to intermacromolecular reactions.

The important presence of $-NH_2$ groups in the resulting fibers can cause the further loss of NH_3. In the FTIR spectrum at 1000 °C (Fig. 5(b)), the C–H bands disappearance and the absorption bands at 1410, 1120 and 800 cm^{-1} become well-defined peaks.

The intermediate temperature step from 400 to 1000 °C can be seen as a polymer–mineral transition. Fused ring structures displaying $-NH_2$ groups are gradually formed in the second stage from intramacromolecular rearrangements due to borazine ring openings. A slightly hydrogenated ceramic fiber is fabricated at 1000 °C.

2.4. FTIR study above 1000 °C

FTIR spectra of fibers corresponding to 1500 and 1800 °C are presented in Fig. 6. The absorption bands ascribed to $-NH_2$ groups decrease in intensity with increasing temperature above 1000 °C. The high-temperature step starting around 1000 °C occurred with a probable loss of NH_3 from resulting material with intermacromolecular reactions. At 1500 °C (Fig. 6(a)), the amino stretching bands are weak demonstrating that the borazine-ring openings are entirely accomplished. The thermal analysis completed by elemental analysis and FTIR data indicate that the formation of planar BN units is complete at 1500 °C. At 1800 °C (Fig. 6(b)), the infrared spectrum shows a strong and broad absorption band centered at 1370 cm^{-1} and a sharp weak band at 805 cm^{-1} which are characteristic of specific types of chemical bonds B–N of h-BN [14]. The bands are assigned to plane ring vibration at 1370 cm^{-1} (E_{1u} mode) and out of the plane ring vibration at 805 cm^{-1} (A_{2u} mode), respectively [15]. These two bands change position with the increase of the pyrolysis temperature from 20 to 1800 °C due to the modification of the atomic environment and the crystallization process studied by X-ray diffraction techniques.

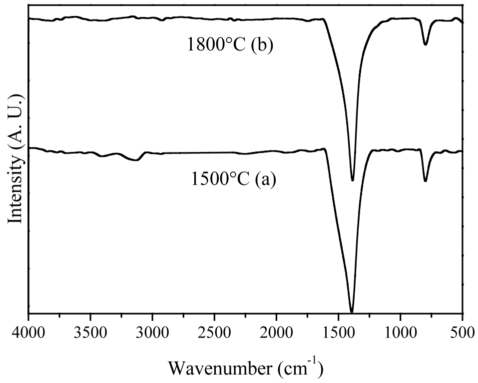


Fig. 6. FTIR spectra of polyMAB-based fibers at 1500 and 1800 °C.

2.5. X-ray diffraction of polyMAB-based fibers pyrolyzed up to 1800 °C

X-ray diffractograms of fibers pyrolyzed up to 1800 °C are presented in Fig. 7. As evidenced in Fig. 7, the X-ray diffractograms of the pyrolyzed fibers from 1000 to 1800 °C show that the diffraction peaks sharpen above 1300 °C. The crystallization of the amorphous polyMAB-based fibers becomes apparent in the temperature range 1300–1500 °C while a variation of the peak width and position angle are clearly observed. The peaks obtained at 1800 °C are characteristic of h-BN material [16].

The Table 2 summarizes the microstructural parameters calculated from the diffractograms. The microstructural parameters such as the crystallite size in the c-axis ($\bar{L}_c$) and the interplanar spacing (d_{002}) strongly increase in the temperature range 1300–1500 °C. This

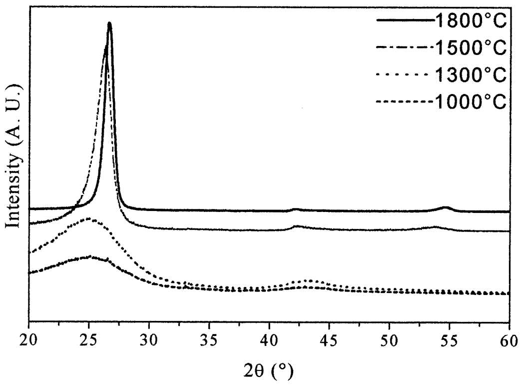


Fig. 7. X-ray diffractograms of polyMAB-based fibers from 1000 to 1800 °C.

