Pyrolysis chemistry of polysilazane precursors to silicon carbonitride
Part 2.[†]—Solid-state NMR of the pyrolytic residues

Corine Gérardin,[*a‡] **Francis Taulelle**[a‡] **and Djamila Bahloul**[b]

[a]*Laboratoire de Chimie de la Matière Condensée, Université P. et M. Curie, 75252 Paris, France*
[b]*Laboratoire de Matériaux Céramiques et Traitements de Surface, URA CNRS 320, Faculté des Sciences, 87060 Limoges, France*

The chemistry of pyrolytic conversion has been studied for three polysilazanes, $(\mathrm{ViSiHNH})_n$, $(\mathrm{ViSiHNMe})_n$ and $[(\mathrm{ViSiHNH})_{0.5}\text{–}(\mathrm{MeSiHNH})_{0.5}]_n$, precursors to silicon carbonitride ceramics. ^{13}C and ^{29}Si MAS and CPMAS NMR spectroscopies were used to clarify the processes leading to the formation of the silicon-based mineral network as well as the segregation of a free carbon phase. The assignment of ^{29}Si NMR signals corresponding to $\mathrm{SiC}_n\mathrm{N}_{4-n}$ sites was essential to follow the number of Si—C and Si—N bonds that are cleaved or formed. It was shown that at the organic–mineral transition temperature (*ca.* 900 °C) the final amount of free carbon as well as the final composition of the silicon-based network were already reached. Above this temperature, redistribution reactions around silicon atoms inside the amorphous silicon-based matrix take place in order to favour nitrogen-rich environments, *i.e.* crystallized $\mathrm{Si_3N_4}$ regions. Above 1400 °C, all ceramics contain a similar amorphous silicon carbonitride structure, whose composition is close to $\mathrm{SiN_{0.85}C_{0.35}}$ and which coexists with a crystallizing $\mathrm{Si_3N_4}$ phase. Finally, the relative amounts of the three possible final carbon states, at 1400 °C, *i.e.* gas products, carbon incorporated in the silicon-based network and free carbon, could be related to the nature of the carbon-containing substituents in the precursor backbones and to the occurrence of the cross-linking reactions below the mineral transition temperature.

Polysilazane polymers whose backbones consist of alternating Si—N bonds with carbon-containing substituent groups are widely used as precursors of silicon carbonitride ceramics.[1–8] The conversion chemistry of these polymeric precursors is still not completely understood. The derived ceramics obtained at 1400 °C are often formed with three phases: a silicon carbide or nitride phase, an amorphous silicon carbonitride structure and a free carbon phase. The thermomechanical properties of the ceramics depend largely on the proportions of these phases and a goal is to be able to predict the amount and the nature of the different combined structures knowing the backbone structure of the precursor. To achieve this objective, one must elucidate the various chemical transformations of the preceramic polymer in the course of pyrolysis. The difficulties arise from the characteristics of the intermediate solid residues which cannot be completely characterized by conventional solid-state analysis methods such as X-ray diffraction techniques. The lack of long-range order in the ceramics obtained below 1400 °C severely limits the investigation by XRD. The most common investigation techniques used to characterize the pyrolytic conversion are thermogravimetry (TG), mass spectrometry (MS), IR spectroscopy and chemical analyses.[4–12] These techniques give insights into the global changes in the materials; they answer the questions: what are the gas-phase products? When are the gaseous products released and in what amounts? But very little information is generally obtained on the chemical bondings present in the solid inorganic intermediates and in the final amorphous ceramics.

Few studies centred on the NMR characterizations of the solid-phase intermediates have been reported.[13–20] Solid-state NMR studies of the pyrolytic residues provide a description of local arrangements around atoms. ^{13}C NMR spectroscopy is very useful for examining the evolutions of C sp^3 and C sp^2 environments. It can indicate when carbon atoms leave the silicon-based network and segregate as a free carbon phase. ^{29}Si NMR spectroscopy can lead to quantitative studies of local Si sites. The fractions of $\mathrm{SiC}_n\mathrm{N}_{4-n}$ environments in the pyrolytic residues can be obtained and those values can be used to estimate a chemical composition of the mineral silicon-based network.

