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Thermal behaviour of a series of poly[*B*-(methylamino)borazine] for the preparation of boron nitride fibers

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Abstract

The thermal behaviour of a series of poly[*B*-(methylamino)borazine] prepared at various temperatures ranging from 140 to 200 °C is studied in the present paper as potential BN fiber precursors. It was shown that the softening capability of poly[*B*-(methylamino)borazine] can be tailored by controlling the temperature at which polymers were prepared to achieve melt-spinning and produce high quality green fibers. Thus as-spun fibers could be next converted into boron nitride fibers using ammonia (25–1000 °C) and nitrogen (25–1800 °C) atmospheres. The quality of boron nitride fibers was shown to depend on the first part of the pyrolysis step (25 and 1000 °C; ammonia atmosphere) in which the great majority of the weight loss necessary for boron nitride production occurs. Ideal poly[*B*-(methylamino)borazine] as BN fiber precursors are those prepared between 170 and 180 °C. They display appropriate melt-spinnability and ceramic conversion capability.

Keywords: Poly[*B*-(methylamino)borazine]; TMA; Softening; Spinnability; TGA; Pyrolysis; Fibers

1. Introduction

The polymer-derived ceramics (PDCs) route has seen an increasing interest during the past decade for the preparation of non-oxide ceramics.[1,2] Using this chemical approach, the chemistry and the polymerization of the starting molecular precursor may be tailored to adjust the composition and the viscoelastic properties of the derived preceramic polymer and therefore prepare complex polymer shapes in a wide variety of non-oxide systems. Thus as-obtained green shapes may be merely decomposed into PDCs with retention of this shape by controlling the further curing and pyrolysis processes which are performed under oxygen-free atmospheres. Because the preparation of ceramic fibers is one of the most demanding prospects, a great interest was focused on the synthesis of preceramic polymers displaying a tailored melt-spinnability and an appropriate chemical and thermal reactivity for the conversion of green fibers derived therefrom into ceramic fibers.[3–6]

In our group, we showed that preceramic polymers of the type poly[*B*-(methylamino)borazine] are well suited to fill the requirements for the preparation of boron nitride fibers.[7–14] However, a lack of reproducibility in the mechanical performances of these fibers can be encountered if the viscoelastic and thermal properties of polymers are not defined.

It is therefore the aim of this work to help to the understanding of the melt-spinnability and ceramic conversion capability of preceramic polymers based on a thermal study dedicated to a series of poly[*B*-(methylamino)borazine] as BN fiber polymers. In the present paper, we study the plastic deformation of such polymers by means of thermo-mechanical analyses (TMA) in order to provide the synthesis conditions and structural features which allow us to develop stable and melt-spinnable polymers. In addition, we focus our study on the transformation of the derived green fibers into ceramic fibers through thermogravimetric analyses (TGA) in order to select the melt-spinnable polymers which allow us to produce boron nitride fibers with desired and reproducible final properties. This paper highlights that TMA and TGA are appropriate tools to predict both melt-spinnability and ceramic conversion capability of preceramic polymers as ceramic fiber precursors.

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2. Experimental procedure

2.1. General comment

All syntheses were carried out in a purified argon atmosphere, using argon/vacuum lines, and Schlenk-type glasses. Ammonia and nitrogen were used in the as-received state (>99.999%). Thermal behaviour of polymers was investigated in a nitrogen atmosphere ($P_{N_2} = 1$ bar) by thermo mechanical analysis (Mettler Toledo TMA/SDTA 840) on polymer pellets ($S = 0.25\,\mathrm{cm}^2$) using compressive load from 30 to 200 °C (300 °C/h). Thermogravimetric analysis of the ceramic transformation was taken on a Setaram TGA 92 16.18 from 25 to 1000 °C (60 °C/h) under ammonia atmosphere at $P_{NH_3} = 1$ bar using silica crucibles.

