



Solid-state NMR applied to Si-based polymer derived ceramics: A review

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ABSTRACT

In this contribution, a review of the use of solid state NMR in the field of Si-based Polymer Derived Ceramics is presented. This synthetic approach allows to prepare a large variety of precursors leading to a wide range of ceramics, both in terms of composition and microstructure: multinuclear solid state NMR is obviously a pertinent spectroscopic tool of investigation since its versatility provides a detailed description of the structure of the polymeric precursors and their pyrolysis products. In a first introductory section, the relevant nuclei that can be probed in such systems are presented with their advantages and drawbacks, as well as the main NMR sequences that have been used to obtain as much structural information as possible in terms of local environments and connectivities. All along this article, examples are then given to illustrate which solid state NMR techniques are currently available to characterise the structure of a large variety of PDCs screening Si-C, Si-C-O, Si-/Ti/B/Al-C-O, Si-C-N, and Si-B/Al/Ti/Zr-N systems.

1. Introduction

The production of ceramics from polymeric precursors commonly called the PDC (Polymer Derived Ceramics) route is a synthesis strategy that consists in preparing a polymer whose skeleton prefigures as well as possible the target ceramic material that is then obtained after pyrolysis in a suitable atmosphere. This approach has several advantages: the enormous potential offered by organometallic chemistry can allow the elaboration of precursors with very varied architectures and thus lead to ceramic materials with completely new structures (composition and microstructure). Moreover, a material is only useful if it can be shaped and the use of soluble or fusible pre-ceramic polymers allows the production of fibres, films and also the impregnation of fibrous reinforcements for composite materials. The overall process for the formation of PDCs consists of three major steps: *i*) synthesis of pre-ceramic polymers from suitable monomers; *ii*) polymer cross-linking at moderate temperatures to lead an infusible organic/inorganic pre-ceramic network; *iii*) ceramisation process (pyrolysis) of the cross-linked materials, which are converted into inorganic amorphous materials by heat treatment at temperatures from 1000 °C to 1300 °C. Considering these synthesis steps, a better understanding of the systems at all stages of their development (monomer, more or less cross-linked polymer, pyrolysis products and amorphous or crystallized ceramics) is relevant. It is indeed essential to characterise in detail the structural transformations occurring during pyrolysis to understand polymer-ceramic relationships and optimise the polymer architecture for the target

material. The polymeric precursors and their pyrolysis products being generally amorphous up to 1200 °C, solid-state Nuclear Magnetic Resonance (NMR) appears to be a particularly well adapted characterisation technique.

In this context, the objective of this contribution is to show to what extent solid-state NMR can structurally characterise the different stages from the polymers preparation to their conversion into ceramics. Indeed, this technique allows not only to investigate the local environment of nuclei (taking advantage of specific NMR parameters (such as the isotropic chemical shift δ_{iso} , or the quadrupolar coupling constant C_Q), but also the longer range connectivities between nuclei (using either through-bond (J or scalar) or through-space, (D or dipolar) interactions).

Historically, polymeric routes for obtaining silicon carbide and nitride-based ceramics have developed considerably since Yajima's discovery [1]: they have been initially studied by ^{13}C , and ^{29}Si NMR [2–7]. This has made it possible to follow the changes in the local environments of the carbon and silicon atoms during polymerisation and conversion into ceramic as described more in details later in this manuscript. In particular, ^{29}Si has been widely used in silicon oxycarbide-based systems since it allows to distinguish easily and quantify $\text{SiC}_x\text{O}_{4-x}$ ($0 \leq x \leq 4$) environments (Fig. 1a) thanks to well-resolved signals ranging over 100 ppm. For $\text{SiC}_x\text{N}_{4-x}$ sites in silicon carbonitride-based ceramics, the resolution of the signals is poorer (Fig. 1b) and the chemical shift range drops to 50 ppm but allows nonetheless to evaluate the sites distribution.

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From an NMR point of view, the easiest isotopes to be probed in the solid state are those with a nuclear I spin equal to $\frac{1}{2}$ (due to the absence of quadrupolar interaction) namely ^1H , ^{13}C , ^{15}N and ^{29}Si for the usual PDC systems. Proton is a bit particular due to the usual presence of strong ^1H - ^1H dipolar couplings and a relatively small chemical shift range which lead generally to a poor resolution of the spectra. A substantial improvement can nonetheless be achieved by high-speed MAS (Magic Angle Spinning) experiments coupled with high field spectrometers. Regarding ^{13}C , ^{15}N and ^{29}Si , these three nuclei are characterised by their low natural abundance (1.10%, 0.37%, and 4.67% respectively) and their moderate gyromagnetic ratio which will contribute to their low or even very low sensitivity. To deal with this, a possibility is isotopic enrichment (in particular for ^{15}N which has been used for example to probe nitrogen in Si_3N_4 polymorphs [10]) or the use of the so-called Cross Polarisation (CP) technique [11] which leads to an improvement in sensitivity while reducing the acquisition time of the spectra obtained. Moreover, this sequence based on a transfer of magnetisation between protons and the low sensitivity spin systems (^{13}C , ^{15}N or ^{29}Si) through the dipolar coupling between both, allows to probe the proximity between the two types of nuclei and is therefore a good tool for structural investigation [12,13]. Nonetheless, the differences in polarisation dynamics between the sites appear at relatively small contact times between both spins, which corresponds to relatively weak magnetisations: differentiation is therefore not very easy. The IRCP sequence [14] makes it possible to circumvent this problem: it consists firstly of polarising the rare spins (^{13}C , ^{15}N ...) for an optimal contact time in order to reach a maximum magnetisation M_0 , and then to reverse the phase by 180° during the inversion time (t_i). The magnetisation will then decrease, cancel and change sign to tend towards M_0 as t_i increases. As the inversion dynamics are similar to those of standard CP, they are strongly dependent on the dipolar interactions and consequently on the spin proximities. The determination of the characteristic parameters of the polarisation dynamics is consequently more accurate using the IRCP sequence. In the field of PDCs, it has been used in ^{13}C NMR to distinguish between CH_3 - and $-\text{CH}_2-/-\text{CH}-$ groups [15–20], in ^{29}Si to differentiate protonated Si nuclei (SiH_2CX and SiHXC_2) from non protonated ones [21], $\text{Me}_x\text{Si}(\text{N}=\text{C}=\text{N})_y(\text{N}<)_{(4-x-y)}$ according to the x value [18], and in ^{15}N to identify NH_x sites depending on the x value (from 0 to 3) [22–25] or NXSi_2 , NXBSi and NXB_2 environments (with $X = \text{H}$ or C) [26].

Quadrupolar nuclei (with a spin quantum number $I > \frac{1}{2}$ such as ^{11}B ($I = 3/2$) and ^{27}Al ($I = 5/2$)) have a quadrupolar moment resulting from the elliptical distribution of nuclear electric charges, and not spherical as in spin $I = 1/2$. As a result, quadrupolar nuclei are polarised by the magnetic field but also subjected to any electric field gradient. This quadrupolar moment-electric field gradient interaction gives rise to quadrupolar effects, characterised by the quadrupolar coupling constant C_Q and the asymmetry factor η_Q . C_Q reflects the strength of the quadrupolar interaction while η_Q provides information on the symmetry of the electric field gradient and by extension the observed site: thus a

nucleus in an axially symmetric site will lead to $\eta_Q = 0$. The second-order quadrupolar interaction affects the central transition: it shifts it from its isotropic value and broadens the resonance spectrum, giving rise to a broad, asymmetric shape, illustrated in Fig. 2a for different values of the asymmetry parameter η_Q .

It is important to note that rotation at the magic angle only partially averages the second order quadrupolar interaction. This makes access to a high-resolution spectrum difficult: in samples with different sites, the line shapes of each of them may overlap and complicate the interpretation of the spectrum. To overcome these effects, a first possibility is to increase the magnetic field because the intensity of the quadrupolar interaction is inversely proportional to the latter, which has become easier in the last years thanks to technological progress. Recording spectra at different fields is also an asset to confirm the consistency of the NMR parameters (δ_{iso} , C_Q and η_Q) used for the simulation (Fig. 2b). In the field of PDCs and in particular in Si-B-C-N quaternary systems, ^{11}B NMR appeared useful in combination with ^{29}Si NMR to discriminate $\text{SiC}_x\text{N}_{4-x}$ ($0 \leq x \leq 4$) and $\text{BC}_x\text{N}_{3-x}$ ($0 \leq x \leq 3$) environments [29–35]. In addition, for a precise quantification of boron sites, more sophisticated techniques such as DOR (Double Rotation) [36], DAS (Dynamic Angle Spinning) [37] or MQMAS (Multiple Quantum Magic Angle Spinning) [38] have been developed. The latter is a two-dimensional experiment which combines sample rotation with manipulation of the nuclear spins and allows to obtain an isotropic spectrum on the second dimension (Fig. 2c). It has been used to investigate boron environments in B-N [39, 40], Si-B-C-N [41,42] and Si-B-C-O [27] systems as well as aluminum sites in Si-Al-C-N PDCs [43].

While one-dimensional NMR spectra provide information on the number and proportions of different species in terms of chemical environments, more detailed structural information can be obtained using two-dimensional correlation experiments. In the latter, magnetisation is transferred between nuclear spins, either by dipolar coupling (through space) or by J-coupling (through chemical bonds), enabling the determination not just of local environments but also of spatial correlations. One of the simplest experiments, known as HETCOR (HEteronuclear CORrelation), can be viewed as an adaptation of the above described cross-polarisation (CP) experiment, with the introduction of a second evolution period to encode chemical shift information for the abundant spin, usually proton. For example, The $\{^1\text{H}\}$ - ^{13}C and $\{^1\text{H}\}$ - ^{15}N HETCOR CP MAS NMR spectra were recorded on a ^{13}C - and ^{15}N -enriched polyphenylsilsequicarbodiimide heat-treated sample to correlate ^1H chemical shift with ^{13}C and ^{15}N signals respectively [44]. This permitted to suggest that C-N bonds at the free carbon/ Si_3N_4 interface is probably stabilized by the presence of hydrogen. 2D HETCOR CP MAS $\{^1\text{H}\}$ - ^{13}C NMR experiment was also used to characterise polytitanosilazanes and showed that there are two types of chemical environment that involve the NCH_3 units in this polymer respectively due to the reaction of SiH units and NH units of the polysilazane with $\text{N}(\text{CH}_3)_2$ groups of the titanium precursor [45].

Homonuclear two-dimensional NMR experiments can also be

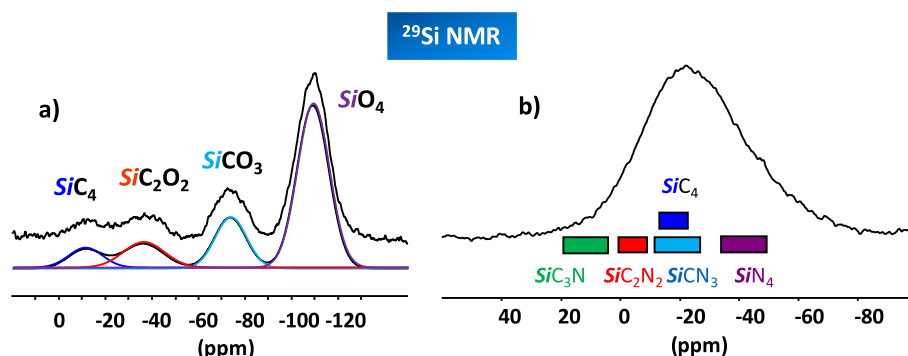


Fig. 1. ^{29}Si MAS NMR spectra of a) Si-C-O and b) Si-B-C-N systems heat-treated at 1000°C . Adapted with permission from Refs. [8,9].