The purpose of this paper is to show how NMR characterizations of the solid residues associated with data obtained previously from chemical analyses, IR spectroscopy, TG, MS analysis and XRD[21] can provide a better description of the major chemical transformations involved in the pyrolytic conversion. It will show how local structural details can give an insight into the chemical bonding and also into the chemical compositions of the structures present in the multiphased materials at all intermediate temperatures. Special emphasis will be given to the influence of the nature of the precursor on the final ceramic structure. The polymer to ceramic conversion chemistry was thus studied for three precursors containing various silazane units, with the same N/Si ratio but different C/Si ratios: $(\mathrm{ViSiHNH})_n$ (VS), $(\mathrm{ViSiHNMe})_n$ (VNMS) and $[(\mathrm{ViSiHNH})_{0.5}\text{–}(\mathrm{MeSiHNH})_{0.5}]_n$ (VS/MS).

Experimental

The synthesis and curing step of the starting oligosilazanes have been reported elsewhere.[8,10,21,22] The three main functionalities present in the polymers are the N—H, Si—H, and Vi (vinyl) groups which can give rise to the typical thermal cross-linking reactions: transamination, hydrosilylation, dehydrogenation and vinyl polyaddition. These reactions were detailed in other papers.[8,21] Note that the VS polymer contains the three reactive functions per silazane unit; in VNMS, the non-reactive NMe group replaces the NH function, and in VS/MS, half of the Vi functions are replaced by Me groups.

The precursors were heated under a nitrogen flow at a pyrolysis temperature in the range 250 to 1450 °C and were kept at that temperature for 1 h.[21] The pyrolysis products were analysed by various techniques such as IR, XRD and chemical analyses and the results were detailed in the preceding paper (Part 1).[21] The atomic ratios C/Si and N/Si of the pyrolytic

---

[†] Part 1, preceding paper.
[‡] Present address: Laboratoire de RMN et Chimie du Solide, UMR CNRS 50, Université Louis Pasteur, Strasbourg, 67000 France.

residues at 1400 °C, which were obtained by chemical analyses, are indicated in Table 1.

The NMR spectra were recorded on a Bruker MSL 400 spectrometer, operating at 100.62 MHz and 79.5 MHz, for ^{13}C and ^{29}Si nuclei respectively. Magic angle spinning (MAS) NMR spectra were acquired at a rotation frequency of 4 kHz. The ^{29}Si one-pulse experiments required a recycle delay varying from 20 to 60 s with a 25° pulse angle. Some spectra were recorded with a recycle delay of up to 1 h and showed no difference in relative intensities from those of spectra acquired with a recyle delay of 1 min. The ^{29}Si MAS NMR spectra could be quantitatively analysed, they were deconvoluted using the Winfit Bruker software program. Lorentz–Gaussian peaks were used to fit the experimental spectra; the three parameters, position, linewidth and amplitude, could be varied or fixed. The ^{13}C MAS NMR spectra were acquired with a recycle delay of 60 s and a pulse angle of 20°. The ^{13}C repetition times were not optimized in order to gain quantitative ^{13}C MAS NMR spectra. A contact time of 1.5 ms and a repetition time of 10 s were used for both ^{13}C and ^{29}Si cross-polarization (CP) MAS NMR spectra. In ^{29}Si and ^{13}C NMR, the compound used as chemical shift reference was tetramethylsilane. For all spectra, between 600 and 1000 scans were accumulated.

Results

^{13}C NMR spectroscopy

The chemical shifts of the signals present in the ^{13}C NMR spectra lie between δ 0 and 200. Signals from δ 0 to 50 are due to carbon atoms in sp^3 configuration, and signals from δ 100 to 200 to carbon atoms in sp^2 configuration. More precisely, between δ 0 and 25–30 appear signals from $Si{-}C(sp^3)$ sites; at δ *ca.* 30 signals from $N{-}C(sp^3)$ sites; and at δ 135 signals from $C{=}C$ sites in vinyl groups. The very broad signal centred at δ 110 observed in ^{13}C MAS NMR spectra without cross-polarization (indicated with an asterisk on the figures), is due to carbon atoms present in the probe, and so it does not represent the sample.