2.2. Fiber preparation

Synthesis procedure and characterization of the precursor, *B*-tri(methylamino)borazine (Fig. 1), have been described elsewhere.[12]

B-tri(methylamino)borazine is thermolyzed at moderate temperatures to yield preceramic networks, namely poly[*B*-(methylamino)borazine], with different chemical and structural properties.[12] This thermolysis step is carried out in an argon atmosphere (3 L/h) at $P_{Ar} = 1$ bar up to the desired temperatures ($T_{\text{thermolysis}}$) ranging from 140 to 200 °C. These polymers are delivered as air- and moisture-sensitive glassy solids at RT. Seven polymers are studied in the present paper. All poly[*B*-(methylamino)borazine] samples display the same IR bands and positions as well as NMR signals in FT-IR and NMR spectra.[12] IR data (KBr pellets, cm^{-1}): 3434 (m); 2958 (w) 2928 (w), 2898 (w), 2820 (m); 1597 (s); 1515 (s); 1460 (s); 1411 (s); 1178 (s); 1095 (m), 707 (w). ^{11}B NMR (96.29 MHz, C_6D_6, ppm): 25.7 (br); ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): 1.86 br (–N(*H*)CH$_3$); 2.47 vbr (–N(H)C*H*$_3$); 2.56 vbr (Bridging –N(C*H*$_3$)–); 2.70–4.10 br (N*H* borazine). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm) 27.6, 27.9 (–N(H)*C*H$_3$); 31.2 (Bridging –N(*C*H$_3$)–). It should be mentioned that attempts to have a precise idea of the molecular weight failed, since the found values for all polymers are too close to distinguish each compound by their proper molecular weight.[12] Comp. Found (referenced to $B_{3.0}$): $B_{3.0}N_{4.7}C_{2.7}H_{11.6}$ (140 °C); $B_{3.0}N_{4.5}C_{2.4}H_{10.1}$ (150 °C); $B_{3.0}N_{4.5}C_{2.2}H_{10.1}$ (160 °C); $B_{3.0}N_{4.5}C_{2.0}H_{9.3}$ (170 °C); $B_{3.0}N_{4.4}C_{2.0}H_{9.5}$ (180 °C); $B_{3.0}N_{4.3}C_{1.9}H_{9.2}$ (190 °C); $B_{3.0}N_{4.2}C_{1.9}H_{8.7}$ (200 °C). Oxygen content is found to be lower than 2 at.% and was therefore omitted.

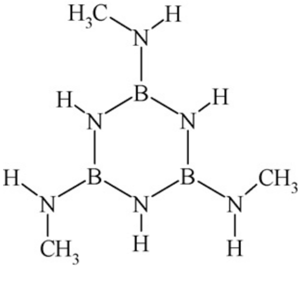

Fig. 1. Structure of the *B*-tri(methylamino)borazine.

For spinning, polymers are placed at RT into a piston-extrusion chamber set up in a nitrogen-filled glove-box, and then heated to the spinning temperature T_{spinning} at which the polymer melt flow is forced along the extrusion line through a spinneret with a single capillary of 200 μm in diameter. The emerging molten filament is drawn by a take-up spool and continuously recovered onto the spool as a fine-diameter solid filament. Thus as-spun fibers are subsequently heated in a silica tube furnace under ammonia atmosphere from 25 to 1000 °C (60 °C/h; dwell time of 2 h), then in a graphite furnace under nitrogen atmosphere from 25 to 1800 °C (100 °C/h; dwell time of 2 h) to yield crystalline BN fibers.

3. Results and discussion

3.1. Thermo-mechanical behaviour

Once solid poly[*B*-(methylamino)borazines] have been prepared, it is desired to assess their capability to form polymer fiber by melt-spinning. Thermo-mechanical analysis (TMA) has been used in a nitrogen atmosphere to investigate the softening capability of poly[*B*-(methylamino)borazine] using compressive load through the observation of the dimensional changes of the polymer upon heating. Fig. 2 presents the TMA curves using a compressive load of 0.1 N. For clarity, only five polymers prepared at different temperatures ($T_{\text{thermolysis}}$) ranging from 140 to 200 °C are presented in Fig. 2.

