Chemically Derived BN Ceramics: Extensive ^{11}B and ^{15}N Solid-State NMR Study of a Preceramic Polyborazilene

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Polyborazilene, a precursor for hexagonal boron nitride (h-BN) ceramics, has been extensively characterized by ^{15}N and ^{11}B MAS NMR. The various B and N sites have been identified according to their first neighboring 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 better understanding of such complex BN preceramic polymer structures.

I. 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] Production of SiC or SiCN-based ceramics was first developed but new systems such as Si−E−C−N (E = Al, B, P, Ti, Zr, etc.), AlN, BN, or B−C−N were also studied.[1−3] Recently, Fazen et al. proposed a new route to hexagonal boron nitride (h-BN) from a polyborazilene obtained by thermal polymerization of borazine.[4] This polymer can then be pyrolyzed under an inert atmosphere and transformed into turbostratic BN around 900 °C (Figure 1).

The influence of the polymer architecture on the structure of the final ceramic has been clearly demonstrated for Si−C[5] and Si−C−N[6] systems. It is therefore essential to control as much as possible the polymerization and ceramization steps and consequently to have effective characterization tools that can follow the changes in local environments during polymer-to-ceramic conversion. Solid-state NMR studies (^{13}C, ^{15}N, and ^{29}Si) have been shown to be extremely useful in this field.[7−10] The objective of this work is to show that ^{11}B and ^{15}N solid-state NMR techniques are particularly useful and relevant for probing BN-based materials.

^{15}N is a $^1/_2$ spin 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 polarization (CP) techniques, taking advantage of the ^{1}H−^{15}N dipolar coupling. These techniques are consequently very sensitive to the proton environment of the nitrogen sites through the ^{1}H−^{15}N distances and to molecular motion. Recent studies on B−N-containing reference compounds have shown it is possible to distinguish N sites depending on their degree of protonation by using the inversion recovery cross polarization (IRCP) sequence.[11]

^{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 that 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.[11] Nonetheless, recently developed sequences such as multiple quantum magic angle spinning (MQ MAS) are able to remove second-order quadrupolar broadening.[13] It appears also very useful to record spectra at higher fields because the intensity of the quadrupolar interaction is inversely proportional to the static field. Using different fields will also improve confidence in the simulation of the resonance signals.

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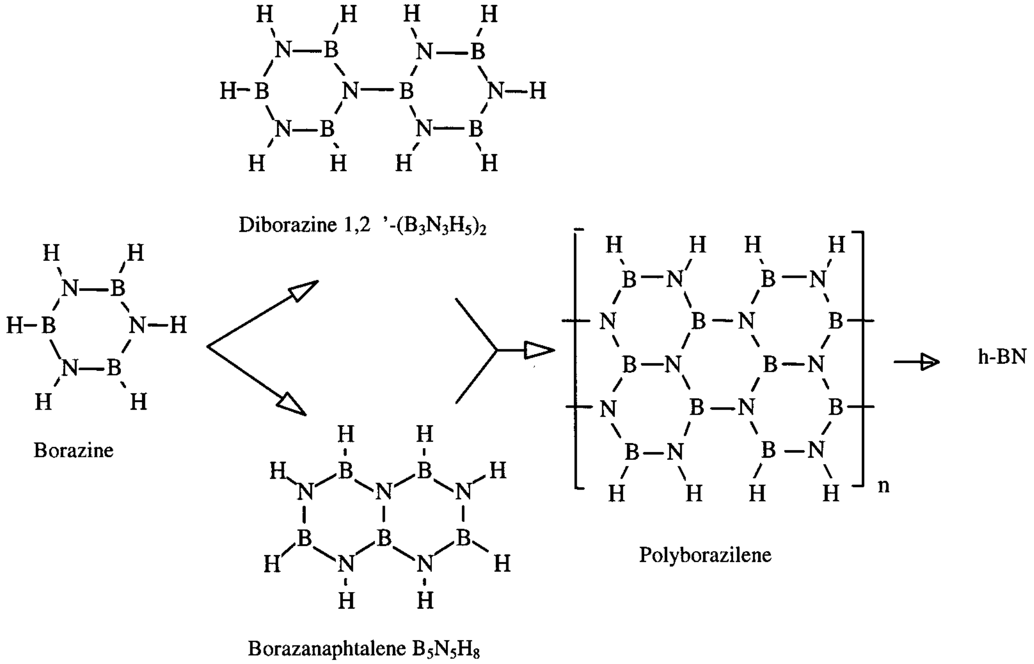

Figure 1. Schematic representation of the transformation of borazine into h-BN.

In this paper, we present a detailed solid-state NMR characterization of the polyborazilene. Combination of CP-derived sequences and sample enrichment lead to ^{15}N spectra with improved sensitivity, while the use of the MQ-MAS sequence and high magnetic field (18.8 T) gives rise to ^{11}B MAS NMR spectra with improved resolution. The various ^{15}N and ^{11}B sites were identified and even quantified.

II. Experimental Section

Sample Preparation. The polyborazilene was prepared by a procedure proposed in the literature[14] that consists of thermal dehydropolymerization of borazine. A quick one-step procedure to obtain borazine from sodium borohydride and ammonium sulfate 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.

NMR Experiments. Liquid-state ^{11}B and ^{15}N NMR experiments were performed on Bruker Avance-400 and AM-300 spectrometers, respectively, operating at a frequency of 128.28 MHz (^{11}B) and 30.41 MHz (^{15}N) with polyborazilene ^{15}N enriched at 10% dissolved in a mixture of THF and C_6D_6.