VS/MS. Fig. 1A and B show the ^{13}C MAS and CPMAS NMR spectra of VS/MS pyrolysates. The spectra of the precursor show the presence of vinyl groups (signal at δ 135) and of $Si{-}CH_3$ groups (at δ *ca.* 0). The ^{13}C CPMAS spectrum enhances the resonances between δ 10 and 30 characteristic of $Si{-}CH_n$ ($n = 1$ and/or 2) sites; the $^1H \rightarrow ^{13}C$ polarization transfer is indeed more efficient in these groups compared to the case of mobile methyl groups. These sites are the result of the transformation of vinyl groups by polyaddition or hydrosilylation leading to $Si{-}C{-}C{-}Si$ or $Si{-}C{-}Si$ bridging groups. The transformation of vinyl groups is shown to take place mainly below 250 °C and it continues up to 500 °C; at this temperature, all vinyl sites have disappeared. Between 250 and 500 °C, a major rearrangement in the C sp^3 environments is observed, the carbon sites newly formed from vinyl groups (signal centred at δ 30) change considerably. The loss of resolution of the peak representing the methyl function (δ *ca.* 0) may be the result of two different phenomena: first, a decrease of the peak may come from the loss of the methyl group through the evolution of methane; secondly, the loss of resolution may reflect the thermal cross-linking leading to progressively less protonated C sites such as CH_2Si_2 bridges or $CHSi_3$ environments as the temperature increases. In the latter case, carbon insertion into the silicon-based network can occur. The ^{13}C NMR resonances corresponding to C sp^3 sites are still observed up to 650 °C under CPMAS conditions and up to 500 °C under MAS conditions. At temperatures higher than 850 °C, the number of protons close to carbon atoms is too low to obtain a sufficient proton magnetization transfer towards ^{13}C nuclei and cross-polarization is inefficient. The signal-to-noise ratio of ^{13}C CPMAS NMR spectra at 650 and 850 °C is rather low, but no significant signal corresponding to a still-protonated graphitic-type carbon structure can be detected in these samples.

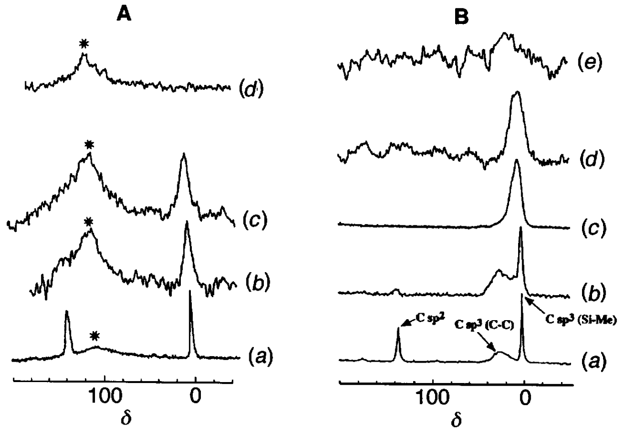

Fig. 1 NMR spectra of the VS/MS residues at different pyrolysis temperatures. **A**, ^{13}C MAS (without cross polarization): (*a*) precursor, (*b*) 250 °C, (*c*) 500 °C, (*d*) 650 °C; **B**, ^{13}C CP MAS (with cross polarization): (*a*) precursor, (*b*) 250 °C, (*c*) 500 °C, (*d*) 650 °C, (*e*) 850 °C.

Table 1 N/Si and C/Si atomic ratios in the precursors (theoretical) and in the ceramics at 1400 °C (determined by chemical analyses)

	starting silazane (theoretical)		global material at 1400 °C chemical analyses)	
sample	N/Si	C/Si	N/Si	C/Si
VNMS	1	3	1.19	1.75
VS	1	2	0.98	1.59
VS/MS	1	1.5	0.86	1.08