In a first approximation, Fig. 2 shows that the plastic deformation of polymer is closely related to the temperature at which they are prepared, *i.e.*, $T_{\text{thermolysis}}$. In particular, an increase of $T_{\text{thermolysis}}$ from 140 to 200 °C shifts the plastic deformation to higher temperatures and reduces the dimensional change.

In more detail, Fig. 2 identifies three distinct sets of thermo-mechanical behaviours. First, polymers prepared at $T_{\text{thermolysis}}$ ≤150 °C are seen to strongly shrink in thickness as illustrated by the large dimensional change which is measured

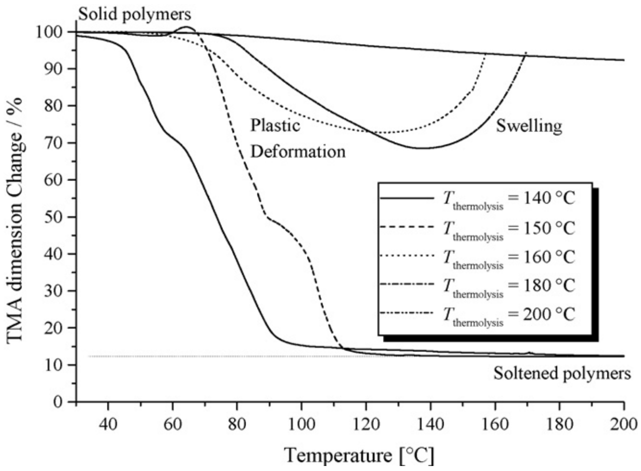

Fig. 2. TMA curves for poly[*B*-(methylamino)borazines] isolated at different $T_{\text{thermolysis}}$.

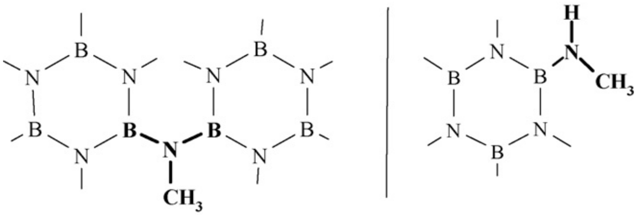

Fig. 3. –N(CH$_3$)– units and –N(H)CH$_3$ groups identified in poly[*B*-(methylamino)borazine] by ^{1}H and ^{13}C liquid-state NMR.

(∼85%). TMA curves obtained for these polymers show that softening starts to occur at ∼48 °C ($T_{\text{thermolysis}} = 140\,°\text{C}$) and ∼70 °C ($T_{\text{thermolysis}} = 150\,°\text{C}$) and is complete at ∼92 °C ($T_{\text{thermolysis}} = 140\,°\text{C}$) and ∼115 °C ($T_{\text{thermolysis}} = 150\,°\text{C}$). We suggest that the appearance of two ranges of melting for these polymers is most probably caused by different molecular weight species which melt in different temperature ranges. Second, the magnitude of the plastic deformation of polymers synthesized at $T_{\text{thermolysis}} \leq 190\,°\text{C}$ is reduced (30–35% in dimensional change) and this partial softening occurs in an one-step process starting from ∼70 °C ($T_{\text{thermolysis}} = 160\,°\text{C}$) and ∼80 °C ($T_{\text{thermolysis}} = 180\,°\text{C}$). Third, the polymer obtained at $T_{\text{thermolysis}} = 200\,°\text{C}$ remains almost dimensionally stable under load, *i.e.*, no softening was observed in the temperature range investigated here.

The thermo-mechanical behaviour can be understood by considering the structural elements which compose the polymer structure.

Poly[*B*-(methylamino)borazines] are composed of at least two decisive structural elements, *i.e.*, bridging –N(CH$_3$)– units and –N(H)CH$_3$ groups (Fig. 3), as determined by ^{1}H (300 MHz, CD$_2$Cl$_2$, ppm; 1.86 br (N(*H*)CH$_3$); 2.47 vbr (N(H)C*H*$_3$); 2.55 vbr (NC*H*$_3$)) and ^{13}C (75 MHz, CD$_2$Cl$_2$, ppm; 27.6, 27.9 (N(H)*C*H$_3$); 31.2 (Bridging N*C*H$_3$)) liquid-state NMR spectroscopy. The identification of these two structural elements means that polymerization occurs *via* methylamine condensation forming bridging –N(CH$_3$)– units from two –N(H)CH$_3$ groups. However, it is important to mention that ^{15}N solid-state NMR shows that this major mechanism occurs in complement with minor mechanisms through establishment of inter-ring B–N bonds and the occurrence of ring-opening process.[12]