Solid-state ^{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 a 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 $\omega_{1H}/2\pi$ and $\omega_{15N}/2\pi$ were carefully set so that $|\omega_{1H}|/2\pi = |\omega_{15N}|/2\pi = 42$ kHz. Proton decoupling was always applied during acquisition and a repetition time of 10 s was used. The ^{15}N MAS NMR spectra were recorded with a pulse angle of 90° and a recycle delay between pulses of 60 s. The relaxation times T_1 of the different sites of the polymer were measured by a saturation recovery technique. All the sites did not have exactly the same T_1 values that were nonetheless all in the same range: $T_1 = 11 \pm 1$ s. Therefore, the longest was chosen to obtain quantitative results.

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 ($\delta = 0$ ppm)).

^{11}B MAS NMR experiments were performed at room temperature on Bruker MSL-300 and MSL-400 spectrometers, at a frequency of 96.216 and 128.28 MHz, respectively, 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 a dried argon atmosphere. ^{11}B MAS experiments were also performed at 11.7 T on a Bruker ASX500 spectrometer and 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. The ^{11}B MQ-MAS experiment has been acquired using a Bruker DSX400 equipped with a 4-mm Bruker CP-MAS probe head. The Z-filter pulse sequence[16] was used with triple quanta coherence transfer achieved under RF fields of 160 kHz (excitation pulse $p_1 = 5.5$ μs, conversion pulse $p_2 = 1.25$ μs). The TPPM composite decoupling pulse sequence was applied with a 20° phase modulation.[17] Acquisitions of multiple quantum experiments have been synchronized with the spinning rate[18] in the first dimension and 128 t_1 slices were acquired. A 3-ms Z-filter pulse was applied with a repetition time of 6 s and 528 scans accumulated. The ^{11}B CP/MAS experiments were also performed on a Bruker DSX400 spectrometer with a spinning rate of 10 kHz. Under MAS conditions, the efficiency of cross-polarization from a spin $I = {}^{1}/_{2}$ nucleus to a quadrupolar nucleus depends on the spin-locking of the quadrupolar nucleus. It has to be maintained in the presence of the rotor-driven modulation of the quadrupolar splitting parameter $Q(t)$. This has been discussed theoretically by Vega[19,20] who has introduced the adiabatic-passage parameter $\alpha = \omega_1{}^2/\omega_Q\omega_R$ with ω_1 the RF field strength, ω_Q the quadrupolar frequency, and ω_R the spinning rate. Spin-locking

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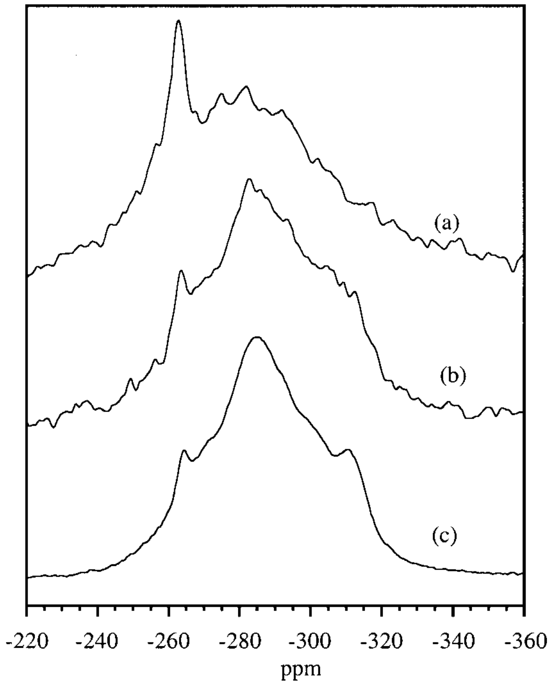

Figure 2. ^{15}N (a) MAS spectrum of the enriched polymer; (b) CP MAS spectrum of the nonenriched polymer; (c) CP MAS spectrum of the ^{15}N-enriched polymer.

is possible if $\alpha \gg 1$ or $\alpha \ll 1$ and is prevented in the intermediate condition ($\alpha \approx 1$). In our case, $\omega_Q \approx 1.4$ MHz, $\omega_R = 10$ kHz, and $\omega_1 \approx 37$ kHz; thus, α (0.1) $\ll 1$. All ^{11}B chemical shifts were determined relative to liquid BF_3OEt_2 ($\delta = 0$ ppm). The FIDs were analyzed with the WIN NMR Bruker program and simulations of the spectra were done with the WIN-FIT program.[21]

III. Results

Fazen et al. have studied the polymerization of borazine, using essentially mass spectrometry and infrared spectroscopy:[4] they have isolated several oligomers that are formed during polymerization. Two intermediates, diborazine, 1.2′-$(B_3N_3H_5)_2$ and borazanaphthalene, $B_5N_5H_8$ have even been isolated and identified by X-ray crystallography. The diborazine can be obtained from the condensation of two borazine rings and elimination of H_2 that has been clearly identified as a reaction product. The formation of borazanaphthalene strongly suggests ring opening and then reformation of cyclic structures. This indicates that the polymerization process of borazine implies complex reactions in which B and N sites can experience different environments with various neighboring atoms as well as coordination number. Anyway, at least four types of environments can be expected in this polymer: BN_3, BHN_2, NB_3, and NHB_2.