VS. The ^{13}C, ^{29}Si, ^1H, ^{15}N and ^{14}N NMR spectra of the VS precursor in solution in C_6D_6 have been detailed elsewhere.[13] It was shown that 15% of the vinyl groups already transformed into C sp^3 sites during the curing step. Fig. 2A shows the ^{13}C CPMAS NMR spectra of VS residues pyrolysed from 500 to 900 °C. At 500 °C, no signal from vinyl groups can be observed but a broad signal at δ 9 is present, it is due to the C sp^3 sites formed from the transformation of vinyl sites. This resonance does not change much up to 600 °C. Broad and weak signals appear at low field; they are characteristic of protonated $C{=}C$ bonds and are certainly due to polyaromatic compounds which are precursors of a free carbon phase. The occurrence of such carbonaceous units was discussed in a previous paper.[21] Vinyl polymerization can lead to ring-type hydrocarbon species; then, $Si{-}C$ cleavage can give rise to six-membered rings containing C sp^2 atoms. At 900 °C, it can be seen that C sp^3 sites are present in a minor amount compared to the abundant C sp^2 atoms. The very broad signal centred at δ 120 is due to still protonated C atoms such as $C{-}CH{=}C$.

VNMS. Fig. 3A and B show the ^{13}C MAS and CPMAS NMR spectra of VNMS pyrolysates. The weak signal at δ 135 in the ^{13}C CPMAS NMR spectrum shows that most vinyl elements were consumed at 250 °C, they transformed into aliphatic carbon sites whose signal appears at δ *ca.* 10. A large number of carbon atoms in $N{-}Me$ groups (at δ 30) are still present at this temperature, but most are transformed between 250 and 500 °C; the consumption of $N{-}Me$ bonds still continues up to 650 °C. At 650 °C, a broad signal centred at δ 130 appears. It presents a large chemical shift anisotropy; several spinning sidebands separated by the spinning speed frequency

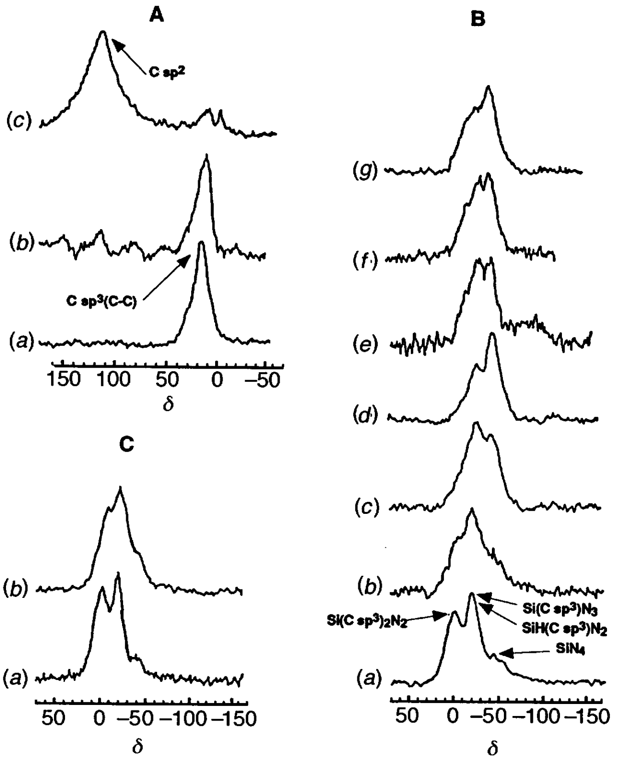

Fig. 2 NMR spectra of the VS residues at different pyrolysis temperatures. **A**, ^{13}C CP MAS: (*a*) 500 °C, (*b*) 600 °C, (*c*) 900 °C; **B**, ^{29}Si MAS: (*a*) 500 °C, (*b*) 600 °C, (*c*) 900 °C, (*d*) 1200 °C, (*e*) 1300 °C, (*f*) 1400 °C, (*g*) 1450 °C; **C**, ^{29}Si CP MAS: (*a*) 500 °C, (*b*) 600 °C.

are observed. These resonances do not appear in spectra without cross-polarization and are due to protonated C sp^2 atoms. This observation shows the presence of abundant C atoms in an aromatic carbon structure. These structures may be formed by breaking of Si—C bonds, as explained earlier. From 650 to 850 °C, the signals due to C sp^3 sites disappear and the resonances due to C sp^2 sites become weaker; the main reason for this is the progressive deprotonation of all carbon atoms leading to a less efficient $\{^1H\}$-^{13}C cross-polarization. By 850 °C, a complete loss of sp^3 carbon occurs in the ^{13}C CPMAS NMR spectrum of VNMS, in contrast to the case of VS pyrolytic residues for which a C sp^3 signal is still observed at 900 °C.