Experimental and simulated ^{13}C CP MAS NMR spectra (Bruker Avance 300 spectrometer at frequencies of 75.47 MHz) of three polymers prepared at 140, 160 and 180 °C (Fig. 4) confirm the formation of bridging –N(*C*H$_3$)– units ($\delta_{\text{iso}} = 30.5$ ppm) and the presence of –N(H)*C*H$_3$ groups ($\delta_{\text{iso}} = 28$ ppm) in poly[*B*-(methylamino)borazine]. The identification of a relatively high intensity signal for –N(H)*C*H$_3$ groups means that these groups are still present in the polymer, and therefore that the polymerization remains incomplete even at $T_{\text{thermolysis}} = 200\,°\text{C}$.

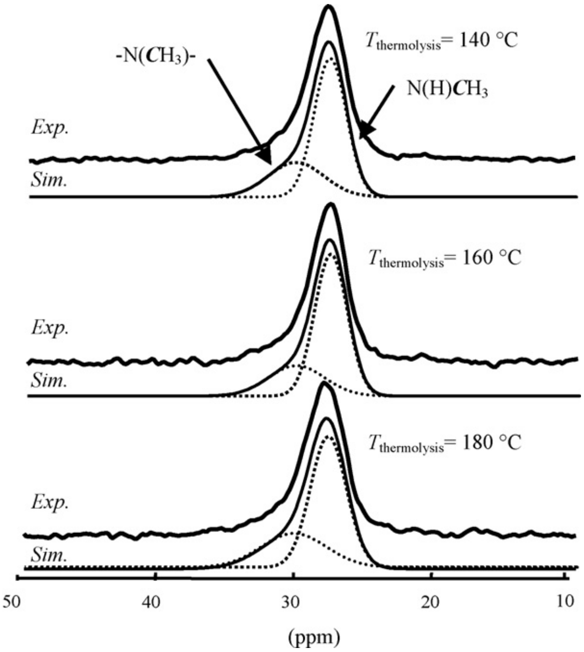

Fig. 4. Experimental and corresponding simulated ^{13}C CP MAS NMR spectra for samples isolated during the thermolysis process at various $T_{\text{thermolysis}}$.

Although cross-polarization (CP) is not quantitative, *i.e.*, the relative amount of –N(H)CH$_3$ groups is overestimated due to the high amount of protons around the BN(H)CH$_3$ site, the estimation of the relative amount of –N(H)CH$_3$ groups is a good indicator of the polymerization progress. As indicated in Table 1, a decrease of the relative amount of –N(H)CH$_3$ groups is observed going from 140 to 200 °C. The relative amount of the –N(H)CH$_3$ groups and bridging –N(CH$_3$)– units extracted from the simulation of the ^{13}C CP MAS NMR spectra are detailed in Table 1.

Based on data reported in Table 1, it is therefore reasonable to postulate that the shift of the polymer softening and the decrease of the plastic deformation magnitude with increasing $T_{\text{thermolysis}}$ are attributed to the polymerization progress, *i.e.*, a decrease of the relative amount of unreacted –N(H)CH$_3$ groups. Keeping in mind that molecular weights are unchanged going from one polymer to the other (see experimental section and Ref. [12]), we suggest that thermolysis occurs *via* intramolecular condensation decreasing the free volume in the polymer network, thereby reducing the softening capability of polymers.