III.1. ^{15}N NMR Experiments. The ^{15}N MAS NMR spectrum of the ^{15}N enriched polymer (Figure 2a) shows a composite signal made of overlapping peaks ranging from −250 to −350 ppm and characteristic of tricoordinated N sites. This spectrum is obviously difficult to interpret, and cross polarization (CP) techniques were used to differentiate each individual signal through its CP response.

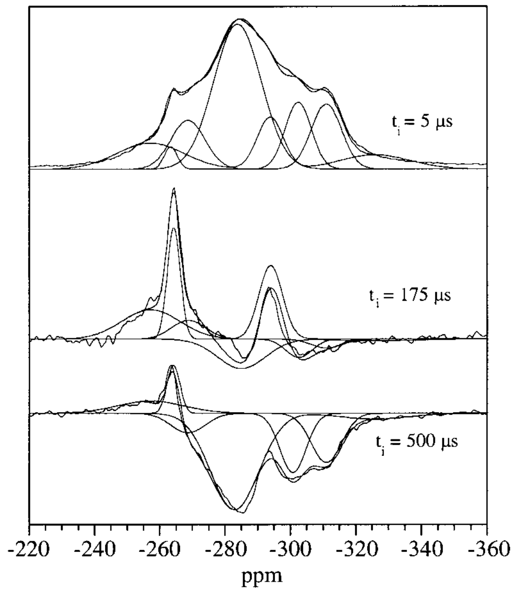

Figure 3. Experimental and simulated ^{15}N IRCP MAS NMR spectra of the polymer for various inversion time values.

The ^{15}N CP MAS spectra of the nonenriched and enriched polyborazilenes (Figure 2b,c) are very similar but, in the latter case, with a much better S/N ratio for a shorter acquisition time (1 h, 30 min vs 10 h). This allowed us to run a series of inversion recovery cross polarization (IRCP) spectra[22−25] to distinguish the N sites from their proton environments. This sequence has already been successfully used to identify $^{15}NH_x$ sites ($x = 0-3$).[11] IRCP MAS NMR spectra of the enriched polymer were thus recorded for various inversion times t_i ranging from 5 μs to 1 ms (Figure 3). All the signals are inverted for $t_i = 1$ ms except a very narrow signal around −263 ppm that can probably be assigned to residual borazine trapped in the polymer structure. Nonetheless, it is clear that all the individual components do not invert at the same rate. We have tried to simulate all the spectra with a single set of peaks, by keeping the chemical shifts, line widths, and shapes constant and by fitting only the amplitudes for each spectra. It was necessary to introduce eight peaks to reproduce the shape of the spectra for each inversion time. The integrated intensities of each signal (except the narrow signal at −263 ppm) were then normalized and plotted against inversion time. The resulting polarization curves show a two-regime inversion behavior with a rapid decrease of the magnetization at low inversion time (Figure 4). They can thus be interpreted within the frame of the I^*-I-S model,[26] where strongly coupled $I-S$ spin pairs interact with an abundant I^* spin reservoir through homonuclear $I-I^*$ dipolar cou-

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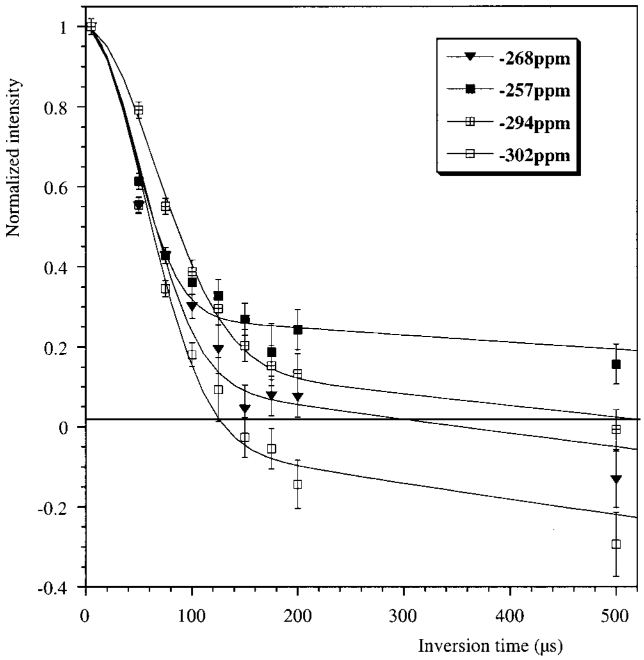

Figure 4. Evolution versus inversion time of the ^{15}N IRCP MAS NMR signal intensities of different sites of the polymer (solid lines correspond to the simulations according to eq 1).

Table 1. CP Characteristic Times Extracted from the ^{15}N IRCP MAS Spectra

δ_{iso} (ppm) ($\pm$1)	T_C (μs) ($\pm$2)	T_D (ms) ($\pm$0.1)	t_i^0 (μs) ($\pm$10)	n ($\pm$0.05)
−257	63	5.6	1000	0.5
−268	76	2.9	370	0.8
−284	81	2.4	150	0.9
−294	95	3.6	590	0.7
−302	81	2.1	140	1.0
−311	81	2.2	150	1.0
−326	69	6.2	150	1.0

pling. In that case, the polarization inversion behavior can be simulated with the following equation,[23,24]

$$M_S(t_i) = M^0(t_c)\left[\frac{2}{n+1}\exp\left(-\frac{t_i}{T_D}\right) + \frac{2n}{n+1}\exp\left(-\frac{3t_i}{2T_D}\right)\exp\left(-\frac{t_i^2}{T_C^2}\right) - 1\right] \quad (1)$$

where T_C is related to dipolar coupling to nearby protons ($I-S$), leading to a coherent transfer of polarization;[25] T_D describes the decay caused by isotropic spin diffusion between I and I^* spins ($T_C \ll T_D$) and n corresponds to the number of strongly coupled protons. The results of the simulation are summarized in Table 1.