^{29}Si NMR spectroscopy

^{29}Si NMR spectra were registered under MAS conditions with and without cross-polarization. The comparison between both types of acquisitions was helpful for the assignment of peaks; it was essentially used to indicate strong ^1H–^{29}Si dipolar couplings which arise from direct Si—H bonds. ^{29}Si CPMAS NMR spectra were not acquired for samples pyrolysed above 800 or 900 °C because the hydrogen contents were too low at these temperatures.

In the spectra analysis, only $SiH_xC_yN_z$ sites will be considered. The oxygen amount in the materials is indeed small. As was shown in Part 1, the chemical analyses indicated less than 5 atom% of oxygen. As was also discussed in Part 1, the oxygen contamination occurs during handling and the oxygen atoms are then present in the amorphous Si—C—N(O) structure. The low oxygen content leads to a distribution of different $SiC_xN_yO_z$ sites (with $z=1$ or 2) which exist in too small an amount to be identified in the NMR spectra as peaks distinguishable from the main SiC_nN_{4-n} ones. As a consequence, the oxygenated sites cannot be taken into account in our spectral analysis and it would be too hazardous to discuss the oxygen evolution from the NMR results.

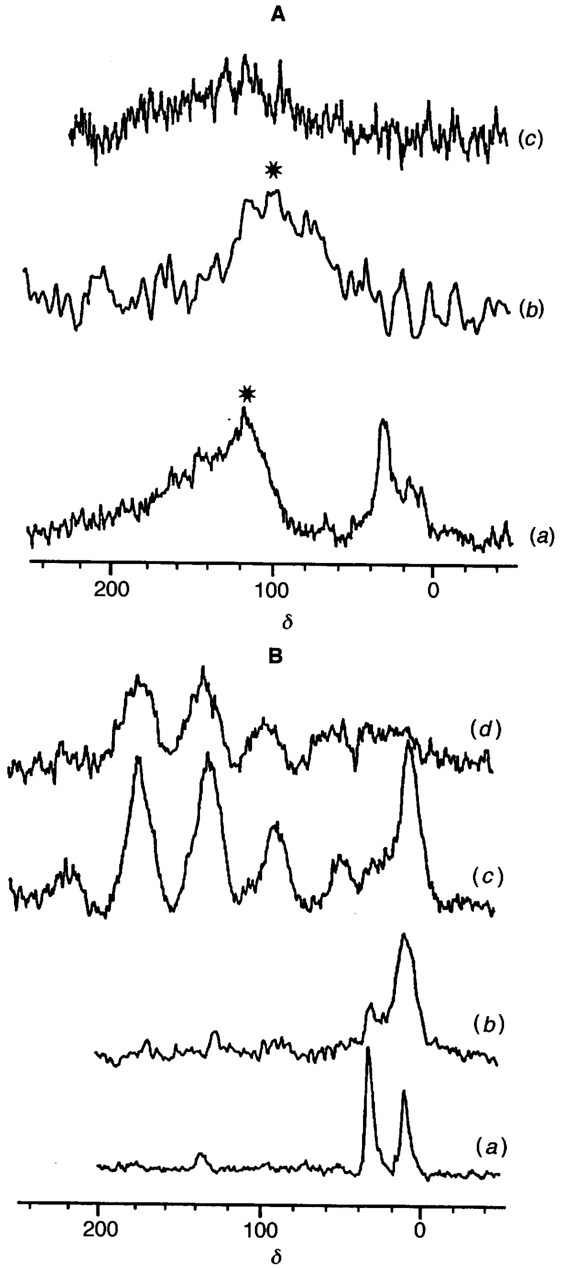

Fig. 3 NMR spectra of the VNMS residues at different pyrolysis temperatures. **A**, ^{13}C MAS (without cross polarization): (*a*) 250 °C, (*b*) 500 °C, (*c*) 650 °C; **B**, ^{13}C CP MAS (with cross polarization): (*a*) 250 °C, (*b*) 500 °C, (*c*) 650 °C, (*d*) 850 °C.