Besides, it is interesting to observe in Fig. 2 that the TMA curves for polymers prepared at $160\,°\text{C} \leq T_{\text{thermolysis}} \leq 180\,°\text{C}$ rose above 120 °C due to the swelling of polymers. This phenomenon appears when low values of load are used during TMA experiments. As an illustration, Fig. 5 shows the general thermo-mechanical behaviour of a polymer prepared at

Table 1
Proportion of –N(*C*H$_3$)– and –N(H)*C*H$_3$ units as a function of $T_{\text{thermolysis}}$ measured by ^{13}C solid-state NMR

$T_{\text{thermolysis}}$ (°C)	Relative intensity (%) (±2)	
	$\delta_{\text{iso}} = 30.5$ ppm	$\delta_{\text{iso}} = 28$ ppm
140	23	77
150	27	73
160	29	31
170	30	70
180	31	69
190	32	68
200	32	68

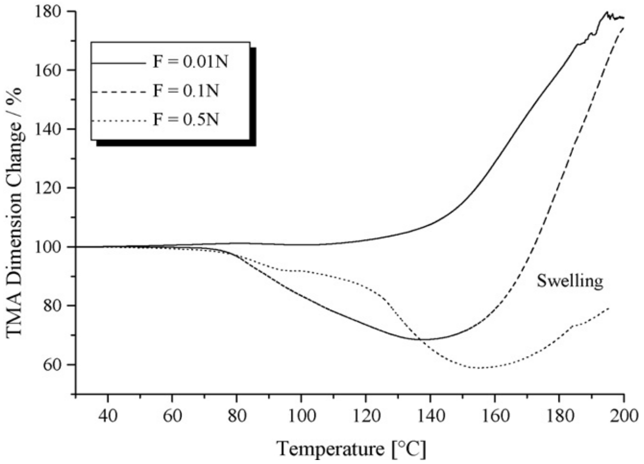

Fig. 5. TMA curves for a poly[*B*-(methylamino)borazine] ($T_{\text{thermolysis}} = 180\,°\text{C}$) using different loads.

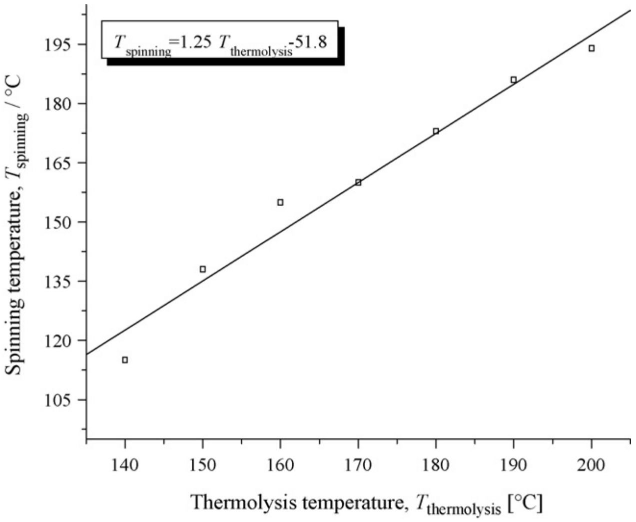

Fig. 6. Variation of T_{spinning} as a function of $T_{\text{thermolysis}}$.

$T_{\text{thermolysis}} = 180\,°\text{C}$ using different values of load in the range 0.01–0.5 N.

It is clearly observed that polymer swelling is reduced when the load used during TMA experiments is increased from 0.01 to 0.5 N.

In addition, increasing the load from 0.01 to 0.1 N, and then 0.5 N allows the polymer softening to be identified. Lastly, it is observed that the temperature at which softening is achieved, *i.e.*, dimensional change is maximum, increases. All these observations reflect the strong dependence of the polymer softening with the value of the load used during TMA experiments. Spinning experiments reflect such findings.

Melt-spinning of poly[*B*-(methylamino)borazine] is generally carried out under load >30 daN for a polymer surface of 1 cm^2. Using such conditions, a polymer prepared at $T_{\text{thermolysis}} = 180\,°\text{C}$ is extruded into a softened filament in a narrow range of T_{spinning} between 170 and 172 °C. In comparison, the temperatures at which the softening of this polymer is maximum (Fig. 5) are ∼140 °C (0.1 N) and ∼155 °C (0.5 N). Therefore, a very specific softening temperature must be exceeded by ∼15 °C for spinning poly[*B*-(methylamino)borazine] compared with TMA results obtained using a load of 0.5 N. In accordance with the narrow temperature range over which spinning occurs, this effect has to be considered.