Table 2
Microstructural parameters of pyrolyzed polyMAB-based fibers obtained by X-ray analysis

	1000 °C	1300 °C	1500 °C	1800 °C
$\bar{L}_c$ (nm)	1.2	1.2	6	10
d_{002} (nm)	0.353	0.353	0.342	0.334

behavior may be attributed to the progressive crystallization of the BN fibers from 1400 to 1800 °C.

3. Experimental

Standard inert atmosphere techniques are used in the syntheses and manipulations of all compounds. The melt-spinning process is realized under inert atmosphere.

3.1. Preparation of the ex-polyMAB BN fibers

The polyMAB is prepared by thermal condensation of MAB [9,17]. Its exact structure is not well known but it seems that the condensation products present the two structural models schematically illustrated in Fig. 1. MAB (44.2 g; 263 mmol) was heated up to 200 °C during 58 h and a yellow solid was obtained (33.6 g). The condensation degrees of oligomeric MAB condensates are described in terms of weight loss between initial monomer (MAB) and final polymer (polyMAB). They can vary as a function of the final reaction temperature and the thermal cycle of the MAB condensation. Degree of condensation (wt.%): 24. Second-order transition (T_g (°C)): 84. Anal. Found (wt.%): C, 19.4; H, 7; N, 49; B, 24.6. FTIR (cm^{-1}): 3430 (ν_{N-H}), 2920, 2840 (ν_{C-H}), 1460 ($\nu_{B-N}+\delta_{C-H}$), 1120 ($\nu_{C-N}+\delta_{N-H}$), 730 (BN out-of-plane bending).

The polyMAB is spun in the molten state under nitrogen atmosphere as continuous fibers by a laboratory scale apparatus. The continuous polyMAB-based fibers winded around a reel are heated under a pure ammonia atmosphere from 25 to 1000 °C and heated up to 1800 °C under a flow of pure nitrogen. Anal. Found at 400 °C (wt.%): C, 10; H, 6.5; N, 54; B, 29.5; at 1000 °C: C, 3.8; H, 1; N, 55; B, 40.2; at 1500 °C: N, 54.3; B, 45.7. Calc. for *h*-BN: N, 56.4; B, 43.6%. FTIR (cm^{-1}) at 400 °C: 3430 (ν_{N-H}), 3210 (ν_{NH_2}), 2920, 2840 (ν_{C-H}), 1460 ($\nu_{B-N}+\delta_{C-H}$), 1120 ($\nu_{C-N}+\delta_{N-H}$), 760 (BN out-of-plane bending); at 500 °C: 3430 (ν_{N-H}), 3210 (ν_{NH_2}), 2920, 2840 (ν_{C-H}), 1460 ($\nu_{B-N}+\delta_{C-H}$), 1120 ($\nu_{C-N}+\delta_{N-H}$), 770 (BN out-of-plane bending); at 1000 °C: 3430 (ν_{N-H}), 3210 (ν_{NH_2}), 1410 (ν_{B-N}), 1120 (δ_{N-H}), 800 (BN out-of-plane bending); at 1500 °C: 3430 (ν_{N-H}), 3210 (ν_{NH_2}), 1400 (ν_{B-N}), 805 (BN out-of-plane bending), at 1800 °C: 1370 (ν_{B-N}), 805 (BN out-of-plane bending). XRD (2θ (°)) at 1000 °C: (002) 25.15, (10) 42.8; at 1300 °C: (002) 25.21, (10) 42.9; at 1500 °C: (002) 26.1, (10) 42.3, (004) 54.3; at 1800 °C (JCPDS card): (002) 26.62 (26.76), (10) 42.06 (41.6), (004) 54.49 (55.16).

3.2. Characterizations

DSC analyses are performed on a TA8000 Mettler-Toledo apparatus.

The pyrolytic yield of the polyMAB-based fibers are obtained by heating samples at 0.8 °C min^{-1} under an ammonia–nitrogen mixture (1:1) from 20 to 1000 °C thus, from 1000 to 1500 °C in flowing nitrogen (TGA 92 16.18 by SETARAM).

Fourier transform-infrared (FTIR) spectra of the fibers heated from 20 to 1800 °C are obtained using a Nicolet Magna 550 Fourier transform-infrared spectrometer in the range of 4000–500 cm^{-1}. The fibers are pulverized, mixed with KBr powder and finally pressed as pellets.