The method to determine ^{29}Si NMR chemical shifts corresponding to SiC_nN_{4-n} first coordination spheres was already developed elsewhere,[23,24] it will not be detailed here. The chemical shifts of SiC_nN_{4-n} sites were calculated using the partial charge model[24] and the classical theory of nuclear shielding. It was shown that replacing a carbon atom by a nitrogen atom in the Si environment does not lead to a regular chemical shift variation. The shape of the curve of $\delta(^{29}Si)$ (SiC_nN_{4-n}) *vs.* n is mainly governed by the nature of the first coordination sphere. The nature of the second coordination sphere mainly shifts that curve to lower or higher field depending on the substituents on the C and N atoms. This is clearly observed in Fig. 4 which represents the chemical shifts of two series: the first one considers $SiMe_n(NMe_2)_{4-n}$ molecules and the second one presents SiC_nN_{4-n} environments with C atoms being CSi_4 sites (as in SiC) and N atoms NSi_3 sites (as in Si_3N_4). In a non-protonated silicon carbonitride structure with only Si, C (as CSi_4 sites) and N (as NSi_3) atoms (which is expected at high pyrolysis temperatures such as 1400 °C),

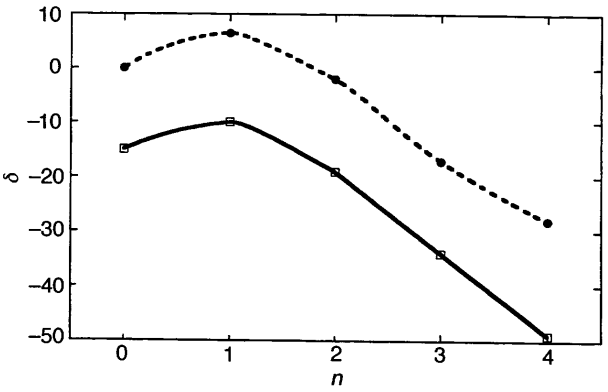

Fig. 4 ^{29}Si NMR chemical shifts corresponding to SiC_nN_{4-n} sites as a function of n for two series: $SiMe_n(NMe_2)_{4-n}$ molecules (●) and SiC_nN_{4-n} sites hacing CSi_4 and NSi_3 environments (☐)

the chemical shifts of SiC_nN_{4-n} sites were calculated to be: δ −15 (n=4), −10 (n=3), −19 (n=2), −34 (n=1) and −49 (n=0) with a precision of ±2 ppm. The exact positions of the peaks corresponding to these environments are then experimentally adjusted while fitting the spectra. As will be seen later, the main Si environments present in the samples studied here, from 500 to 1400 °C, are SiC_2N_2, $SiCN_3$ and SiN_4. Fitting the spectra using these three components leads to the exact positions of the individual signals as the temperature increases. It is shown that SiC_nN_{4-n} chemical shifts decrease when the temperature increases and this corresponds to the change in the Si second coordination sphere, *i.e.* the decrease in the number of protons. At temperatures higher than 500 °C, a very small amount of N atoms exist as $NHSi_2$ sites, most of them were already transformed into NSi_3 environments. The protonation state of nitrogen atoms changes only slightly from 500 to 1400 °C, which is why the chemical shift corresponding to SiN_4 sites does not change much with temperature (Fig. 5). In contrast, C atoms are still highly protonated at 500 °C. As T increases, carbon deprotonation occurs. In our samples, it is clear that SiC_nN_{4-n} ^{29}Si chemical shifts increase with a T increase in proportion with n, the number of C atoms in the Si sphere (Fig. 5).

VS/MS. Figs. 6 and 7 show the ^{29}Si CPMAS and MAS NMR spectra of VS/MS pyrolysates. The assignment of the main signals present in the CPMAS spectra is given in Fig. 6. Numerous environments are present in the precursor: $SiH_2(C\ sp^2)N$ sites are due to ends of chains, the other Si environments can be explained as shown in Fig. 8. The Si sites indicated with an asterisk represent the initial sites present in the non-cross-linked oligomers. All the sites formed by hydrosilylation and/or Vi polyaddition give the NMR signals shown in Fig. 6. It is emphasized that both types of cross-linking reactions can lead to the same types of Si first coordination spheres, and so it is not easy to distinguish here which cross-linking reaction is predominant. The comparison between ^{29}Si CPMAS and ^{29}Si MAS NMR spectra shows whether Si first coordination spheres are protonated. It appears that $SiH(C\ sp^2)N_2$ and $SiH(C\ sp^3)N_2$ environments are still present at 250 °C, with resonances at δ *ca.* −35 and −20 respectively. $Si(C\ sp^3)N_3$ sites may be present at 500 °C and appear in the same chemical shift range as $SiH(C\ sp^3)N_2$ sites. SiN_4 environments appear at 500 °C, at δ *ca.* −45. With increasing temperature to 850 °C, $Si(C\ sp^3)N_3$ and $Si(C\ sp^3)_2N_2$ become the major Si first coordination spheres, while Si—H bonds are consumed. Between 850 °C and 1400 °C, the intensity of the signal due to SiN_4 sites increases but never becomes predominant.