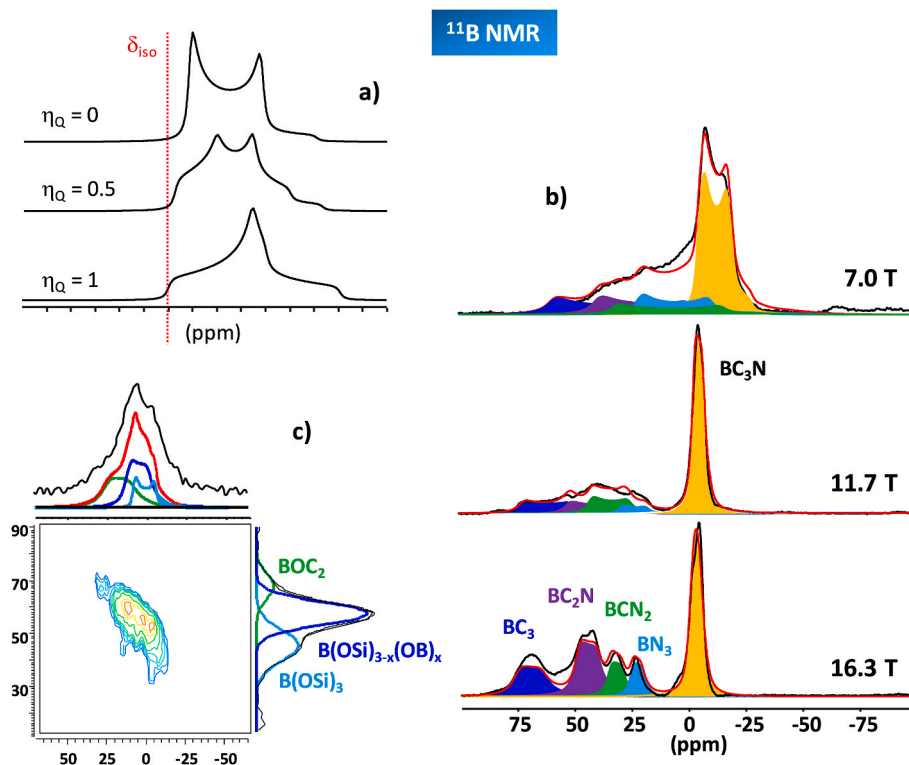


Fig. 2. a) Evolution of the MAS NMR spectrum of a spin $I = 3/2$ according to the quadrupolar asymmetry factor (η_Q) value; b) Experimental and simulated ^{11}B MAS NMR spectra of an Si-B-C-N preceramic polymer recorded at different magnetic fields; c) 2D ^{11}B MQMAS spectrum of an Si-B-C-O system heat-treated at 700 °C. Partially adapted with permission from Refs. [27,28].

relevant in PDCs. In silicon oxycarbide systems, ^{29}Si correlation spectroscopy (COSY) [46] and double quantum (DQ) NMR experiments [47] were used to investigate connectivities between various $\text{SiC}_x\text{O}_{4-x}$ environments.

Finally, it is worth mentioning REDOR (Rotational Echo Double Resonance) experiments [48] which reintroduce heteronuclear dipolar coupling between two types of spins, causing the I spins close to the S spins to « dephase », i.e. decrease in intensity. The latter can then provide information on the inter-nuclear distances between the I and S nuclei. This technique has been used to elucidate the atomic network and proximities through $\{^{15}\text{N}\}\text{-}^{13}\text{C}$ [49,50] to probe the evolution of C-N bonds but also $\{^{13}\text{C}\}\text{-}^{11}\text{B}$ and $\{^{15}\text{N}\}\text{-}^{11}\text{B}$ experiments on ^{13}C , ^{15}N enriched samples to investigate boron environments [49].

It appears that solid-state NMR experiments offer interesting perspectives in terms of local structure of PDCs but an additional tool can be necessary to fully exploit the information available and assign all NMR signals. DFT NMR calculations can be very helpful in this context and can also provide the necessary link between structural models and experimental NMR data. Combination of modeling and calculation of NMR parameters has been used to investigate mixed $\text{SiC}_x\text{O}_{4-x}$ environments in silicon oxycarbide ceramics and possible correlation between structural parameters and ^{29}Si NMR chemical shift values [47,51]. A similar study was conducted to correlate the local structure to the ^{29}Si NMR signal in silicon nitride-based systems [52]. NMR calculations were also used to assign ^{27}Al signals among $\text{AlH}_x\text{N}_y\text{C}_{N-x-y}$ ($3 \leq N \leq 6$) sites in poly(vinylmethyl-co-methyl)silazanes precursors of Si-Al-C-N ceramics [43] and ^{11}B NMR parameters of BH_xC_y ($0 < x \leq 4$, $0 \leq y < 4$) sites to characterise boron-modified polycarbosilanes [53].

The next section will be devoted to a review of solid-state NMR investigations in the field of Si-based Polymer-Derived Ceramics in Si-C, Si-C-O, Si-Ti/B/Al-C-O, Si-C-N, and Si-B/Al/Ti/Zr-N systems with the aim to highlighting the type of informations that can be obtained with this spectroscopy.

2. Silicon carbides (Si-C)

After Yajima's discovery [1], the preparation of silicon carbide ceramic fibers derived from organometallic polymer precursors has become an intense subject of research [54]. One of the first ceramic precursor studied by NMR is a commercial polycarbosilane characterized by $-\text{CH}_2\text{-Si}(\text{CH}_3)_2\text{-CH}_2-$ and $\text{CH}_2\text{-Si}(\text{H})(\text{CH}_3)\text{-CH}_2-$ units that could be clearly distinguished by ^{29}Si CP MAS NMR spectroscopy [2]. NMR was also used to follow the polymer to ceramic conversion which permitted to identify by ^{13}C CP MAS NMR (in samples heat-treated above 700 °C) a signal around 135 ppm that could be assigned to the presence of aromatic carbon atoms: this was one of the first experimental signature of precursor bonds for graphitic carbon that is formed around 1200 °C according to Raman data. In addition, ^{29}Si MAS NMR allows to follow the transformation from amorphous silicon carbide to crystalline one. Indeed, ^{13}C and ^{29}Si MAS NMR has been successfully applied to distinguish between the different SiC polytypes [55–57]. ^{13}C and ^{29}Si NMR was also used to characterise the polysilane-to-polycarbosilane transformation of poly(methylchlorosilanes) [16]: in particular a detailed investigation using the IRCP sequence [14] permitted a precise identification of the various NMR peaks, even in case of extensive overlap of the signals and showed the formation of Si-CH₂-Si carbosilane sites in the low-temperature range without Si-Si bond cleavage. “Kumada-rearrangement” occurs above 380 °C leading to the replacement of Si-Si by Si-C bonds transforming the polysilane into a polycarbosilane. This study illustrated for the first time the interest of advanced solid-state NMR techniques for the fine characterisation of the first steps of the polymer-to-ceramic transformation.

More recently, ^{13}C and ^{29}Si MAS NMR was used for example to investigate the local environments of Si and C sites in the pyrolysis products of a novel cyano-polycarbosilane, used as a precursor of ceramic fibers [58].

3. Silicon oxycarbides (Si-C-O)

As mentioned in the introduction, ^{29}Si NMR has been widely used to quantify $\text{SiC}_x\text{O}_{4-x}$ ($0 \leq x \leq 4$) environments in Si-C-O-based systems [59–69], usually obtained from polymeric organosilicon gels synthesized by hydrolysis and condensation (sol-gel synthesis) of modified silicon alkoxides ($\text{R}_x\text{Si}(\text{OR}')_{4-x}$). Early studies [70–72] used NMR to show the cleavage of the Si-C bonds and their conversion into Si-O bonds above 300 °C and monitor the maximal temperature below which Si-C bonds are retained in the silica network, leading to a silicon oxycarbide phase with a random distribution of $\text{SiC}_x\text{O}_{4-x}$ units and an additional free carbon phase (graphitic or turbostratic sp^2 hybridized carbon). Up to 1300 °C, the system undergoes redistribution reactions between Si-C and Si-O bonds leading to a phase separation between domains rich in SiC_4 units and others rich in SiO_4 units. Above 1300 °C, Si-C bonds are formed again by carbothermal reduction of the silica matrix which is related to a decrease in the free carbon content, leading to the crystallisation of silicon carbide above 1500 °C. It should be noticed that NMR was also used in combination with RAMAN spectroscopy to investigate in details the free carbon phase in carbon-rich Si-C-O PDCs [17] since it plays a crucial role on the mechanical and electrical properties but also on the oxydation resistance at high temperature. Similarly, Si-C-O samples with different carbon contents prepared from commercially available polysiloxanes have been studied by NMR [73]: a special attention was given to the structural heterogeneity at the nanometer length scale and for this purpose, ^{29}Si NMR spectra were recorded with increasing delay to determine the spin-lattice relaxation characteristic times T_1 . It was consequently shown that the structure could be described as a fractal spatial distribution of $\text{SiC}_x\text{O}_{4-x}$ structural units (with an average dimensionality of $D \sim 2.4$ to 2.5) at length scales on the order of a few nanometers. This fractal network is interspersed with « voids » occupied by sp^2 -hybridized free carbon nanodomains. Influence of the amount of mixed $\text{SiC}_x\text{O}_{4-x}$ ($1 \leq x \leq 3$) environments on the thermodynamic stability of silicon oxycarbides was also investigated by comparing two PDCs prepared from two silanes containing or not an Si-C direct bond [74]. NMR was used to quantify mixed bonding and it was shown that the system with none of them was also energetically stable, suggesting that other factors, such as the presence of Si-OH groups, detected by ^{29}Si NMR, may contribute to

stability. Finally, a very detailed high field ^{29}Si NMR investigation of a silicon oxycarbide network structure was recently reported [47]. Two types of 2D experiments were conducted: i) ^{29}Si double-quantum correlation NMR spectra which permitted to highlight the absence of connectivity between the SiO_4 and the SiC_4 units and the significant connectivity of SiO_3C units and all other units in the structure (Fig. 3a); ii) ^{29}Si extended CSA amplification spectrum (Fig. 3b) which showed i) the higher chemical shift anisotropy (Δ) of the mixed-bond $\text{SiO}_x\text{C}_{4-x}$ units compared to SiO_4 ones and ii) the unusually high Δ -value for the SiC_4 units, supported by DFT calculations, indicative of local asymmetry compatible with the connectivity of the SiC_4 units to the sp^2 C atoms at the interface between the Si-O-C network and free carbon domains.

It is also interesting to notice that apart from the most frequently probed ^{13}C and ^{29}Si nuclei, ^1H MAS NMR has been used to measure the hydrogen content in Si-C-O systems prepared by sol-gel route [75] that were then characterized by calorimetric measurements, for which the composition needs to be determined as precisely as possible.