The observed T_C values are quite similar for all the detected ^{15}N sites and close to those observed for NH sites,[11] suggesting for each detected site the existence of a strong ^{15}N$-$^{1}H heteronuclear dipolar coupling. For four of the peaks, at −284, −302, −311, and −326 ppm, the extracted n value is 1, indicating that the corresponding sites should be NHB_2 groups. For the other three peaks, at −257, −268, and −294 ppm, their corresponding curves do not follow the expected behavior for rigid NHB_2 groups: this may suggest either that these groups are indeed NH sites but belonging to species subjected to molecular motions or that they are nonprotonated NB_3 sites but with protons in their close environment.

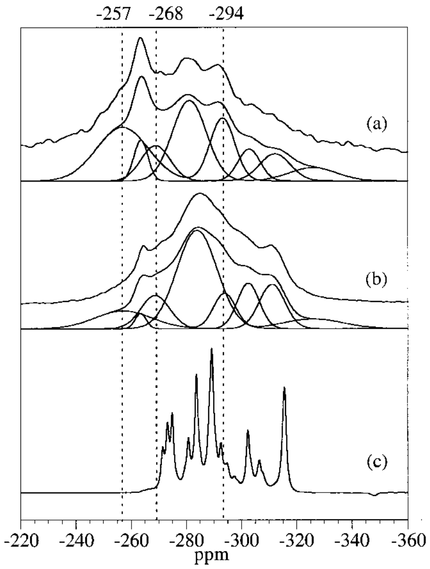

Figure 5. ^{15}N spectra of the polymer: (a) solid-state MAS; (b) solid-state CP MAS; (c) liquid-state DEPT in THF, C_6D_6.

To tackle this question, the ^{15}N CP MAS NMR spectrum of the polymer (Figure 5b) was compared with the solution-state NMR spectrum (Figure 5c) recorded with the DEPT sequence. The protonated NH sites appear with positive signals and the NH_2 sites with negative signals, while the nonprotonated N sites are not detected.[27] The spectrum shows positive signals and particularly major peaks at −271.2, −272.9, −274.8, −280.6, −283.6, −284.8, −289.1, −290.1, −302.2, and 315.2 ppm, suggesting that the assignments to NHB_2 sites of the peaks centered at −284, −302, −311, and −326 ppm in the CP-MAS spectrum is reasonable. Interestingly, no peak is present in the solution spectrum around −257 ppm, suggesting that the peak observed at these chemical shifts in the ^{15}N CP MAS spectrum is certainly due to NB_3 sites. For the peaks observed in the CP MAS spectrum at −268 and −294 ppm, it is difficult to assign them in an unambiguous manner to NB_3 sites because some minor peaks are present in the same chemical shift ranges in the solution state spectrum.

Figure 5 shows also the comparison between the ^{15}N CP MAS spectrum (b) and the SPE MAS spectrum (a), which have been simulated with the same peaks, previously extracted from the IRCP experiments. As expected, the signals at −257 and −268 ppm, previously assigned to NB_3 sites, are indeed more intense in the SPE spectrum. Interestingly, the peak at −294 ppm seems to show similar behavior, suggesting that it is also due to nonprotonated NB_3 sites because it can be underestimated by cross polarization at contact times optimized for protonated N.[28] The percentages of the various sites extracted from the simulation of the SPE MAS spectrum (which was recorded as to be quantitative, taking into account the relaxation time T_1 mea-