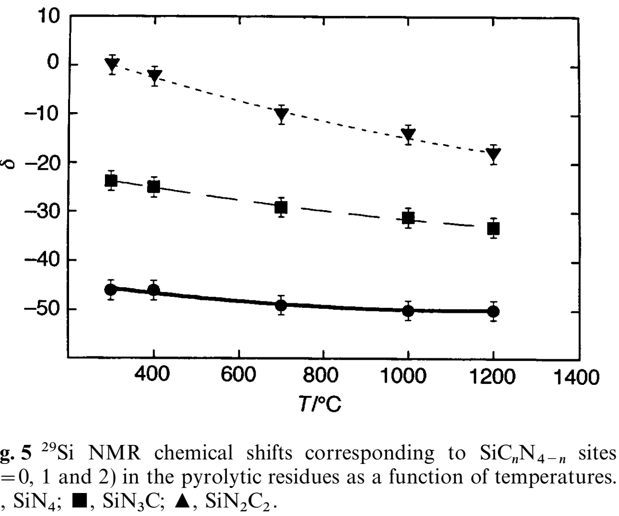

Fig. 5 ^{29}Si NMR chemical shifts corresponding to SiC_nN_{4-n} sites (n=0, 1 and 2) in the pyrolytic residues as a function of temperatures. ●, SiN_4; ■, SiN_3C; ▲, SiN_2C_2.

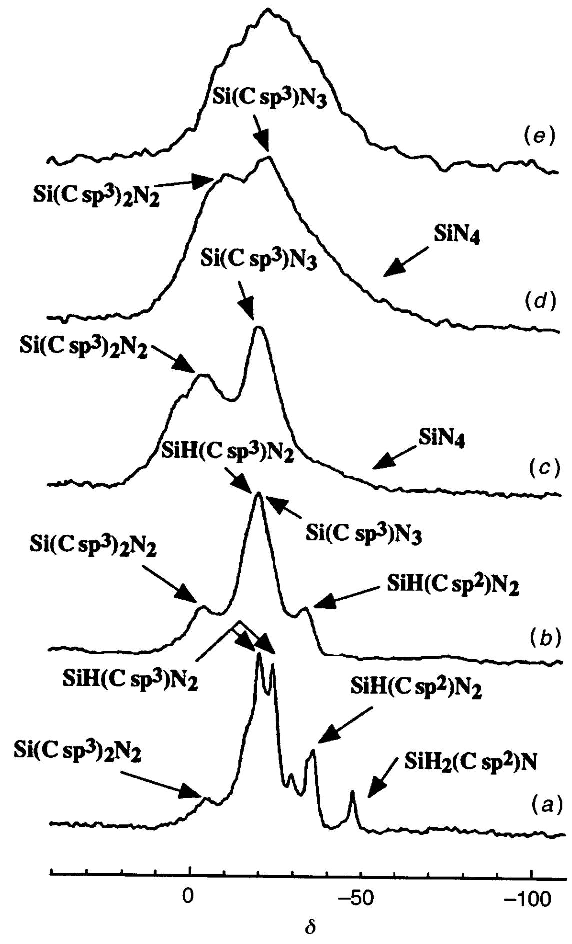

Fig. 6 ^{29}Si CP MAS (with cross polarization) NMR spectra of the VS/MS residues at different pyrolysis temperatures: (*a*) precursor, (*b*) 250 °C, (*c*) 500 °C, (*d*) 650 °C, (*e*) 850 °C