4. Silicon-X-oxycarbides (Si-C-O-Ti/B/Al)

4.1. Silicon-titanium oxycarbides

The major advantage of using a polycarbosilane to be converted to SiC as proposed in the pioneering work of Yajima is the possibility to prepare ceramic fibres. They have high tensile strength and Young's modulus but their mechanical properties deteriorate at temperatures above 1200 °C. Consequently, to improve the mechanical properties at higher temperatures, a new precursor (namely a polytitanocarbosilane prepared from polycarbosilane and titanium n-butoxide) has been used to prepare Si-Ti-C fibres for which the crystallisation process is delayed, compared to the fibres prepared from polycarbosilane, with maximum mechanical properties around 1400 °C [76]. According to ^{29}Si MAS NMR, during the pyrolysis process, the local environment of silicon atoms is strongly modified compared to the initial polycarbosilane since Si-O bonds are formed via a cleavage of Si-C bonds, leading to the formation of $\text{SiC}_x\text{O}_{4-x}$ ($0 \leq x \leq 4$) environments. This reaction occurs up to 700 °C then Si-O bonds react with carbon resulting in a decrease of SiC_2O_2 and SiCO_3 units and mainly SiO_4 units remain. Above 1200 °C, the consumption of Si-O bonds increases and at 1500 °C, the system

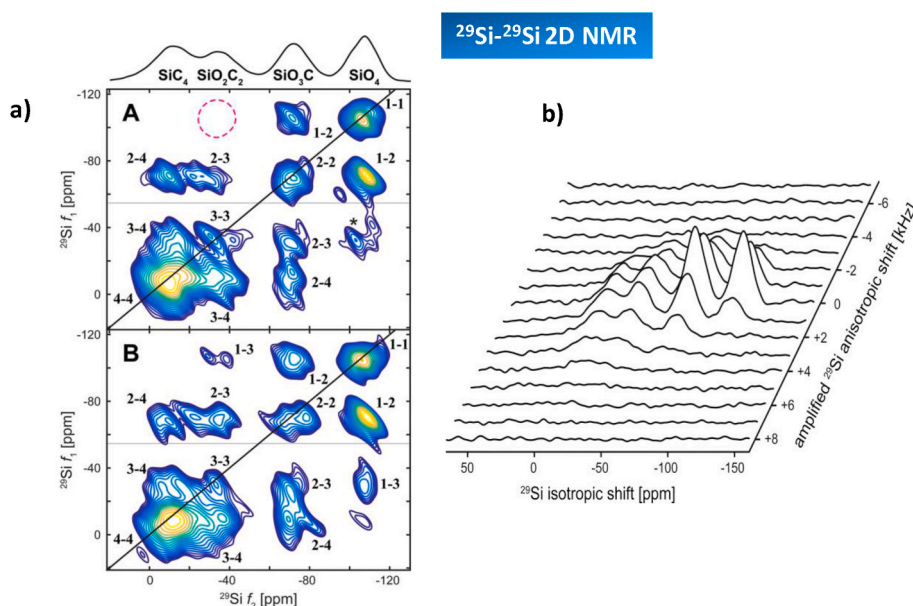


Fig. 3. a) 2D ^{29}Si DQ correlation spectra collected with DQ excitation times of (A) 6.7 and (B) 9.3 ms and b) stacked plot of the 2D ^{29}Si xCSA spectrum, recorded on an amorphous silicon oxycarbide polymer-derived ceramic of the composition $\text{SiO}_{0.94 \pm 0.11}\text{C}_{1.13 \pm 0.08}$. Reprinted with permission from Ref. [47]. Copyright 2021 American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

consists of SiC and TiC crystalline phases. Similarly, more recently, a precursor of titanium-containing polycarbosilane was prepared by reacting an hyperbranched polycarbosilane (HBPCS) and tetrabutyl titanate (TBT) [77]. The cross-linking reaction was investigated by different techniques including ^{29}Si MAS NMR indicating condensation between the Si-H bond of HBPCS and butoxy group in TBT leading to the formation of Si-O-Ti bonds. In this system, the crystallisation of SiC crystals starts only above 1600 °C and is probably inhibited by the formation of titanium carbide.

4.2. Silicon-boron oxycarbides

The introduction of B atoms in Si-O-C networks may positively affect the thermal stability of the systems that can be obtained from sol-gel-derived polyborosiloxanes. Indeed, an increase of the decomposition temperature and a decrease of the silica crystallisation has been observed in the presence of boron [78,79]. In this context, it is important to probe the distribution of boron atoms in the siloxane network which can be achieved thanks to ^{11}B MAS NMR [27,80–82]. Indeed, trigonal $\text{BC}_x\text{O}_{3-x}$ ($0 \leq x \leq 3$) have significantly distinct ^{11}B NMR parameters (as shown by 2D ^{11}B MQMAS experiments) and it is even possible to differentiate and quantify B(OSi) sites from B(OSi) $_{3-x}$ (OB) $_x$ ($x = 1, 2$) ones (Fig. 2c). A good dispersion of B atoms in the siloxane network has been achieved for example by pyrolysis of gels obtained from ethyltriethoxysilane and triethylborate [81]: ^{11}B NMR showed a progressive replacement of borosiloxanes bridges by B-C bonds with temperature, suggesting at 1000 °C the formation of a silicon-boron oxycarbide network containing mixed silicon oxycarbide (identified by ^{29}Si NMR) and boron oxycarbide units. In addition, the influence of boron content and pyrolysis temperature on the thermodynamic stability was investigated [8] and it appeared that addition of boron could decrease the stability which, on the basis of ^{29}Si and ^{11}B NMR data, is possibly due to the formation of $\text{BC}_x\text{O}_{3-x}$ units in the silicon oxycarbide phase. The increase in the pyrolysis temperature leads to demixing of mixed silicon oxycarbide and boron oxycarbide units, leading to a stabilization assigned to a greater stability of the B-free Si-O-C glass.

4.3. Silicon-aluminum oxycarbides

Modification of a polycarbosilane by reaction with an aluminum alkoxide leads to a precursor of Si-Al-C-O ceramics in which AlO_4 , AlO_5 and AlO_6 environments (with distinct chemical shift values at 65, 29, 4 ppm respectively) could be identified by ^{27}Al NMR [83]. Formation of Al-C bonds characterized by a signal around 150 ppm is observed after pyrolysis indicating the formation of an aluminum oxycarbide phase while a pure silicon carbon (3C polytype) starts to crystallize around 1200 °C as shown by XRD and ^{29}Si MAS NMR spectra. Around 1300 °C, the aluminum oxycarbide phase seems to react with the SiC one, favoring the formation of the silicon carbide 2H polytype at the expense of the 3C one. SiC(OAl) and SiC(Al) fibers were also characterized by ^{13}C , ^{27}Al and ^{29}Si multinuclear NMR [84] showing the presence of $\text{SiC}_x\text{O}_{4-x}$ environments, Al-C and Al-O bonds as well as a free carbon phase. All in all, ^{27}Al NMR is used in these systems to confirm the introduction of aluminum into silicon oxycarbide network as for example in the glass obtained from a xerogel based on ladder-like silsesquioxanes obtained from a modified alkoxy silane and butoxy derivative of aluminum [85].

5. Silicon carbonitrides (Si-C-N)

Similarly to silicon oxycarbide, multinuclear NMR is one of the most accurate spectroscopy to identify the type of coordinations in silicon carbonitride and in particular, ^{29}Si MAS NMR was extensively used to quantify $\text{SiC}_x\text{N}_{4-x}$ ($0 \leq x \leq 4$) environments [6,86–92] and follow the amount of Si-C and Si-N bondings either cleaved or formed during the polymer to ceramic transformation. The most common PDC precursors to Si-C-N ceramics are polysilazanes, polysilsesquiazanes,

polysesquicarbodiimides and polysilylcarbodiimides [93,94].

5.1. Poly(organosilazanes)

Seyferth and his collaborators prepared cyclic $(\text{CH}_3\text{SiH}_2\text{NH})_n$ oligomers by ammonolysis of methylchlorosilane [95] and the method was extended to other cyclotetrasilazanes, which could be characterized by NMR [96]. The polymer-to-ceramic transformation was also followed by ^{29}Si CP MAS NMR to get information on the hydrogen distribution at lower temperatures and by ^{29}Si MAS NMR up to 1500 °C, showing the progressive phase separation into SiC and Si_3N_4 domains. Ziegler et al. also proposed the synthesis of silazane-based polymers by ammonolysis of chlorosilanes leading to $\text{H}(\text{NH})_2\text{SiCH}_3$, $\text{CH}_3(\text{NH})_2\text{SiCH}=\text{CH}_2$ or $(\text{NH})_3\text{SiCH}=\text{CH}_2$ environments that could be easily identified by ^{29}Si NMR [97]. Pyrolysis of such precursors with tailored structures were then investigated by solid-state NMR [98]. At 300 °C, the appearance of a ^{29}Si signal characteristic of $(\text{N})_2\text{Si}(\text{C}^{\text{sp}3})_2$ units suggests crosslinking via hydrosilylation reaction between Si-H and vinyl groups and/or polymerisation of the vinyls, leading to Si-CH $_2$ -CH $_2$ -Si bonds. This can be confirmed by ^{13}C NMR showing a decrease of the vinyl signal and new signals corresponding to aliphatic carbons. Below 800 °C, an homogenous Si-C-N phase is observed as indicated by a broad ^{29}Si signal due to a distribution of $\text{SiC}_x\text{N}_{4-x}$ ($0 \leq x \leq 4$) environments as well as a free carbon phase characterized by ^{13}C MAS NMR. Progressive phase separation is then observed between 800 and 1500 °C with mainly SiC_4 , SiCN_3 , SiN_4 environments and the crystallisation of SiC is observed above 1500 °C.

Similarly, various polyvinylsilazanes were prepared by ammonolysis of vinylchlorosilazanes, cross-linked by different procedures and characterized by solid-state NMR with the help of the comparison with model compounds [99]. NMR results suggest that hydrosilylation is the main reaction occurring in the cross-linking but transamination reactions leading to NSi_3 environments can not be excluded. In the presence of potassium hydride as a catalyst, dehydrocoupling reaction between SiH and NH adjacent functions were identified. Structural modifications during the ceramisation of these hydrogenovinylsilazanes $[-\text{NH}-\text{Si}(\text{H})(\text{CH}=\text{CH}_2)-\text{NH}-]$ were studied by ^{13}C CP MAS, ^{29}Si MAS and CP MAS [5] showing progressive transformation of silicon environments from $\text{SiH}(\text{C}^{\text{sp}2})\text{N}_2$ to $\text{SiH}(\text{C}^{\text{sp}3})\text{N}_2$, $\text{SiH}(\text{C}^{\text{sp}2})(\text{C}^{\text{sp}3})\text{N}_2$ and finally $\text{SiC}_x\text{N}_{4-x}$ ($0 \leq x \leq 2$). After elimination of hydrogen and decrease in the number of Si-C bonds, the final composition at 1400 °C is estimated to be 32% of amorphous silicon nitride phase, 28% of silicon carbonitride phase and 40% of free carbon.

The polymer to ceramic conversion of other copolymers based on silazanes such as $[-\text{NH}-\text{Si}(\text{H})(\text{CH}=\text{CH}_2)-\text{NH}-]_{0.5} - [-\text{NH}-\text{Si}(\text{H})(\text{CH}_3)-\text{NH}-]$ was also investigated by NMR [100] and compared to $[-\text{NH}-\text{Si}(\text{H})(\text{CH}=\text{CH}_2)-\text{NH}-]$ and $[-\text{NH}-\text{Si}(\text{H})(\text{CH}_3)-\text{NH}-]$ precursors with a careful quantitative analysis of the fraction of silicon sites. Assuming that at high temperatures (above 900 °C), hydrogen content is not significant (as confirmed by ^1H NMR), atomic compositions of the matrix can be estimated taking into account C atoms as CSi_4 sites and N atoms as NSi_3 sites. The proportions of $\text{SiC}_x\text{N}_{4-x}$ environments are obtained from ^{29}Si NMR spectra, and compositions can be calculated as follows: if $p = \text{SiC}_2\text{N}_2$ (%), $q = \text{SiCN}_3$ (%) and $r = \text{SiN}_4$, then: $\text{Si}(\%) = (p+q+r)/\Sigma$; $\text{C}(\%) = (2p+q)/4\Sigma$ and $\text{N}(\%) = (2p+3q+4r)/3\Sigma$ with $\Sigma = (p+q+r) + (2p+q)/4$. This leads to a more precise description of the different phases forming the material, considering also the free carbon phase that can be estimated from the fractions of C atoms which are no longer bonded to Si atoms, obtained from the comparison of the global C/Si ratio (from chemical analyses) and in the $\text{SiC}_x\text{N}_{4-x}$ distribution obtained by NMR.