Fig. 6 reports the spinning temperature (T_{spinning}) of polymers as a function of the temperature, *i.e.*, $T_{\text{thermolysis}}$, at which they are prepared.

In good agreement with the shift of the polymer softening to higher temperatures with increasing $T_{\text{thermolysis}}$ (see Fig. 2), T_{spinning} is seen to increase with increasing $T_{\text{thermolysis}}$. In addition, as found during TMA experiments, there are three distinct sets of melt-spinning behaviours. Polymers synthesized at 140 and 150 °C were easily extruded at 115 and 138 °C, respectively. Several meters of fibers could be produced, but the derived softened filament emerging from the capillary exhibited a low viscosity which caused capillary instability. Therefore, such polymers are not appropriate candidates to produce high quality green fibers.

Poly[*B*-(methylamino)borazines] prepared below 190 °C were readily spinnable, since fine-diameter fibers ($17.5 \le d\ (\mu\text{m}) \le 21$) could be produced by stretching the emerging softened filament without spinning instability. In contrast, the spinning of the poly[*B*-(methylamino)borazine] obtained at 200 °C was not successful, since the derived filament which emerged from the capillary with difficulty was highly viscous. Stretching was not possible. Such results can be linked to rheological experiments which have been achieved for the same polymeric systems.[13]

3.2. Polymer-to-ceramic conversion

Thermogravimetric analysis of the poly[*B*-(methylamino) borazines] prepared between 140 and 200 °C has been carried out under ammonia atmosphere up to 1000 °C (60 °C/h). The ceramic yields of each polymer, which were deduced from the overall weight losses recorded at 1000 °C, are reported in Table 2. It should be mentioned that 95% of the weight loss occurs in the temperature range RT-1000 °C as described in ref. [11] and [14].

As expected, an increase of $T_{\text{thermolysis}}$ causing intramolecular cross-linking involved an increase of the ceramic yield of the corresponding polymer. Different thermal behaviours of the

Table 2
Ceramic yields of polymers prepared at different $T_{\text{thermolysis}}$

$T_{\text{thermolysis}}$ (°C)	Ceramic yield (%)
140	47.9
150	50.8
160	52.5
170	53.1
180	54.5
190	57.3
200	58.2

Fig. 7. Fibers derived from polymers prepared at 140–150 °C.

derived green fibers were therefore observed during their conversion into ceramic fibers. It should be mentioned that fibers are maintained around a spool during heat-treatment to prevent the shrinking effects which are caused by the weight loss of polymers and the density increase of fibers.

Green fibers derived from polymers prepared below 160 °C broke during the first step of the conversion (25–1000 °C) under ammonia atmosphere (Fig. 7).

This is caused by the very high overall weight loss, *i.e.*, low ceramic yield, of the corresponding polymers which occurred at 1000 °C (see Table 2). In contrast, it was observed that a thermolysis above 160 °C was required to increase the degree of cross-linking of poly[*B*-(methylamino)borazine] up to a certain level, thus enhance ceramic yields, and therefore preserve the integrity of fibers during the whole ceramic transformation process (25–1800 °C). Reproducible tensile strength around 1.4 GPa were obtained for the boron nitride fibers derived from these polymers.[7]

4. Conclusion

The thermo-mechanical behaviour of a series of poly[*B*-(methylamino)borazine] has been studied in the present paper. Thermo-mechanical properties of such polymers can be tailored by adjusting the temperature at which they are prepared in order to achieve melt-spinning and produce fine-diameter green fibers. The ceramic transformation of these green fibers into boron nitride fibers was studied by TGA experiments in ammonia atmosphere up to 1000 °C. The quality of the boron nitride fibers depends on the control of the weight loss which occurs in the temperature range 25–1000 °C. Fibers derived from polymers prepared below 160 °C broke during heat-treatment due to the important shrinking effects which occurs below 1000 °C. In contrast, polymers prepared between 170 and 190 °C are ideal candidates as BN fiber precursors.

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