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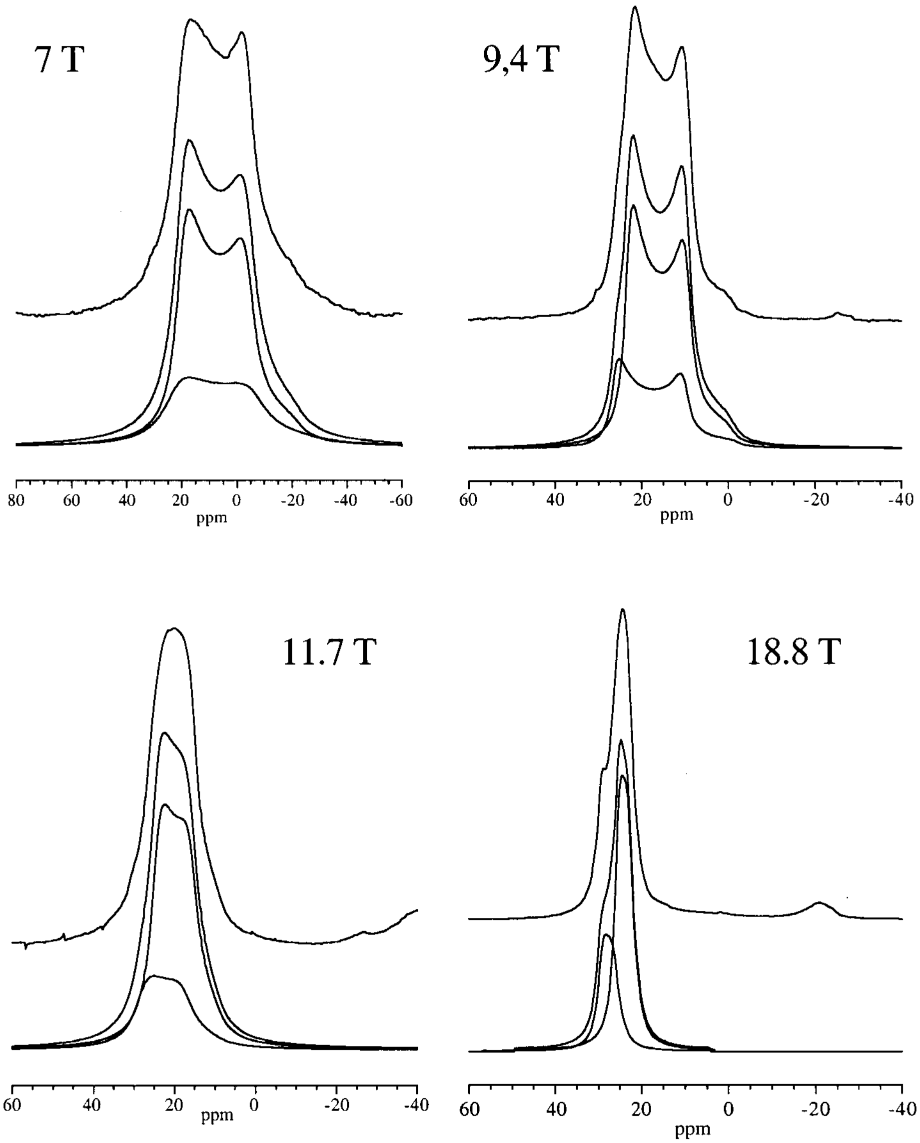

Figure 6. Experimental and simulated ^{11}B MAS NMR spectra of the polymer recorded at different fields.

Table 2. Partition of the Various Sites Extracted from the Simulation of the ^{15}N SPE MAS Spectrum

δ_{iso} (ppm) (±1)	proportions (%) (±2)	assignment
−257	27	NB_3
−268	10	NB_3
−284	27	NB_2H
−294	15	NB_3
−302	7	NB_2H
−311	8	NB_2H
−326	6	NB_2H

sured for ^{15}N in this compound, $T_1 = 11 \pm 1$ s) are summarized in Table 2. Assuming that the peak assignments are correct, it turns out that the polymer is composed of two types of N sites (if only the first neighboring atoms are considered), NB_3 and NB_2H, in a 50:50 ratio.

III.2. ^{11}B NMR Experiments. The ^{11}B MAS NMR spectrum of the polymer recorded at 9.4 T (Figure 6) shows a large signal in the region of tricoordinated borons.[11] From the expected structure of the polymer (Figure 1), two types of boron sites should be present, BN_2H and BN_3, which are clearly observed in the corresponding solution state NMR spectra[29] (Figure 7). The signal around 31 ppm, which is present as a doublet in the nondecoupled spectrum ($^1J(^1H-^{11}B) = 135$ Hz) can be assigned to BN_2H sites, while the other one around 26 ppm is present as a singlet corresponding to BN_3 sites. These values are in agreement with those found in oligomers that have been isolated during the polymer synthesis.[4] But these two signals, whose chemical shift difference is only 5 ppm, are difficult to identify from the MAS NMR spectrum because of the large quadrupolar interaction that broadens the peaks over a much larger chemical shift range.

To overcome this problem, the ^{11}B MAS spectra of the polymer were recorded at different fields, 7.05, 9.4, 11.7, and 18.8 T (Figure 6). The central transition is perturbed only to second-order by the quadrupolar interaction and this perturbation scales inversely proportional to the applied magnetic field so it is reduced at higher fields.[30] Indeed, the spectrum recorded at 18.8 T shows two signals that can be attributed to BN_3 and BN_2H

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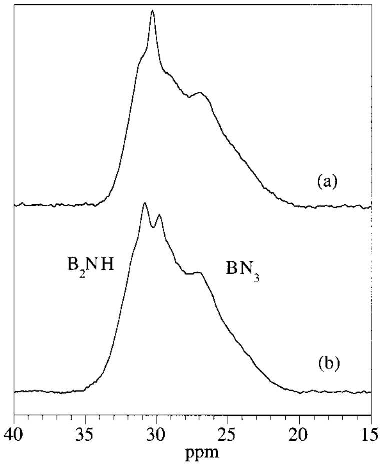

Figure 7. ^{11}B liquid-state NMR spectra of the polymer in solution in THF, C_6D_6 (a) with proton decoupling and (b) without proton decoupling.

sites respectively by comparison with the solution state spectrum (Figure 7).