Appart from vinylsilazanes, hydridopolysilazanes (synthesized by reaction of trichlorosilane with hexamethyldisilazane $(\text{Me}_3\text{Si})_2\text{NH}$) can also be converted into Si-C-N ceramics [101]. The initial polymer contains two types of silicon environments $\text{NSi}(\text{Me})_3$ and N_3SiH clearly evidenced by ^{29}Si CP MAS NMR which permits to discriminate the silicon sites directly bonded to a proton. ^{15}N CP MAS NMR spectroscopy

shows the presence of Si_2NH and Si_3N units after heat-treatment at 300 °C. Above 400 °C, SiN_2C_2 signals and the progressive formation of SiN_3 are observed by ^{29}Si NMR while ^{15}N CP MAS spectra show a decrease of Si_2NH signals in favour of Si_3N ones. Above 1200 °C, a minority of mixed Si-C-N bonds are observed while the ceramic contains predominantly SiC and Si_3N_4 .

The conversion into ceramics of poly(N-methylsilazane) $[\text{H}_2\text{SiNMe}]_x$ - and poly-(Si-methylsilazane) $[\text{MeHSiNH}]_x$ -was also investigated by solid-state NMR [102] showing that poly(N-methylsilazane) converts into Si_3N_4 and a free carbon phase at 1000 °C while poly-(Si-methylsilazane) leads to an amorphous compounds still containing mixed $\text{SiC}_x\text{N}_{4-x}$ units.

Various polysilazanes are commercially available but without a precise description of their structure. Consequently, Seitz et al. characterized two of them via NMR spectroscopy [103]: NCP200 is a commercial polyhydridomethylsilazane based on $[\text{NH-SiHMe-NH}]_m[\text{NH-SiMe}_2\text{NH}]_n$ units and clear identification of both silicon sites could be achieved thanks to ^{29}Si CP MAS experiments enhancing the NH-SiHMe-NH signal due to the presence of the direct Si-H bond. It should be noticed that the position of the peak corresponding to the SiN_2C_2 environments is characteristic of a six-membered cyclosilazane ring [99] and different from a four- or eight-membered ring or even a chain. The ceramic conversion of another commercial polyvinylsilazane (VT50) was investigated by comparison and it appears that the later leads to a ceramic containing predominantly Si_3N_4 and free carbon while NCP-derived ceramic shows a distribution of $\text{SiC}_x\text{N}_{4-x}$ ($0 \leq x \leq 4$) environments. Another polysilazane, namely a poly(ureamethylvinyl) silazane, commercialized as Ceraset was investigated by NMR [88] and shows ^{13}C and ^{29}Si signals characteristic of $[\text{NH-Si}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{NH}]$ and $[\text{NH-Si}(\text{H})(\text{CH}_3)\text{NH}]$ units with a majority of the later. Cross-linking at 270 °C induces the formation of Si-CH_2 - or $\text{Si-CH}_2\text{-CH}_2\text{-Si}$ arising from hydrosilylation of vinyl groups or Kumada-like rearrangement reactions as described previously. At 1100 °C, ^{29}Si NMR allows to quantify the presence of SiN_4 (16%), SiN_3C (73%) and SiN_2C_2 (11%) suggesting an amorphous Si-C-N phase is obtained.

5.2. Poly(organosilylcarbodiimides)

Apart from polysilazanes, a second type of precursors that yield Si-C-N ceramics after thermal decomposition are poly(organosilylcarbodiimides) than can be obtained by the reaction of various chlorosilanes with cyanamide or bis(trimethylsilyl)carbodiimide [104–106]. Among them, reaction mechanisms for the ceramisation of polymethylsilylcarbodiimides based on $\text{SiH}(\text{CH}_3)(\text{NCN})_2$ units were investigated by multinuclear solid-state NMR [21]. This study demonstrates the similarity of the ^{29}Si NMR shifts in polysiloxanes and polysilylcarbodiimides, therefore suggesting to treat the NCN units as pseudo-oxygens. Using both ^{29}Si MAS and IRCP MAS measurements to distinguish protonated from non protonated silicon sites, identification of $\text{SiC}(\text{NCN})_2(\text{NCHN})$, $\text{SiC}(\text{NCN})_3$ and $\text{SiH}_2\text{C}(\text{NCN})$ units after heat-treatment at 200 °C indicate that cross-linking occurs through hydrosilylation reactions and a disproportion process of the $\text{SiH}(\text{CH}_3)(\text{NCN})_2$ moieties. Above 200 °C, SiCX_3 , SiCNX_2 , SiCN_2X , and SiCN_3 sites ($\text{X} = \text{NCN}$, NCHN) sites are identified and only SiN_4 and SiCX_3 sites ($\text{X} = \text{NCN}$, NCHN) at 600 °C, suggesting a progressive cleavage of the Si-C bonds. At 1000 °C, the ^{29}Si MAS NMR spectrum is dominated by a signal at -46.0 ppm characteristic of SiN_4 units in amorphous Si_3N_4 while ^{13}C NMR suggests the formation of free carbon phase.

Similarly, the pyrolytic transformation of a poly(methylsilsesquicarbodiimide) based on $\text{Si}(\text{CH}_3)(\text{NCN})_3$ units was followed by ^{13}C , ^{15}N and ^{29}Si CP and IRCP MAS NMR [18] which permitted to identify $\text{CH}_3\text{Si}(\text{N}<)_x(\text{N}=\text{C}=\text{N})_{3-x}$ ($0 \leq x \leq 3$) and $\text{Si}(\text{N}<)_x(\text{N}=\text{C}=\text{N})_{4-x}$ ($1 \leq x \leq 4$) environments (Table 1) depending on the temperature. This suggests two steps in the pyrolysis process: i) cleavage of the Si-CH₃ bonds between 550 ad 600 °C and complete

rearrangement of the $\text{Si-N}=\text{C}=\text{N-Si}$ backbone leading to the formation of Si-N bonds; ii) decomposition of the residual carbodiimide units between 800 and 1200 °C. As for the previous silylcarbodiimides based-system described, no mixed $\text{SiC}_x\text{N}_{4-x}$ ($1 \leq x \leq 3$) units are retained at 1200 °C and the fraction of the carbon from the starting polymer remains as free carbon while amorphous Si_3N_4 is also observed.

At this point, considering the results previously described, it is interesting to mention that ^{29}Si MAS NMR measurements in polysilazanes and polysilylcarbodiimides have shown significantly different microstructures of the resulting ceramics since polysilazanes lead rather to a single-phase amorphous SiCN characterised by mixed $\text{SiC}_x\text{N}_{4-x}$ ($1 \leq x \leq 3$) units while polysilylcarbodiimides form a two-phase system composed predominantly of amorphous Si_3N_4 interconnected with a free carbon phase.

More recently [107], solid-state NMR was used to characterise carbon-rich Si-C-N ceramics derived from phenyl-containing poly(silylcarbodiimides). The carbon content was varied by the second substituent being either a phenyl ring, a methyl group, an hydrogen atom or a vinyl group. Polymers were first investigated by ^{29}Si CP and ^{13}C MAS NMR which allowed to assign $\text{R}(\text{Ph})\text{Si}(\text{NCN})_2$ groups as well as aromatic carbons and NCN units if not hidden by the phenyls signals. The polymer decomposition starts at 600 °C as suggested by the ^{29}Si NMR spectrum characteristic of the presence of $\text{SiC}_x(\text{CN})_y\text{N}_z$ sites. At 1000 °C, the diphenyl system shows only SiN_4 units, while $\text{SiC}_x\text{N}_{4-x}$ ($x = 1$ or 2) signals are observed in the methyl/phenyl mixed system. At 1500 °C, contrary to the studies on polysilylcarbodiimide-derived ceramics reported previously, no crystalline Si_3N_4 phases were detected since ceramics are amorphous up to 1500 °C when a fraction of amorphous Si_3N_4 transforms to crystalline SiC. The C-rich systems exhibit a better temperature resistance than that of the reported Si-C-N ceramics with lower C-content. The crystallisation of the poly(diphenylsilylcarbodiimide)-based system occurs even beyond 1500 °C. The formation of β -SiC was detected at 1700 °C.

Moreover, poly(phenylvinylsilylcarbodiimide) and poly(phenylsilsesquicarbodiimide) were isotopically enriched in nitrogen-15 [44] which permitted to probe by ^{15}N MAS NMR the presence of three-coordinated nitrogen sites in NCSi_2 and NSi_3 environments in the 800 and 1100 °C heat-treated ceramics. Two dimensional $\{^1\text{H}\}$ - ^{15}N and $\{^1\text{H}\}$ - ^{13}C HETCOR CP MAS NMR experiments allowed to probe the distribution of protons (Fig. 4). This multinuclear NMR study provided self-consistent structures with coexisting nanometric domains of α - Si_3N_4 and amorphous carbon with an interfacial region characterized by mixed $\text{SiC}_x\text{N}_{4-x}$ units in the case of the poly(phenylsilsesquicarbodiimide)-derived system while the carbon domains form a matrix that embeds α - Si_3N_4 nanodomains in the poly(phenylvinylsilylcarbodiimide)-derived ceramic.

It can be noticed that the characterization of the free carbon phase in different Si-C-N ceramics depending on the polysilazane precursor has been carefully detailed combining ^{13}C MAS NMR with other spectroscopies such as Raman and ESR as well as high resolution TEM imaging [108]. As previously explained, the segregation of the free carbon is also

Table 1

Assignments of the silicon-29 chemical shift data obtained by ^{29}Si CP and IRCP MAS NMR experiments on a poly(methylsilsesquicarbodiimide) and its pyrolysis products up to 800 °C. Reprinted with permission from Ref. [18]. Copyright 1999 American Chemical Society.

^{29}Si Chemical shift range (ppm)	Assignment
-59	$\text{MeSi}(\text{N}=\text{C}=\text{N})_3$
-48 to -43	$\text{MeSi}(\text{N}<)(\text{N}=\text{C}=\text{N})_2$
-36 to -33	$\text{MeSi}(\text{N}<)_2(\text{N}=\text{C}=\text{N})$
-20 to -17	$\text{MeSi}(\text{N}<)_3$
-88	$\text{Si}(\text{N}<)(\text{N}=\text{C}=\text{N})_3$
-78 to -71	$\text{Si}(\text{N}<)_2(\text{N}=\text{C}=\text{N})_2$
-60	$\text{Si}(\text{N}<)_3(\text{N}=\text{C}=\text{N})$
-49 to -45	$\text{Si}(\text{N}<)_4$

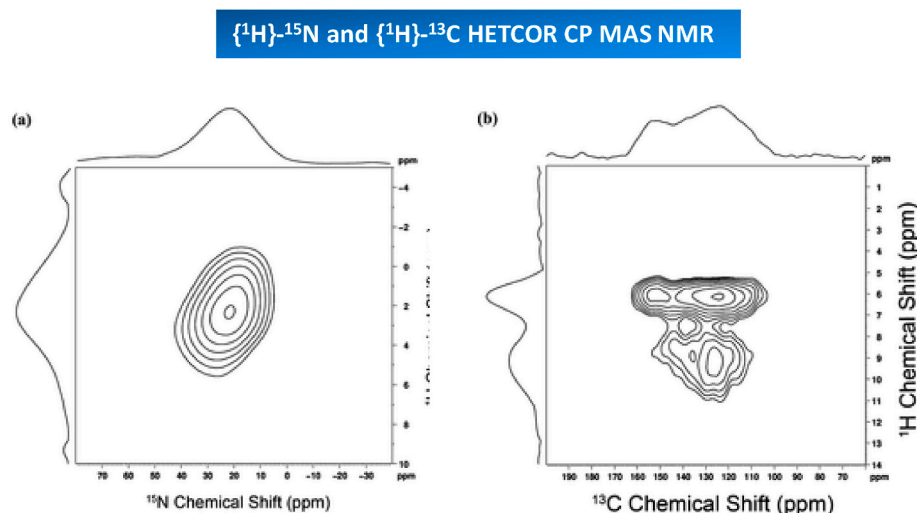


Fig. 4. Two dimensional $\{^1\text{H}\}\text{-}^{15}\text{N}$ and $\{^1\text{H}\}\text{-}^{13}\text{C}$ HETCOR CP MAS NMR experiments recorded on a polyphenylsilsequicarodiimide heat-treated at 800°C . Reprinted with permission from Ref. [44]. Copyright 2012 American Chemical Society.

indirectly visible in ^{29}Si NMR spectra by a high-field shift of the peaks indicating an increase of the number of Si–N bonds compared to Si–C ones since ^{29}Si chemical shift value of $\text{SiC}_x\text{N}_{4-x}$ decreases when x increases from 1 to 4 (Fig. 1b). Moreover, ^{13}C NMR experiments can give informations on the relaxation behavior: indeed sp^2 carbons are characterized by a faster spin-lattice relaxation in comparison with the CSi_4 components (due to the presence of paramagnetic centers demonstrated by ESR spectroscopy). The different relaxation times allow to probe the possible heterogeneity of the ceramics, with two phases namely the free-carbon and the Si-C-N phase.

