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^{11}B and ^{15}N solid state NMR investigation of a boron nitride preceramic polymer prepared by ammonolysis of borazine

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Abstract

A poly(aminoborazine), precursor for hexagonal boron nitride (h-BN) obtained by reaction of borazine $B_3N_3H_6$ with ammonia, and its pyrolysis derivatives have been extensively characterised by ^{15}N and ^{11}B MAS NMR. The various B and N sites have been identified according to their first neighbouring atoms, as well as to the second ones in the case of ^{15}N, and have also been quantified. This study demonstrates that a suitable choice of NMR techniques together with the use of isotopic enrichment can lead to a large improvement in spectral resolution, which allows a better understanding of such complex BN preceramic polymer structures and permits to follow the polymer-to-ceramic transformation.

Keywords: Polymer; Ceramic; Solid State; NMR; Boron nitride; Poly(aminoborazine)

1. Introduction

Polymeric approach to refractory non oxide ceramics is a process of great interest offering possibilities of obtaining composite and shaped materials such as fibers, films or bulk pieces from soluble or fusible starting polymers.[1] It has first been developed to produce SiC or SiCN-based ceramics, starting from polysilanes, polycarbosilanes and polysilazanes.[2,3] More recently, this approach was extended to the preparation of hexagonal boron nitride (h-BN), a ceramic widely used in high temperature technology.[4] Different families of polymeric precursors have been developed by several groups, starting from borazine[5] ($B_3N_3H_6$); or N- and B-substituted borazines.[4,6–8]

While polyborazilene has proven to be an excellent precursor for the production of boron nitride coating, films and shaped materials, this cross-linked polymer appears less adapted to applications requiring melt-processing due to the need to control the dehydrocoupling reactions. One strategy is to reduce the number of reactive BH and NH groups, by functionalising the polymer with suitable substituents as amines.[9] A good knowledge of the structure of fusible polymers or copolymers seems to be the key to obtain BN fibers with high properties. It is therefore essential to control as much as possible the polymerisation and ceramisation steps and consequently to have effective characterisation tools that can follow the changes in local environments during polymer-to-ceramic conversion. Solid-state NMR studies have been shown to be extremely useful in this field and more particularly, ^{11}B and ^{15}N solid-state NMR techniques are particularly relevant to probe BN-based materials.[10,11]

^{15}N is a spin 1/2 with a very low sensitivity in natural abundance (3.8×10^{-6} compared with ^{1}H) but this drawback may be overcome by ^{15}N enrichment and the use of Cross Polarisation (CP) techniques, taking advantage of the ^{1}H–^{15}N dipolar coupling. These techniques are consequently very sensitive to the proton environment of the ni-

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trogen sites through the ^{1}H–^{15}N distances and to molecular motion.

^{11}B is an abundant isotope (80.22%) but measurement of high-resolution spectra of this half-integer quadrupolar nucleus (I = 3/2) can be difficult because of the second order quadrupolar interaction which distorts the signals and can only be partially averaged by MAS.[12] Moreover, the ^{11}B chemical shift range observed in BN compounds is relatively small.[13] Nonetheless, recording spectra at higher field permits to minimise the second order quadrupolar broadening since the intensity of the quadrupolar interaction is inversely proportional to the static field. Using different fields will also improve the confidence in the simulation of the resonance signals.

In this paper, we report therefore a detailed solid-state NMR characterisation of a poly(aminoborazine) obtained by reactions of borazine $B_3N_3H_6$ with ammonia and its pyrolysis derivatives. This polymer offers several advantages for the impregnation of matrices,[14] and could be a good candidate in the formation of new generation BN fibers.

2. Experimental

2.1. Sample preparation

2.1.1. Poly(aminoborazine) POL(NH_3)

Under an atmosphere of dry nitrogen, 1.30 g (76.5 mmol) of NH_3 (Alphagaz, 3.6 nv) were condensed at −80 °C in a reactor. When the temperature was warmed to −40 °C, 2.00 g (25.0 mmol) of ^{15}N-enriched borazine were added. A quick one-step procedure to obtain borazine from sodium borohydride $NaBH_4$ and ammonium sulfate $(NH_4)_2SO_4$ was recently proposed.[15] The ^{15}N enriched polymer was obtained from enriched borazine synthesized with ammonium sulfate ^{15}N enriched at 10 at.% purchased from Isotec. The mixture was warmed to room temperature in 1 h. The crude was only composed of a white powder, dried under vacuum (0.05 mmHg) to remove the trace of borazine. 2.90 g of a white solid were collected (88% weight yield). The isotopic enrichment was evaluated by mass spectrometry and was estimated to 10%. The structure of this poly(aminoborazine) polymer is compared to a polyborazilene POL(Δ) prepared by a procedure proposed in the literature[16] that consists in thermal dehydropolymerisation of borazine. Pyrolysis of these polymers was then performed by inserting a quartz tube loaded in the glovebox and equipped with a dried argon gas flow into a tubular furnace. The heating rate was 10 °C/min.