Because the access to a high-field spectrometer is difficult, we tried to see whether the use of the 2D MQ-MAS sequence could also bring resolution in the ^{11}B NMR spectra. This experiment was recently proposed by Frydman and Harwood[31] who discovered that an isotropic spectrum of a quadrupolar nucleus broadened by the second-order quadrupolar interaction could be obtained from a skew projection of a two-dimensional (triple quantum, single quantum) correlation spectrum. The 2D 3Q-MAS NMR spectra of the polymer is presented in Figure 8 with and without high proton decoupling. Considering that the ^{11}B−^{1}H dipolar coupling (estimated to be 22.6 kHz, if one just considers a BH group and a B−H distance of 1.2 Å[32]) is multiplied by the coherence order (3 for triple quantum),[33] the resolution in the isotropic ω_1 dimension is greatly improved under composite decoupling.[34] Two signals are clearly resolved at 71 and 85.5 ppm: for an $I = {}^{3}/_{2}$ nucleus such as ^{11}B, the observed shift in the isotropic dimension is given by

$$\delta\omega_1^{\text{obs}} = \frac{17}{8}\delta_{\text{iso}}^{\text{CS}} + \frac{10^6}{32}\frac{C_Q^{\,2}}{\omega_0^{\,2}}\left(\frac{\eta^2}{3} + 1\right) \tag{2}$$

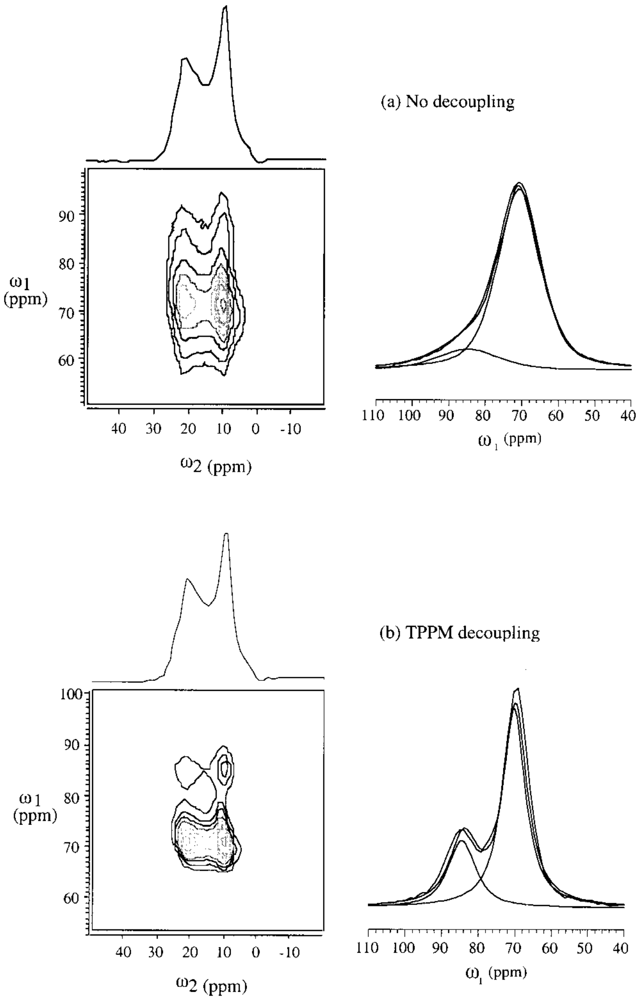

Figure 8. Two-dimensional ^{11}B 3Q-MAS spectrum of the polymer recorded at 9.4 T (a) without decoupling and (b) with TPPM ^{1}H decoupling.

Table 3. NMR Parameters Obtained from the Modeling of the ^{11}B Experimental Spectra of the Polymer

δ (ppm) (±1)	C_Q (MHz) (±0.1)	η	$\Delta_{\omega 1}$ (Hz) no decoupling	$\Delta_{\omega 1}$ (Hz) TPPM decoupling	assignment	intensity (%) (±2)
27	2.7	~0.1	1800	1100	BN_3	70
31	2.9	~0.1	2400	1100	BN_2H	30

where $\delta_{\text{iso}}^{\text{CS}}$ is the isotropic chemical shift, C_Q the quadrupolar coupling constant, and η the asymmetry parameter.[35] Using this equation and the line shape fitting of the anisotropic cross sections at the corresponding peaks for the two sites, the NMR parameters obtained for each ^{11}B site are reported in Table 3. It is worth noticing that the line width of the peak at $\delta_{\text{iso}}^{\text{CS}} = 31$ ppm is the most affected by ^{1}H decoupling ($\Delta\omega_1$: 2400 → 1200 Hz) showing, in agreement with the solution NMR data, that this peak is due to BN_2H sites. The quadrupolar coupling constants are similar to those found for h-BN (2.8 MHz)[36] and the asymmetry parameters in agreement with a trigonal site. It can be noticed that the η values appear quite similar for both sites, suggesting that the asymmetry parameters are mainly sensitive to the geometry of the sites and less to the substituents. These parameters were then used to simulate the 1D MAS spectra recorded at different fields (Figure 6) and the simulations obtained are quite satisfactory. The extracted percentages of BN_3 and BN_2H sites are respectively 70 and 30%.

The ^{11}B CP MAS NMR spectra of the polymer recorded for three different contact times are presented in Figure 9. They were simulated with the two sites

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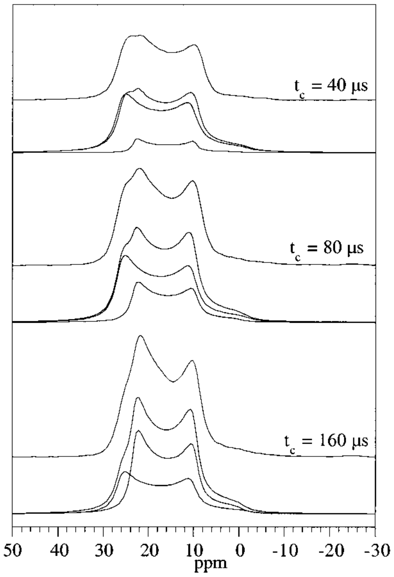

Figure 9. ^{11}B CP MAS spectra of the polymer recorded for contact time values ranging from 40 to 160 μs.