6. Silicon oxycarbonitrides (Si-C-N-O)

In the context of a synthetic strategy to tune the specific surface area of materials by modifying the structure of preceramic polymer in an NH_3 reactive atmosphere, microporous silicon oxycarbonitride ceramics were obtained [109]. In particular, in the case of the ammonolysis of a commercial polysiloxane, ^{29}Si NMR spectra show, in addition to the silicon environments previously described in this manuscript for Si-C-O and Si-C-N systems (Fig. 1), new signals that can be assigned to SiN_2O_2 environments (and possibly minor amounts of SiNO_3 and SiN_3O). Other mixed polysiloxane-silazane networks were investigated by NMR, with a main focus on carbon-13 silicon-29 nuclei [110–113].

7. Silicon-X-carbonitrides (Si-C-N-Ti/Zr/B/Al)

7.1. Silicon-boron carbonitrides

Amorphous Si-B-C-N ceramics prepared by the PDC route can exhibit excellent thermomechanical properties and in particular a very high stability at high temperatures under inert atmosphere [114]. This can be attributed, among other things, to the presence of a $\text{BN}(\text{C})$ phase around SiC and Si_3N_4 , which delays the decomposition of the system [115]. Two main types of synthesis routes have been used to obtain ceramic precursor polymers in the Si-B-C-N system [116,117].

On the one hand, a route that can be described as polymeric, which consists of reacting a boron-containing compound with a silazane or any other Si, C and N-based polymer, and on the other hand, a monomer route in which polymerisation takes place during the reaction. For example, silazanes were substituted by borazine [118] and hydridopolysilazanes were reacted by boranes [119] but conversion to ceramic was not followed by solid-state NMR. Another proposed possibility is to react TADB (trichlorosilylaminodichloroborane) with methylamine to

form a N-methylpolyborosilazane that can be converted into $\text{Si}_3\text{B}_3\text{N}_7$ or SiBN_3C ceramics depending on the conditions of pyrolysis [120] with a boron-11 NMR spectrum characteristic of BN_3 environments. Boron-containing polysilylcarbodiimides were characterized by ^{13}C CP MAS, ^{11}B and ^{29}Si MAS NMR [121]. Similar polymers can also be obtained from a boron-substituted chlorosilane of the type $\text{B}[\text{C}_2\text{H}_4(\text{R})\text{SiCl}_2]_3$, and bis(trimethylsilyl)carbodiimide [115].

Poly(borosilazane) precursors were also synthesized by the hydroboration of vinyl-substituted cyclotrisilazane $[\text{CH}_2=\text{CH}(\text{CH}_3)\text{SiNH}]_3$ with the borane adduct $(\text{CH}_3)_3\text{N-BH}_3$ and the polymer-to-ceramic conversion process was investigated by ^{13}C , ^{29}Si , and ^{11}B solid-state MAS NMR [122]. In addition to the usual carbon and silicon environments identified by ^{13}C and ^{29}Si NMR as previously reported in the Si-C-N systems, ^{11}B NMR allows to distinguish 3- and 4-coordinated boron sites and more specifically H_2BC , HBC_2 , HBCN , BC_2N and BN_3 environments in the polymer whose structure appears relatively complex. ^{11}B NMR shows also the formation of new B-N bonds after heat-treatment, with main signals shifting from BC_2N and HBN_2 to BN_3 environments, typical of amorphous boron nitride domains.

To illustrate the « polymeric » route with systems relatively close to the previously described, it can be mentioned that vinyl-substituted polysilylcarbodiimides $[(\text{H}_2\text{C}=\text{CH})(\text{R})\text{Si}(\text{NCN})]_n$ ($\text{R}=\text{H}$, CH_3 or $(\text{NCN})_{0.5}$) were reacted with borane dimethylsulfide ($\text{BH}_3\cdot\text{S}(\text{CH}_3)_2$) leading to incorporation of boron by hydroboration of the vinyl units [115]. Similarly, borane dimethylsulfide was used for the hydroboration of a polyvinylsilazane $[(\text{H}_2\text{C}=\text{CH})\text{Si}(\text{H})\text{NH}]_n$ [123] and ^{11}B NMR on the precursor suggests a more complex boron environment than the expected BC_3 sites and in particular tetra-coordinated signals suggesting BNC_3 environments. After thermolysis, BN_3 sites consistent with hexagonal boron nitride are observed, suggesting the formation of B-N bonds after cleavage of B-C ones. More recently, related systems were investigated starting from a commercial poly(vinylmethyl-co-methyl)silazane (HTT1800, probably very similar to the previously mentioned Ceraset) based on $[-\text{NH-Si}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{-NH-}]$ and $[-\text{NH-Si}(\text{H})(\text{CH}_3)\text{-NH-}]$ units [124,125]. Similarly, ^{11}B NMR shows that the real structure of boron-modified polymers is complex due to both *i*) hydroboration of the vinyl groups by borane dimethylsulfide and *ii*) dehydrocoupling reaction of B-H bonds with the N centers of the polysilazane. Very interestingly, the boron amount has a big influence on the crosslinking, the lower the Si/B ratio, the higher the crosslinking degree which has a significant effect on the processability. Moreover, boron plays a major role in modifying the mechanisms of the polymer-to-ceramic transformation [125].

An alternative synthesis pathway was developed by Riedel et al. consisting in *i*) the synthesis of boron-containing monomers in a first step by hydroboration reactions of dichloroborane-, monochloroborane- and borane-dimethylsulfide with dichloromethylvinylsilane and trichlorovinylsilane [126]; *ii*) ammonolysis of these monomers leading to polyborocarbosilazanes of the general formula $[B(C_2H_4-Si(NH)CH_3)_x(NH)_{3-x}]_n$ with well-defined Si/B ratios ranging from 1/1 to 3/1 as well as distinct expected boron environments BCN_2 , BC_2N and BC_3 for 1/1, 2/1 and 3/1 systems respectively, as confirmed by ^{11}B NMR which permits to identify BC_xN_{3-x} sites according to the x value (as illustrated in Fig. 2b for another SIBC system [28]). Similarly, $NHSi_2$, $NHBSi$, and NHB_2 nitrogen environments are expected and could be clearly identified by ^{15}N CP MAS NMR (Fig. 5). Since ^{15}N -enriched polymers were obtained using 10% ^{15}N enriched ammonia for the ammonolysis, ^{15}N NMR could be used to follow the ceramisation process which would not have been possible without isotopic enrichment considering the very low natural abundance of nitrogen-15 [26]. Very interestingly, using the IRCP sequence to distinguish protonated from non protonated nitrogen sites, the presence of a mixture of $NXSi_2$, $NXBSi$, and NXB_2 with $X = H$ or C could be identified at 400 °C while removal of hydrogen from the nitrogen atoms is almost complete at 600 °C and a distribution of NB_3 , NCB_2 , $NCBSi$, and $NCSi_2$ sites is suggested at 1000 °C. In parallel, *i*) ^{11}B NMR shows a progressive replacement of B-C bonds by B-N bonds, leading to a mixture of BCN_2 and BN_3 environments only at 1000 °C, whatever the initial Si/B ratio; *ii*) ^{29}Si NMR spectra are typical of a distribution of SiC_xN_{4-x} ($x = 0$ to 4) units; *iii*) ^{13}C CP MAS NMR shows the formation of C-N bonds at 400 °C and of a free carbon phase above 600 °C. All in all, these NMR results suggest that boron atoms are homogeneously dispersed in the silicon carbonitride phase supporting the high thermal stability analyzed in these compounds.

Following on, researchers focused on the development of the processability and improvement of the ceramic yield. As an illustration, $B(C_2H_4SiHCl_2)_3$ is an alternative synthon for the preparation of boron-modified polysilazanes [127]. After ammonolysis, a preceramic polymer displaying a higher degree of cross-linking as well as light-weight pendant groups with latent reactivity was produced. Using ^{15}N -enriched ammonia for ammonolysis, a complete multinuclear ^{11}B ,

^{13}C , ^{15}N and ^{29}Si NMR study could be completed [128] showing that boron exhibits a strong affinity to nitrogen, resulting in a reduction of nitrogen in the vicinity of silicon atoms below 500 °C. The amorphous ceramic at 1050 °C is characterised by the presence of a distribution of SiC_xN_{4-x} environments, (with $x = 0,1,2$), amorphous (graphite-like) carbon and planar BN domains. Domains with mixed Si-C and Si-N bonds is a possible reason for the observed high-temperature stability of Si-B-C-N ceramics. The same is true for the BN domains, which are considered as diffusion barriers at higher temperatures, thus inhibiting decomposition reactions. In the temperature range between 1000 and 2000 °C, a crystallisation of the amorphous ceramic is observed and ^{29}Si NMR suggests a demixing of the silico-carbo nitride domains and formation of silicon carbide and silicon nitride.

In line with these works, improved processability was obtained by reacting similar boron-containing monomers (tris(dichloromethylsilyl)ethyl)borane ($B(C_2H_4SiCH_2Cl)_3$, TDSB) with $LiNH_2$ [129] or methyl amine CH_3NH_2 (MA) [19] instead of ammonia, leading to boron-modified polysilazanes of the type $[B(C_2H_4-Si(NCH_3)CH_3)_3]_n$. In the later case, NMR was used to show that the MA: TDSB ratio fixed during the polymer synthesis strongly modifies the proportion of identified structural units, determines the boron environment and influences the molecular weight of polymers, causing different responses to melt-spinnability. Indeed, these systems can be described as a complex polymeric network bridged via tri-coordinated $BC_{3-x}N_x$ units and tetra-coordinated BC_xN_{4-x} units connecting four and/or six-membered -Si-N- rings. ^{11}B NMR indicates a disappearance of tetracoordinated boron atoms and BC_3 units with the concomitant increased proportion of $BC_{3-x}N_x$ ($0 < x < 3$) units below 200 °C [9]. Thermolysis between 200 and 1000 °C leads to an amorphous ceramic containing mainly BN_3 and BCN_2 environments, SiC_xN_{4-x} ($0 \leq x \leq 3$) and graphite domains according to multinuclear NMR. These polymers show appropriate rheological properties to be spun as a melt but a poor ceramic yield which is an issue in terms of fiber shape retention. Consequently, co-polymers composed of $C_2H_4SiCH_3(NH)_x$ and $C_2H_4SiCH_3(NCH_3)_y$ ($C_2H_4=CHCH_3$, CH_2CH_2 as discussed later) building block in a well defined ratio were combined to tune both rheological properties and thermal behavior [28]. The first attempts led to good extrusion and a significantly higher