The identification of pyrolysis products is performed by a GC system (Hewlett–Packard model Agilent micro-GC M200) connected to a high resolution mass-spectrometer (Agilent 5973 network Mass selective detector). The coupling of the two apparatus permits to assess qualitatively to the nature of the gas evolved during the TG analysis.

Elemental analysis are performed by The Service Central de Microanalyse du CNRS (Vernaison, France) on the crushed polyMAB-based fibers from 20 to 1500 °C.

X-ray diffraction (XRD) is carried out on fibers in a temperature range of 1000–1800 °C. The specimens are placed in the position so that the fiber-axis is perpendicular to incidence plane. A Phillips X-ray diffractometer is used with Cu–K$_{\alpha 1}$ radiation of wavelength 0.15406 nm and a scan range from 20 to 60° with a step size of 0.03. Interplanar spacing d_{002} is calculated using the Bragg equation. The stacking size ($\bar{L}_c$, stacking height layer planes) is calculated using the Scherrer relation, $\bar{L}_c = 0.9\lambda/(B^2 - B'^2)^{1/2} \cos\theta$.

4. Conclusion

The TGA/GC–MS, FTIR and DRX techniques used in this work are suitable to identify changes taking place in poly[2,4,6-tri(methylamino)borazine]-based fibers during pyrolysis. The conversion process into BN fibers can be divided in three major temperature ranges. In the first stage 20–400 °C, weight loss occurs due to the principal evolution of CH_3NH_2. The concentration of cross-linking increases by formation of a considerable amount of branching (interborazinic direct and bridged-bond). The second stage is transitional toward hydrogenated ceramic fibers around 1000 °C: a polymeric–mineral transition is occurred with numerous intramacromolecular rearrangements. In the three stage up to 1800 °C, a crystallization process with increase of grain size leads to carbon-free BN fibers at 1800 °C.

References

[1] R.T. Paine, C.K. Narula, Chem. Rev. 90 (1990) 73.

[2] K.J. Wynne, R.W. Rice, Annu. Rev. Mater. Sci. 14 (1984) 297.

[3] M. Blazso, J. Anal. Appl. Pyrol. 39 (1997) 1.

[4] P. Greil, Adv. Eng. Mater. 2 (2000) 339.

[5] P.J. Fazen, J.S. Beck, A.T. lynch, E.E. Remsen, L.G. Sneddon, Chem. Mater. 2 (1990) 96.

[6] (a) T. Wideman, L.G. Sneddon, Chem. Mater. 8 (1996) 3;
(b) T. Wideman, E.E. Remsen, E. Cortez, V.L. Chlanda, L.G. Sneddon, Chem. Mater. 10 (1998) 412.

[7] Y. Kimura, Y. Kubo, N. Hayashi, Comp. Sci. Technol. 51 (1994) 173.

[8] S. Bernard, B. Bonnetot, D. Cornu, R. Favre, P. Miele, B. Toury, P. Toutois, H. Vincent, French Patent no. 2806422-A1 (2000).

[9] (a) S. Bernard, M.P. Berthet, J. Bouix, D. Cornu, P. Miele, B. Toury, P. Toutois, C. Vincent, French Patent no. 2806423-A1 (2000).;
(b) B. Toury, P. Miele, D. Cornu, H. Vincent, J. Bouix, Adv. Funct. Mater. 12 (2002) 228.

[10] K.J.L. Paciorek, D.H. Harris, R.H. Kratzer, J. Polym. Sci. 24 (1986) 173.

[11] R.H. Toeniskoetter, F.R. Hall, Inorg. Chem. 2 (1963) 29.

[12] R.R. Rye, D.R. Tallant, Chem. Mater. 3 (1991) 286.

[13] Y. Kimura, Y. Kubo, N. Hayashi, J. Inorg. Org. Polym. 2 (1992) 231.

[14] F.A. Miller, C.H. Wilkins, Anal. Chem. 24 (1952) 1253.

[15] R.J. Nemanich, S.A. Solin, R.M. Martin, Phys. Rev. B 23 (1981) 6348.

[16] M. Hubacek, M. Ueki, T. Sato, V. Brozek, Thermochim. Acta 282/283 (1996) 359.

[17] G. Mignani, C. Richard, R. Trichon, French Patent no. 2695645 (1992).