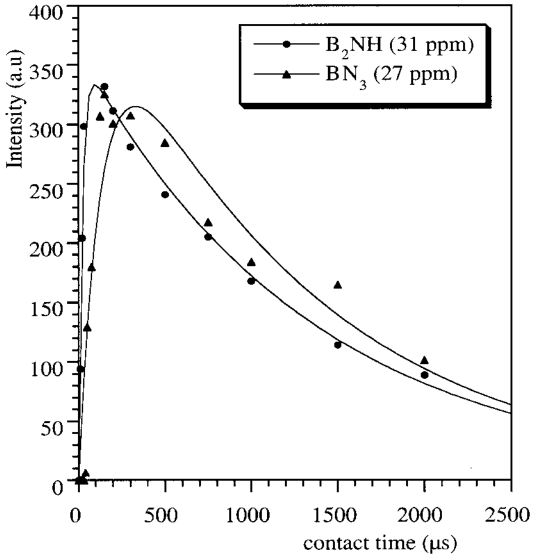

Figure 10. Evolution versus contact time of the ^{11}B CP MAS NMR signals intensities of the two peaks identified in the polyborazilene.

previously described. As expected, the signal of the directly protonated BN_2H site is enhanced for short contact times, and its relative intensity compared to the signal of the nonprotonated BN_3 site then decreases with increasing contact time. The resulting polarization curves (Figure 10) show that the dynamics of the BN_2H and BN_3 sites are not very different as this was observed for NB_2H and NB_3 sites by ^{15}N IRCP MAS experiments. This suggests that boron and nitrogen atoms that are not directly bonded to protons are nonetheless coupled to protons in their close environment.

IV. Discussion

^{11}B and ^{15}N NMR studies have shown that only tricoordinated boron and nitrogen atoms are present in the polyborazilene in the following environments: BHN_2, BN_3, NHB_2, and NB_3. Moreover, the second neighbors of the boron atoms cannot be identified through ^{11}B NMR experiments while the ^{15}N NMR spectra exhibit eight different signals, which suggests that they could give more information about the more distant environment of the observed nucleus despite a poor signal-to-noise ratio. Nonetheless, it is quite difficult to assign more precisely these sites according to the second neighbors of the nitrogen atoms. Only two dimers have been isolated[4] and, unfortunately, ^{15}N NMR chemical shifts were not measured. Recently, Gastreich and Marian[37] have done ab initio calculations of ^{15}N NMR chemical shifts in hydrogen-saturated cutouts of h-BN whose geometries were optimized by means of density functional theory. Chemical shifts calculations have been carried out at the coupled-perturbed Hartree–Fock level of theory, employing gauge-including atomic orbital (GIAO) basis sets. They obtained ^{15}N NMR chemical shifts ranging from −253 to −305 ppm and two types of sites corresponding to nitrogen atoms with direct NH bonds or free of hydrogen in the first coordination sphere. The former seems to appear at a lower field than the latter, in good agreement with our experimental results (Table 2). Further examination of the calculated data permitted three groups of signals in each block, labeled from (**I**) to (**VI**) (Figure 11), to be distinguised. A unique chemical environment could be assigned to each group, including neighbors up to the second coordination sphere. We thus tried to assign the different signals found in the ^{15}N MAS NMR spectrum of the polymer according to this classification and considering the protonation of the sites determined by a ^{15}N IRCP MAS NMR study (Figure 12). The fragment $N(BNH)_3$ is not discussed but it corresponds to the presence of B-boryl bridges that should appear at ^{11}B chemical shift values $\delta \leq 24$ ppm,[38] which is not observed experimentally. Therefore, only boron trigonal sites included in six-membered $[B-N]_3$ rings are considered in this study.

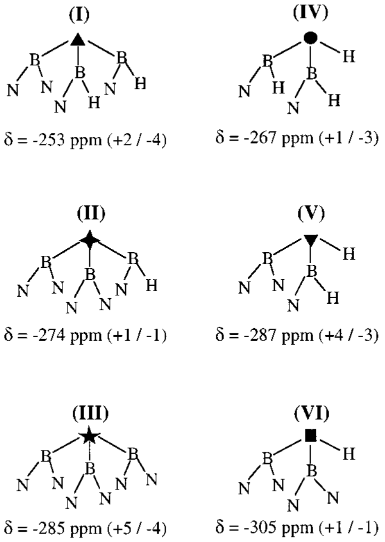

Figure 11. Schematic representations and calculated ^{15}N chemical shifts of nitrogen environments in hydrogen-saturated cutouts of h-BN according to first and second coordination spheres.[36]

The NB_3 sites at −257 and −268 ppm may be attributed to (**I**) and (**II**) environments, corresponding