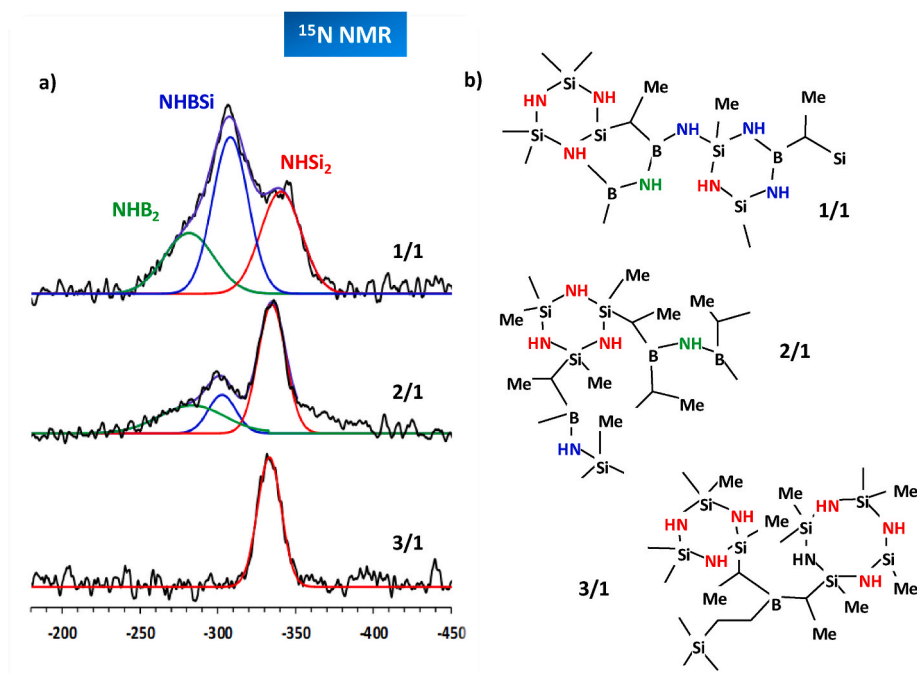


Fig. 5. a) ^{15}N CP MAS NMR experimental and simulated spectra of three polyborocarbosilazanes with 1/1, 2/1 and 3/1 Si/B ratios. b) Proposed structures for these polymers highlighting the different nitrogen environments. Adapted with permission from Ref. [26].

ceramic yield than the melt-spinnable boron-modified polyorganosilazane containing only NCH_3 units but the stretchability of the extruded fibers was not stable. Consequently, a second series of Si-B-C-N precursors was tested by fixing NH amount x at 0.5 while increasing the NCH_3 y values above 0.5 by adding an excess of methyl amine. The chemical structures of the various co-polymers have been characterized, in particular by NMR, showing that excess of MA induces more ending groups and specifically more tetracoordinated boron quantified by ^{11}B NMR which are thought to play a crucial role on the meltspinnability of the precursors.

In addition, boron-modified poly(allylmethylsilazane) $[\text{B}(\text{C}_3\text{H}_6\text{Si}(\text{CH}_3)\text{NH})_3]_n$, which exhibits a larger carbon content due to the longer alkyl chain, also leads to a quaternary Si-C-B-N ceramic [20]. Combination of ^{13}C CP and IRCP MAS NMR sequences shows that the hydroboration reaction of the poly(allylmethylsilazane) is not regio-selective. Boron attacks the β - as well as the γ -carbon atom of the propenyl groups in the polymeric precursor leading to both $\text{B}-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{Si}$ and $\text{B}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}$ bonds. Similarly, ^{13}C IRCP MAS NMR was used to show that hydroboration of vinylsilazanes mentioned previously also consists in α - and β -addition with the formation of $\text{B}-\text{CH}(\text{CH}_3)-\text{Si}$ and $\text{B}-\text{CH}_2-\text{CH}_2-\text{Si}$ environments (Fig. 6) [19,28,128].

It is interesting to notice that a comparative structural study of silicon borocarbonitride polymer-derived ceramics from polyborosilylcarbodiimide and polyborosilazane precursors was conducted using multinuclear, one- and two-dimensional NMR spectroscopy [41]: the structures of both types of PDCs contain sp^2 free carbon nanodomains whose average size decreases with decreasing carbon content.

Moreover the polyborosilylcarbodiimide-derived Si-B-C-N ceramics consists of Si_3N_4 and BN nanodomains while the polyborosilazane-derived one contains mixed silicon- and boron-carbonitride nanodomains with core-shell structures as demonstrated by the presence of $\text{SiC}_x\text{N}_{4-x}$ and $\text{BC}_x\text{N}_{3-x}$ environments according to ^{29}Si and ^{11}B NMR. The bonding scheme suggests that the B-C-N domains occupy the interfacial region that separates the Si-C-N and the free carbon domains.

Most of polymers previously described in this section are built through silazane rings which are cross-linked via $-\text{C}-\text{B}-\text{C}-$ bridges whereas Jansen and his collaborators proposed the synthesis of polyorganosilazanes cross-linked via $-\text{B}-\text{N}-\text{B}-$ bridges, using for example a two-step reaction involving tetrachlorosilane (SiCl_4), hexamethyldisilazane ($\text{Me}_3\text{Si}-\text{NH}-\text{SiMe}_3$) and boron trichloride (BCl_3) which leads to a trichlorosilyl-amino-dichloroborane $\text{Cl}_3\text{Si}-\text{NH}-\text{BCl}_2$. A polyborosilazane is then obtained by ammonolysis with NH_3 or aminolysis by methylamine [130]. This approach has its advantages and drawbacks in terms of polymer processability and tetrachlorosilane can be replaced by MeSiCl_3 or Me_2SiCl_2 . In the same line, a (trichlorosilyl)dichloroboryl ethene, $\text{Cl}_3\text{Si}-\text{CH}(\text{CH}_3)-\text{BCl}_2$ was polymerized with ^{13}C - ^{15}N enriched methylamine which allowed to record $\{^{15}\text{N}\}$ - ^{13}C REDOR NMR experiments (Fig. 7) [42].

The structural organization of the obtained $\text{Si}_2\text{B}_2\text{N}_5\text{C}_4$ ceramic could be derived from this spectroscopic study which shows that a large proportion of carbon is connected to nitrogen through different coordinations, similarly to a SiBN_3C ceramic reported in a former study [49]. ^{11}B MQMAS NMR experiments suggests that boron atoms are

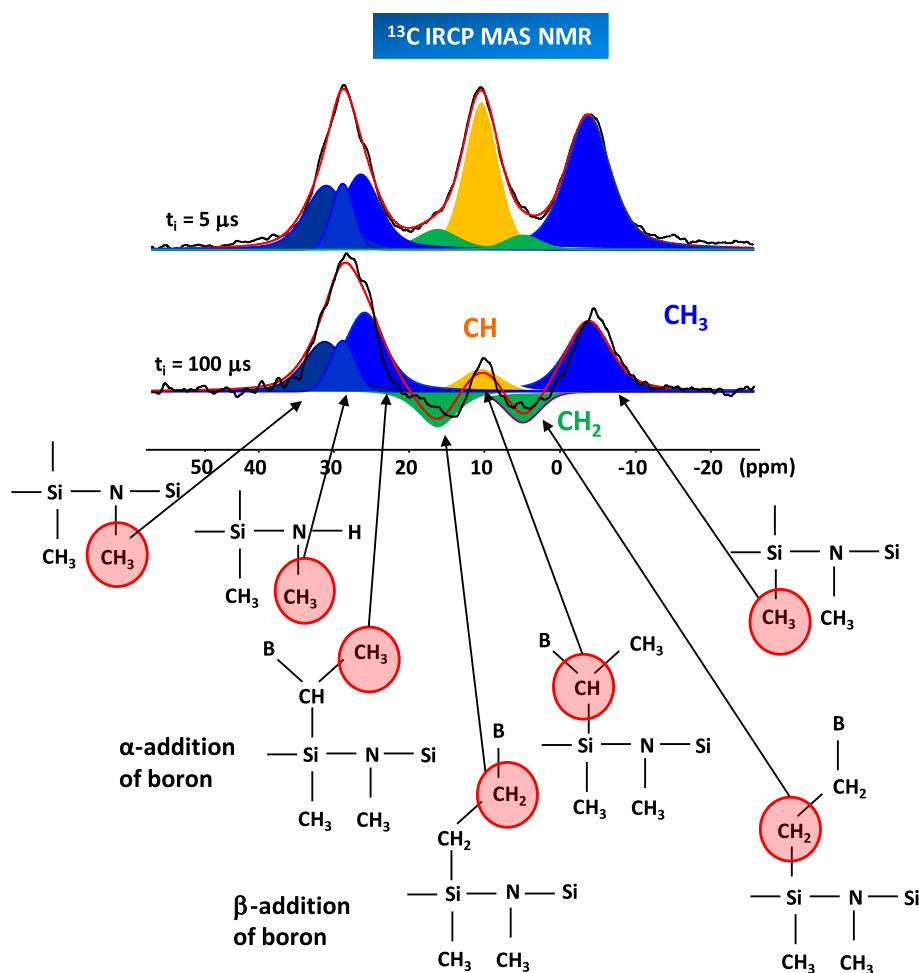


Fig. 6. a) ^{13}C IRCP MAS NMR experimental and simulated spectra recorded at two inversion times t_1 of a boron-modified polysilazanes of the type $[\text{B}(\text{C}_2\text{H}_4\text{Si}(\text{NCH}_3)\text{CH}_3)_3]_n$. Adapted with permission from Ref. [19].

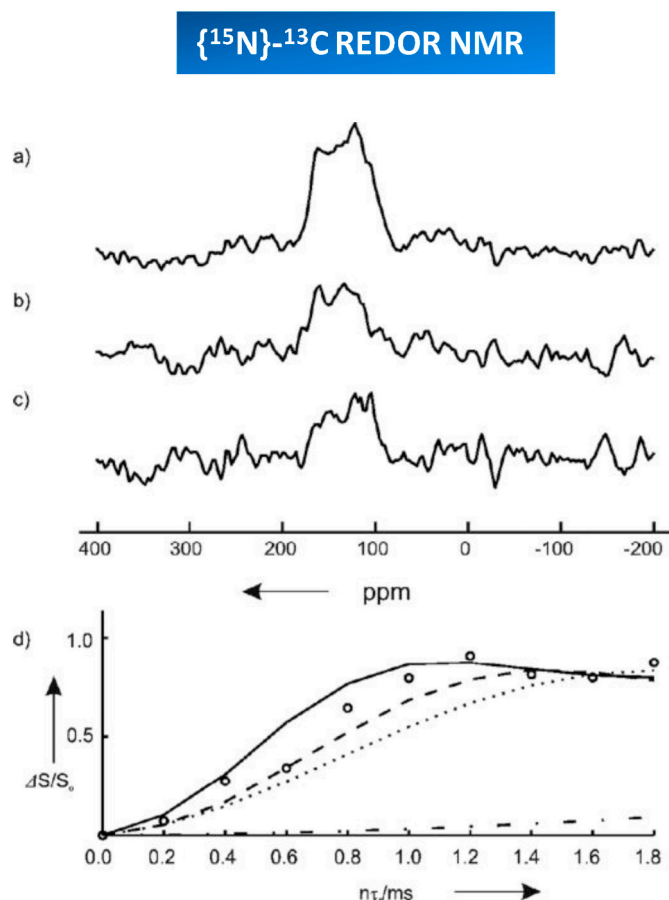


Fig. 7. Experimental and simulated $^{13}\text{C}\{^{15}\text{N}\}$ REDOR curves of an $\text{Si}_2\text{B}_2\text{N}_5\text{C}_4$ ceramic, $\omega_r/(2\pi) = 10$ kHz. $\Delta S/S_0$: normalized intensity difference, n : number of rotor cycles, τ_r : rotor period. a) ^{13}C Hahn echo MAS spectrum. b) $^{13}\text{C}\{^{15}\text{N}\}$ REDOR NMR spectrum at a dephasing time of 0.6 ms. c) difference spectrum. d) experimental REDOR curve with $\text{N}=\text{C}$ (—, 1.34 Å, $\angle = 120^\circ$), $\text{C}=\text{N}$ (····, 1.47 Å), $\text{C}-\text{X}-\text{N}$ (- - -, 2.5 Å). Reprinted with permission from Ref. [42].

incorporated into the network not only via nitrogen but also via carbon while ^{15}N MAS confirms the presence of direct carbon-, boron- and silicon-nitrogen bonds. Similarly, trichlorosilyl-amino-dichloroborane $\text{Cl}_3\text{Si}-\text{NH}-\text{BCl}_2$ was polymerized with methylamine MeNH_2 [131] or ^{13}C - ^{15}N enriched methylamine [50] and $\{^{15}\text{N}\}$ - ^{13}C REDOR experiment also shows that a large proportion of the carbon remains connected to nitrogen in the final ceramic. Moreover, some unsaturated carbon-carbon bonds are present, as confirmed in this work by ^{13}C -2D RFDR (Radio Frequency Driven Dipolar Recoupling) experiments. In addition, Jansen et al. studied by NMR SiBN_3C ceramics obtained from borazine derivatives $[(\text{SiCl}_m\text{Me}_{3-m})\text{NB}(\text{Cl}_n\text{Me}_{1-n})_3]$ ($m = 1-3$) [132,133] cross-linked with methylamine. High temperature stability and crystallisation durability already reported for Si-B-C-N systems are observed but not enhanced.