2.2. NMR experiments

^{15}N CP MAS experiments were performed at room temperature on a Bruker MSL-300 spectrometer, at a frequency of 30.41 MHz (^{15}N) and 300.13 MHz (^{1}H), using a Bruker CP-MAS probe. Solid samples were spun at 5 kHz, using 7 mm ZrO_2 rotors filled up in a glovebox under dried argon atmosphere. All ^{15}N CP MAS experiments were performed under the same Hartmann-Hahn match condition, set up by using a powdered sample of NH_4NO_3: both RF channel levels $\omega_{1_H}/2\pi$ and $\omega_{15_N}/2\pi$ were carefully set so that $|\omega_{1_H}|/2\pi = |\omega_{15_N}|/2\pi = 42$ kHz. Proton decoupling was always applied during acquisition and a repetition time of 10 s was used. The ^{15}N Single Pulse Experiment (SPE) MAS NMR spectra were recorded with a pulse angle of 90° and a recycle delay between pulses of 100 s. Chemical shifts were referenced to solid NH_4NO_3 (10% ^{15}N enriched sample, δ_{iso} ($^{15}NO_3$) = −4.6 ppm compared to CH_3NO_2 (δ = 0 ppm)).

^{11}B MAS NMR experiments were performed at room temperature on a Bruker MSL-400 spectrometer, at a frequency of 128.28 MHz, using a Doty CP-MAS probe with no probe background. Solid samples were spun at 10 kHz, using 5 mm ZrO_2 rotors filled up in a glovebox under dried argon atmosphere. ^{11}B MAS experiments were also performed at 18.8 T on a Bruker DSX800 spectrometer using 4 mm ZrO_2 rotors. A 1 μs single-pulse excitation (while the $t_{90°}$ measured on BF_3OEt_2 is 8 μs) was employed, with repetition times of 5 s. All ^{11}B chemical shifts were determined relative to liquid BF_3OEt_2 (δ = 0 ppm). Spectra were simulated using the DMFIT program.[17]

3. Results

3.1. Chemical analysis

The results of the elemental analysis of the samples pyrolysed at various temperatures are summarised in Table 1 and were obtained from Service Central d'Analyse du CNRS (Vernaison, France). The poly(aminoborazine) POL(NH_3) exhibits a higher degree of protonation than POL(Δ) prepared by thermal dehydropolymerisation of borazine, suggesting a smaller degree of crosslinking. Moreover, the molar ratio N/B remains fairly constant with temperature and the main evolution observed is a deprotonation of the system. Finally, it is worth noticing that, from 200 °C, compositions of the two systems become quite close.

Table 1
Chemical analysis data and molar compositions of the polymers heat-treated at different temperatures

Pyrolysis temperature (°C)	Element (wt.%)			Empirical formula
	B (±0.2)	N (±2)	H (±0.1)	
POL(NH_3)	33.6	45.0	9.5	$B_{1.0}N_{1.1}H_{3.1}$
200	29.8	50.0	4.8	$B_{1.0}N_{1.1}H_{1.7}$
400	34.3	50.5	3.1	$B_{1.0}N_{1.1}H_{1.0}$
600	35.1	59.0	1.8	$B_{1.0}N_{1.3}H_{0.5}$
POL(Δ)	37.6	53.2	5.1	$B_{1.0}N_{1.1}H_{1.5}$
200	31.3	55.5	3.7	$B_{1.0}N_{1.3}H_{1.3}$
400	29.8	50.8	3.4	$B_{1.0}N_{1.3}H_{1.2}$
800	38.6	55.0	1.2	$B_{1.0}N_{1.1}H_{0.3}$
1450	42.7	54.1	0.2	$B_{1.0}N_{1.0}H_{<0.05}$