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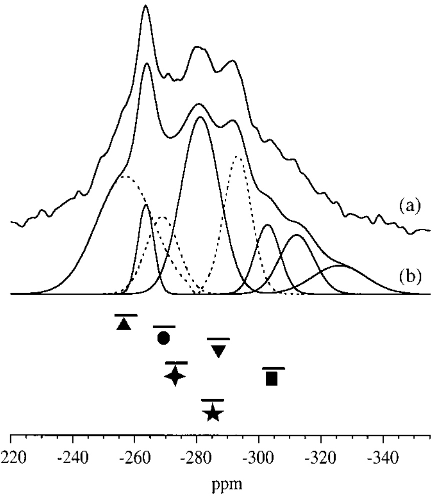

Figure 12. (a) ^{15}N MAS spectrum of the polyborazilene and (b) its simulation: BHN_2 sites in full line and BN_3 sites in dashed lines. The chemical shift range corresponding to nitrogen environments described in Figure 11 is also presented.

to nitrogen atoms surrounded by protonated borons. There is no evidence for the presence of NB_3 sites of type (**III**) corresponding to the bonding situation in h-BN. This suggests that the structure of the polymer is not highly condensed, in good agreement with the results obtained by ^{11}B and ^{15}N CP MAS experiments, showing that nonprotonated boron and nitrogens atoms were nonetheless close to the protons. The NHB_2 sites at −284 and −302 ppm may be assigned to (**V**) and (**VI**) environments while the narrow signal at −267 ppm attributed to residual borazine has indeed a chemical shift of type (**IV**) characteristic of an NH site bonded to protonated borons.

The large number of signals observed by ^{15}N NMR may thus be explained by differences in the second neighboring atoms, but it should be noted that the ^{15}N chemical shift range obtained by these ab initio calculations do not cover the whole ^{15}N MAS polyborazilene spectrum. It remains for instance difficult to explain the presence of the NHB_2 signals at −311 and −326 ppm. The NB_3 site at −294 ppm is also difficult to assign because its chemical shift is very low compared to those calculated. This high-field shift could perhaps be due to a cycle effect. Indeed, ^{14}N chemical shift values for a eight-membered B_4N_4 ring was shown to be 30 ppm lower than those in the corresponding six-membered B_3N_3 ring, while the ^{11}B chemical shift values are very close.[39] The signals observed at −294, −321, and −325 ppm could then possibly be assigned to NB_3 and NHB_2 sites engaged in eight-membered rings.

V. Conclusion

A range of ^{11}B and ^{15}N solid-state NMR techniques have been used to investigate in detail the structure of polyborazilene, a polymer precursor for hexagonal boron nitride. A combination of $^{1}H-^{15}N$ cross-polarization sequences and ^{15}N enrichment allows us to distinguish eight different N sites, revealing the high sensitivity of this isotope not only to the first but also to the second neighboring atoms. Environments were proposed based on the comparison between the experimental chemical shift values and ab initio calculations already reported in the literature. The ^{11}B chemical shift values are much less sensitive to differences in first neighboring atoms. Furthermore, the second-order quadrupolar broadening renders quite difficult the interpretation of the spectra. However, the use of the MQ-MAS sequence coupled to the very efficient TPPM decoupling technique allows us to identify the two expected BHN_2 and BN_3 sites, whose difference in chemical shifts is as little as 4 ppm. This was also confirmed by MAS spectra recorded at various fields as well as by $^{1}H-^{11}B$ CP-MAS experiments.

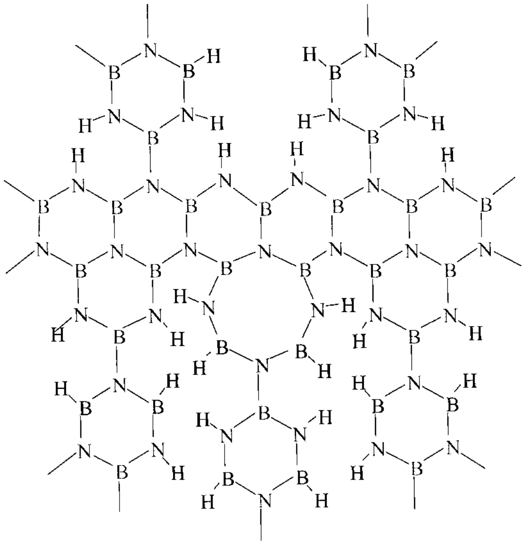

Figure 13. Proposed structure for the polyborazilene considering the results of the ^{11}B and ^{15}N NMR study.

This polymer contains only tricoordinated boron and nitrogen atoms, present in two types of B sites (BHN_2, BN_3) and two types of N sites (NHB_2, NB_3), if only the first neighboring atoms are considered. Quantitative analysis gives the following estimations: BHN_2:BN_3 = 30:70 and NHB_2:NB_3 = 50:50. No tetracoordinated atoms could be evidenced, which indicates that most of the B and N atoms are included in ring structures. However, the formation of borazanaphthalene (which has been reported in the literature[4]) strongly suggests that some ring-opening reactions may occur, followed by reformation of cyclic structures. This reaction seems to lead not only to six-membered-ring but also to eight-membered-ring structures as suggested by the assignment of the large number of ^{15}N signals that were observed. Considering all these elements, a possible structure for this polyborazilene is proposed in Figure 13. It shows $[B-N]_3$ and $[B-N]_4$ ring structures and the resulting ratios BHN_2:BN_3 and NHB_2:NB_3 are 31:69 and 53:49, respectively, in good agreement with the results of the quantitative analysis.

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