7.2. Silicon-aluminum carbonitrides

The addition of Al to silicon carbonitride can also induce remarkably low oxidation rates of the obtained materials possibly due to the formation of a protective oxide layer by incorporation of Al in the silica surface [134,135]. The modification of the microstructure induced by the presence of Al can also result in a potential improvement of the mechanical properties [136]. As for Si-B-C-N systems, two main types of

synthesis routes have been used to obtain ceramic precursor polymers: i) a polymeric approach by mixture of organosilicon and organoaluminum precursors [137]; ii) a single source precursor approach like for example reacting an alkylaluminum compound and hexamethylcyclotrisilazane [138] leading to a poly(aluminosilazane) with different Si/Al ratios: ^{27}Al and ^{29}Si MAS NMR was used to follow the polymers-to-ceramics transformations and the relative proportions of $\text{SiC}_x\text{N}_{4-x}$ and $\text{AlC}_x\text{N}_{4-x}$ units. Several Si-Al-C-N precursors were reported such as $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlNH}_2$ and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Al}(\text{NH}_2)_2$ [139]. Si-Al-C-N PDCs could also be obtained by reaction of tris(trimethylsilyl)aluminum $(\text{Me}_3\text{Si})_3\text{Al} \cdot \text{Et}_2\text{O}$ with ammonia [140] or $[\text{MeSi}(\text{H})\text{NH}]_n$ with Me_3Al or Me_2AlNH_2 [141]. An interesting example of the single source precursor approach is the synthesis of different polyaluminosilazanes from dichlorocarbosilanes (R_2SiCl_2 with $\text{R}=\text{H}$, CH_3 , $\text{CH}=\text{CH}_2$ and $\text{CH}_2-\text{CH}=\text{CH}_2$), ammonia and N,N dimethylethylaminealane ($\text{AlH}_3 \cdot \text{N}(\text{Me})_2\text{Et}$) [142]. ^{13}C CP MAS NMR shows the formation of $\text{Si}-\text{CH}(\text{CH}_3)-\text{Al}$ and $\text{Si}-\text{CH}_2-\text{CH}_2-\text{Al}$ units indicating hydroalumination reactions occur between Al-H and C=C bonds but also that vinyl and allyl groups are still partially present in the polyaluminosilazanes, indicating that is not the only reaction taking place during the polymerisation. Indeed, SiN_3C environments are observed by ^{29}Si NMR, suggesting a possible dehydrocoupling reaction between SiH units and NCH_x groups present in the alane. Hydroalumination is confirmed by ^{27}Al MAS NMR exhibiting AlN_2C_2 signals while the presence of Al-N bonds in AlN_4 , AlN_4C , AlN_3C or AlN_3H environments confirms dehydrocoupling reactions between NH of the silazane and the alane. Pyrolysis up to 1000 °C leads to an Si-Al-C-N amorphous system based on $\text{SiC}_x\text{N}_{4-x}$ ($0 \leq x \leq 4$), $\text{AlN}_4/\text{AlN}_4\text{C}$ units and free carbon according to NMR.

An Si-Al-C-N precursor was also prepared via a mixed approach namely by reaction between $[\text{Me}(\text{H})\text{SiNH}]_4$ and a poly(allyl iminoalane-co-ethyl iminoalane) $[\text{HAlN}(\text{allyl})]_m[\text{HAlN}(\text{ethyl})]_n$. [143]. ^1H and ^{13}C NMR shows that partial hydrosilylation occurs between Si-H groups and C=C bonds of the aluminum precursor while ^{27}Al NMR shows AlN_4 environment around 200 °C, suggesting dehydrocoupling reactions between between NH and AlH groups. Moreover dehydrocoupling reactions between the SiH and NH groups occur above 400 °C leading to SiC_2N_2 , SiHCN_2 and SiCN_3 environments as observed by ^{29}Si NMR.

Finally, different PDCs in the SiAlCN system were also obtained by reactions of polymeric silicon precursors on alanes (typically $\text{AlH}_3 \cdot \text{NMe}_3$ or $\text{AlH}_3 \cdot \text{NEtMe}_2$). For instance, Müller et al. [144] prepared polyaluminosilazanes by hydroalumination with trimethylamine alane ($\text{AlH}_3 \cdot \text{NMe}_3$) of vinyl containing polysilazanes and polysilylcarbodiimides. As mentioned previously, NMR shows that hydroalumination is not the only reaction occurring and that dehydrocoupling with formation of Al-N units is favored contrary to what is observed for the reaction of poly(vinylsilazane) with trialkylamine boranes, $\text{BH}_3 \cdot \text{NR}_3$ for which a selective hydroboration of the vinyl units occurs as previously mentioned [128]. Upon heating, dehydrocoupling reactions involving Si-H and H-N groups are observed and at 1000 °C, a complete transformation into an amorphous ceramic is observed and characterised by the presence of an Si-C-N matrix according to ^{29}Si NMR (with a distribution of $\text{SiC}_x\text{N}_{4-x}$ units), amorphous (graphite-like) carbon probed by ^{13}C NMR, and AlN_x environments with Al in different co-ordinations ($x = 4, 5, 6$) according to ^{27}Al NMR. The same structural Si-C-N/C-Al-N components are present in the polysilazanes and polysilylcarbodiimides-based systems but with significantly different compositions: for instance, the proportion of SiN_4 units compared to $\text{SiC}_x\text{N}_{4-x}$ ($1 \leq x \leq 4$) is higher for polysilylcarbodiimides according to ^{29}Si NMR in accordance with the higher nitrogen content in the initial polymer structure. In the same line, a commercial poly(vinylmethyl-co-methyl)silazane (HTT 1800) was reacted with various amounts of N,N -dimethylethylamine alane ($\text{AlH}_3 \cdot \text{NEtMe}_2$) [43] and as precedently, hydroalumination of vinyl groups by the alane appears to be minor according to ^{13}C (showing a large amount of unreacted vinyl groups) and ^{27}Al NMR (indicating a majority of Al-N rather than Al-C bonds): cross-linking occurs predominantly through dehydrocoupling

reactions between NH of the silazane and AlH of the alane. It should be noticed that a relatively precise assignment of the complex ^{27}Al NMR spectra of the polymer could be obtained thanks to a combination of relatively high-field 2D ^{27}Al MQ MAS NMR spectra and calculation of NMR parameters in structural models based on the different types of aluminum environments that could be expected (Fig. 8).

This study indicates that above a certain Al: Si molar ratio, the alane hydride does not react completely with the polysilazane leading to the formation of additional organic side groups such as Al-NR_3 ($\text{R}=\text{CH}_3$ and C_2H_5), possibly acting as plasticizers particularly appropriate for processing at low temperature. Furthermore, aluminium plays a major role in modifying the mechanisms of the polysilazane-to-ceramic transformation, especially in the low temperature regime of the thermal decomposition by prohibiting the distillation of small polymer fragments which leads to an increase of the ceramic yields compared to the neat polysilazanes.

The same synthesis pathway was used in another contribution [145] but with a different pyrolysis atmosphere (NH_3 instead of N_2) with the objective to get novel hydrogen chemisorption properties. According to ^{27}Al MAS NMR experiments on the pre-treated samples, a reversible H_2 chemisorption and desorption is obtained: this is suggested by the relative intensities of the distorted tetrahedral $\text{AlN}_{4-x}\text{L}_x$ ($\text{L} = \text{N}, \text{O}$ and H , $x = 1-3$), and five-fold coordinated $\text{AlN}_{5-x}\text{L}_x$ ($x = 1-4$).

In addition to polysilazanes, a perhydropolysilazane (PHPS) was reacted to a cage-type poly(ethyliminoalane) $(\text{Et}_2\text{AlNH}_2)_n$ with n mainly equal to 8 [146]. The solid-state NMR spectra and XRD pattern indicate that the residue pyrolyzed at 1600°C contains mainly crystalline AlN , 2H-SiC and $\beta\text{-SiC}$ while amorphous Si_3N_4 is observed at 1000°C [147]. Similarly, PHPS was reacted with trimethylamine alane ($\text{AlH}_3\cdot\text{NMe}_3$) which acts as a cross-link reagent via dehydrocoupling reactions leading to AlN_4 and AlN_5 environments identified by ^{27}Al MAS NMR while $\alpha\text{-Si}_3\text{N}_4$ and 2H-SiC seem to crystallize at 1500°C [148].

It can be noticed that Si-B-Al-C-N systems can also be obtained by the PDC route [149] still with the aim of improving the oxydation resistance of the final system whose structure can be investigated by NMR [150] just as previously reported Si-B-C-N and Si-Al-C-N systems.

7.3. Silicon-titanium/zirconium carbonitrides

Similarly to boron and aluminum, introduction of titanium in a Ti/Si atomic ratio of 0.1 using the PDC route was shown to stabilise amorphous Si-Ti-(C)-N ceramics up to 1873 K [151]. Perhydropolysilazane $[\text{SiH}_2\text{-NH}]_n$ (PHPS) was modified by tetrakisdimethylaminotitanium $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$ (TDMATi) and ^{29}Si MAS NMR indicates the presence of SiH_3N , SiH_2N_2 and SiHN_3 units suggesting dehydrogenation reactions between the N-H and Si-H groups which are apparently accelerated by the very small amounts of $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$ (Ti/Si ratios ranging from 0.001 to 0.1 were studied) [152]. This is possibly due to the formation of highly cross-linked polymer network by N-Ti-N bridges, which makes the configurations of Si-H and N-H groups more favorable for their dehydrogenation reactions. This could lead to enhance the lower temperature formation of SiN_4 tetrahedral units necessary for the crystallisation of $\alpha\text{-Si}_3\text{N}_4$ and higher Ti/Si ratios for doping appear more interesting to delay this crystallisation.

The same synthesis was used but with much higher amount of $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$ (Si: Ti ratio of 2.5) for a completely different objective in terms of final ceramic properties [153]. Indeed, Veprek et al. have shown that silicon-titanium-nitrogen coatings exhibit ultrahardness and high resistance to brittle fracture [154,155]. However, they used physical (PVD) and chemical vapor deposition (CVD) methods which are not suitable to obtain bulk nanocomposites contrary to the PDC route using for example PHPS and TDMATi. ^{13}C CP MAS NMR experiments suggest that once TDMATi has reacted with NH units of PHPS, generating $(\text{Si}_2\text{N})_x\text{-Ti}[\text{N}(\text{CH}_3)_2]_3$ groups, they can further react in the same way with new NH units, forming $(\text{Si}_2\text{N})_x\text{-Ti}[\text{N}(\text{CH}_3)_2]_{4-x}$ groups with x increasing from 2 to 4. Moreover, an additional ^{13}C signal is attributed to $-\text{NCH}_3$ bridges

between silazane units and Ti atoms, i.e., $\text{N}_2\text{Si-NCH}_3\text{-Ti}\equiv$ groups, resulting from the reaction of Si-H units and $\text{N}(\text{CH}_3)_2$ groups. This reaction was confirmed in another study comparing the PDCs obtained reacting either PHPS or a polymethylsilazane (PMSZ) with $\text{Ti}(\text{N}(\text{CH}_3)_2)_4$ [45]. Indeed 2D HETCOR CP MAS $\{^1\text{H}\}\text{-}^{13}\text{C}$ NMR experiment was used to characterise the obtained polytitanosilazanes and showed that there are two types of chemical environment that involve the NCH_3 units in the polymers: i) $\text{N}_2\text{Si}(\text{CH}_3)\text{-N}(\text{CH}_3)\text{-TiN}_3$ units that result from the reaction between SiH units and $\text{N}(\text{CH}_3)_2$ groups of TDMATi with methane elimination and ii) $\text{Si}_2\text{NTi}[\text{NCH}_3]_3$ units that result from the reaction between NH units from PHPS or PMSZ and $\text{N}(\text{CH}_3)_2$ groups of TDMATi with dimethylamine elimination. Moreover, ^{15}N CP MAS experiments allow to identify NCH_3 signal which appear to be more intense in PHPS than in PMSZ for a given amount of Ti precursor, suggesting a higher reactivity of PHPS with TDMATi. The as-obtained polymers were compacted by using warm-pressing and pyrolyzed at 1000°C under ammonia: a comprehensive mechanistic study of the polytitanosilazane-to-nanocomposite transformation could then be proposed based on solid-state NMR data coupled with TG experiments.

In line with this study, TDMATi was also used to modify a commercially available poly(vinylmethyl-co-methyl)silazane (Durazane 1800, probably very similar to the previously mentioned HTT1800) [156]. The combination of multinuclear (^{13}C , ^{15}N and ^{29}Si) solid-state NMR data with FTIR and chemical analysis allows to identify at least three reactions occurring i) between the SiH groups of the polysilazane and methyl groups of TDMATi leading to $-\text{Si-N}(\text{CH}_3)\text{-Ti}[\text{N}(\text{CH}_3)_2]_3$ units; ii) between SiH groups of the polysilazane and methyl groups of TDMATi leading to $-\text{N-Ti}[\text{N}(\text{CH}_3)_2]_3$ units; iii) hydrosilylation between $-\text{Si-CH}=\text{CH}_2$ and $-\text{Si-H}$ units of the silazane leading to $-\text{Si-CH}_2\text{-CH}_2\text{-Si-}$ and $-\text{Si-CH}(\text{CH}_3)\text{-Si-}$ units. This produces a relatively highly crosslinked polymer containing a certain portion of side groups of the type $-\text{Ti}[\text{N}(\text{CH}_3)_2]_x$ that transforms after pyrolysis in an amorphous Si-based ceramic matrix in which TiN_xC_y nanocrystals ($x + y = 1$) are homogeneously formed *in situ* in the matrix during the process and evolve toward fully crystallized compounds as $\text{TiN/Si}_3\text{N}_4$, TiN_xC_y ($x + y = 1$)/SiC and TiC/SiC nanocomposites after annealing to 1800°C depending on the atmosphere.

In a similar way, Zr instead of Ti was introduced by reacting tetrakis(diethylamino)zirconium $\text{Zr}[\text{N}(\text{CH}_2\text{CH}_3)_2]_4$ (TDEAZr) with polymethylsilazane (PMSZ) [157]. As observed in the case of Ti, NMR experiments combined with FTIR suggest that NH and SiH groups in polysilazanes react with $-\text{N}(\text{CH}_2\text{CH}_3)_2$ groups of TDEAZr resulting in the formation of Si-N-Zr and $-\text{Si-N}(\text{CH}_2\text{CH}_3)\text{-Zr-}$ bridges. The pyrolysis under ammonia at 1000°C leads to an amorphous ceramic which then forms highly crystalline $\text{ZrN/Si}_3\text{N}_4$ nanocomposites at 1600°C . The unique nanostructural feature of the nanocomposites made of ZrN nanocrystals distributed in α - and $\beta\text{-Si}_3\text{N}_4$ phases was investigated by HRTEM. Preliminary investigations suggest the possible tuning of the optical properties (in terms of optical band gaps) of these nanocomposites. Finally, mixed Ti/Zr systems were investigated by reacting polymethylsilazane with both TDMATi ($\text{Ti}(\text{N}(\text{CH}_3)_2)_4$) and TDEAZr ($\text{Zr}[\text{N}(\text{CH}_2\text{CH}_3)_2]_4$) [158] in a combined 1:5 at. (Ti+Zr:Si) ratio. Multinuclear (^{13}C , ^{15}N and ^{29}Si) solid-state NMR allows to identify two main types of reactions i) between $-\text{NH}$ units in PMSZ and $-\text{N}(\text{CH}_2\text{CH}_3)_2\text{-N}(\text{CH}_3)_2$ groups in TDEAZr and TDMATi via release of diethylamine/dimethylamine which lead to $-\text{N-TM-}$ ($\text{TM} = \text{Ti}, \text{Zr}$) bonds; ii) between the Si center of PMSZ and $-\text{N}(\text{CH}_2\text{CH}_3)_2\text{-N}(\text{CH}_3)_2$ groups in TDEAZr and TDMATi with evolution of ethane/methane to form $-\text{Si-N}(\text{CH}_2\text{CH}_3)\text{-Zr-}$ and/or $-\text{Si-N}(\text{CH}_3)\text{-Ti-}$ bridges. After a pyrolysis step under ammonia (at 1000°C) and a heat-treatment in flowing nitrogen ($1000\text{--}1700^\circ\text{C}$), TiZrN_2 nanocrystals distributed in α - and $\beta\text{-Si}_3\text{N}_4$ phases are observed. This unique nanostructure is expected to provide noble metal-free catalysts applications or components with high plasmonic quality.

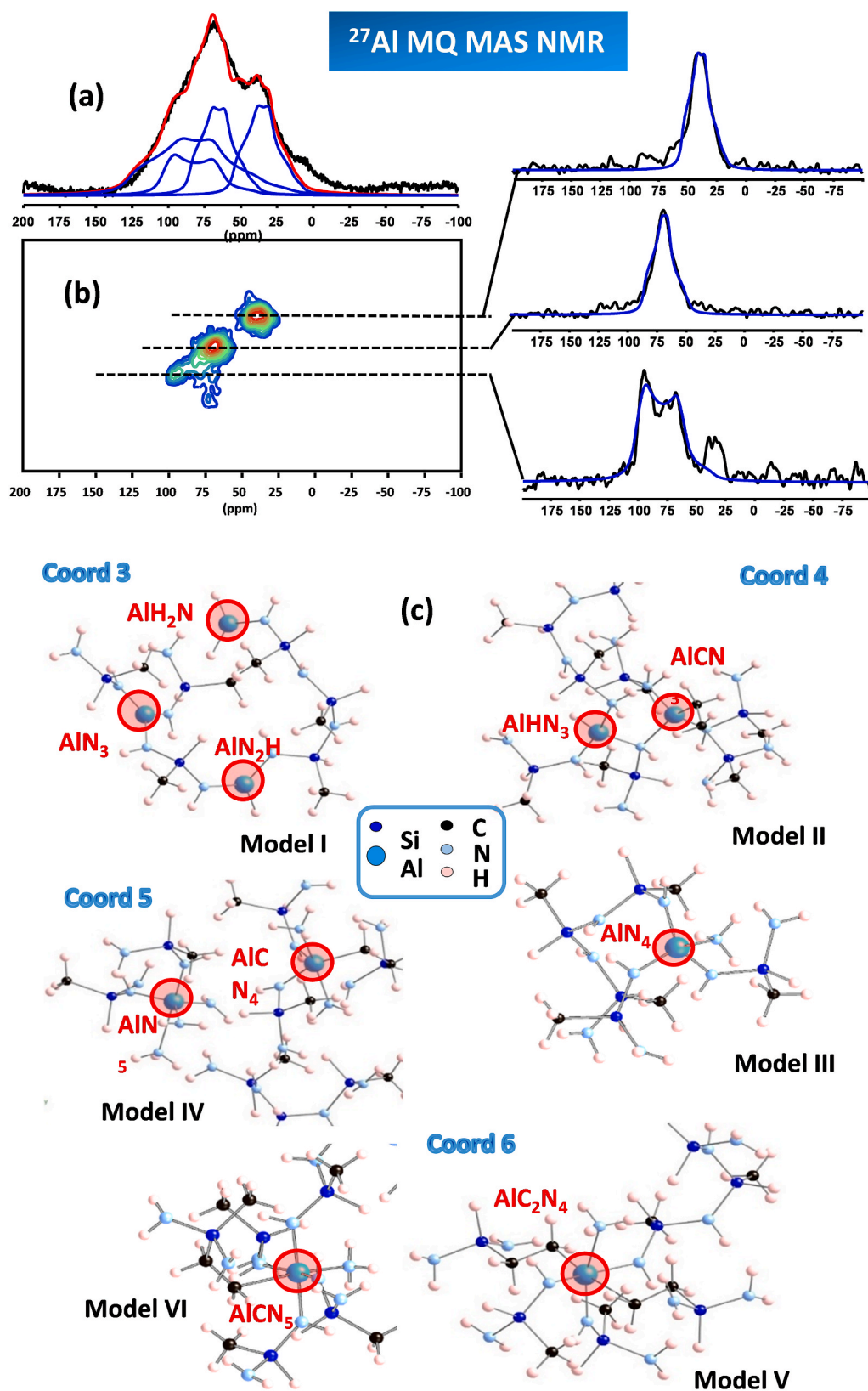


Fig. 8. Experimental and simulated (a) ^{27}Al MAS and (b) ^{27}Al MQ MAS NMR spectra recorded for an aluminum-modified poly(vinylmethyl-co-methyl)silazane. c) Optimized geometries of simple models presenting representative aluminum environments used for the calculation of the corresponding ^{27}Al NMR parameters. Reprinted with permission from Ref. [43].

8. Conclusions

This overview demonstrates how multinuclear solid-state NMR applied to the description of precursors and ceramics intermediates can be extremely useful for a better understanding of these complex materials and highlight their structure that can then be related to their properties. It should be noticed that this contribution is focused on the structural characterisation of these systems but NMR appears to be also useful in a specific application context. In the recent years, Si-(B)-C-O and Si-(B)-C-N based PDCs have been tested as anode materials for rechargeable lithium-ion batteries. NMR can be useful to characterise the matrix probing ^{13}C , ^{29}Si or ^{11}B as previously described [159–162], but also to probe lithium dynamics using ^7Li NMR. Recording ^7Li spectra according to temperature allows indeed to estimate the relaxation characteristic times and activation energies associated with the diffusive motion of Li ions [163,164]. Moreover, analysis of ^7Li signals can also give informations on the presence of electrochemically active sites for lithium storage in the PDC-based matrix [165]. Similarly, polymer-derived silicon carbonitride ceramic has been used as an anode material in Na/Na⁺ cell, and *ex-situ* ^{23}Na NMR appears extremely relevant to identify the interactions between sodium and the matrix during the sodiation/desodiation process [166].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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