VS. The NMR study of the VS precursor in solution[13] showed the presence of $SiH(C\ sp_2)N_2$, $SiH(C\ sp_3)N_2$ and $Si(C\ sp_3)(C\ sp_2)N_2$ sites in the precursor. Let us add that the nitrogen environments present in the precursor were determined by ^{15}N and ^{14}N NMR spectroscopy; the following distribution was found: 30% NH_2Si (at δ −356.2), 46% $NHSi_2$ sites (at δ −346.8) and 24% NSi_3 (at δ −330). The chemical shifts were relative to CH_3NO_2. This result reflected the occurrence of the transamination reaction during the curing step of the starting oligosilazanes. Fig. 2B and C show the ^{29}Si MAS and CPMAS NMR spectra of VS pyrolysates. At 500 °C, the main environments are $Si(C\ sp^3)_2N_2$, $Si(C\ sp^3)N_3$ and

SiN_4, (signals at δ −2, −24 and −46 respectively); there certainly remain some protonated sites of the type $SiH(C\ sp^3)N_2$ but no $SiH(C\ sp^2)N_2$ since all vinyl groups were consumed before 500 °C. Between 600 and 900 °C, a marked consumption of $Si(C\ sp^3)_2N_2$ sites is observed while nitrogen-rich sites form. Between 500 and 1200 °C, the intensity of the signal due to SiN_4 sites increases and becomes predominant. Note that among all SiC_nN_{4-n} environments, only SiC_2N_2 sites can be explained by solely cross-linking reactions such as hydrosilylation and vinyl polyaddition. One possibility is that $SiCN_3$ environments form from $SiHCN_2$ sites by dehydrocoupling between Si—H and N—H bonds. Another explanation is that Si—C cleavage around SiC_2N_2 environments can lead to C-deficient Si sites and the formation of new Si—N bonds, thus explaining the occurrence of $SiCN_3$ sites and particularly the increase of SiN_4 environments.

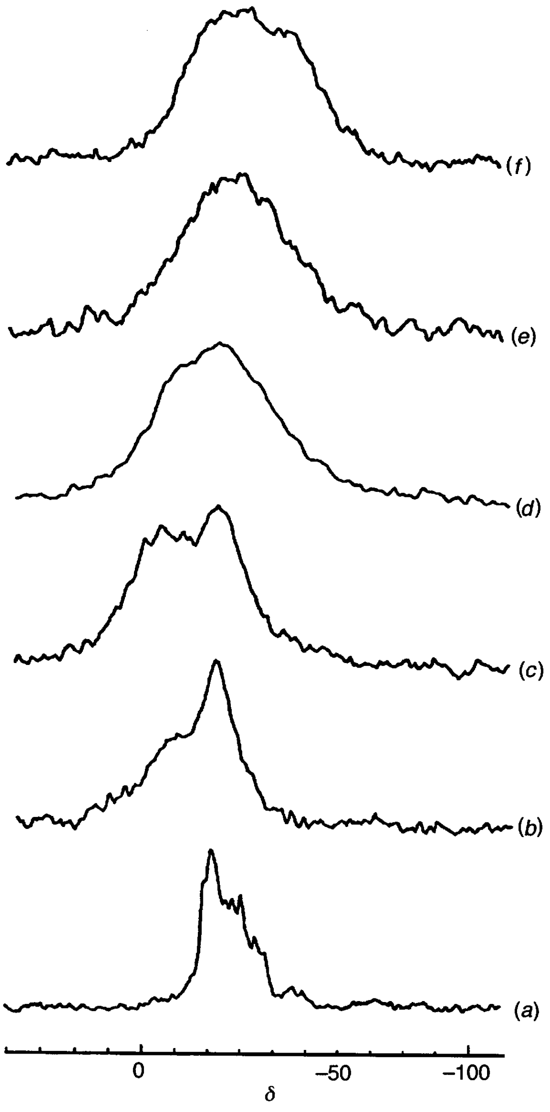

Fig. 7 ^{29}Si MAS (without cross polarization) NMR spectra of the VS/MS residues at different pyrolysis temperatures: (*a*) precursor, (*b*) 250 °C, (*c*) 500 °C, (*d*) 650 °C, (*e*) 850 °C, (*f*) 1400 °C

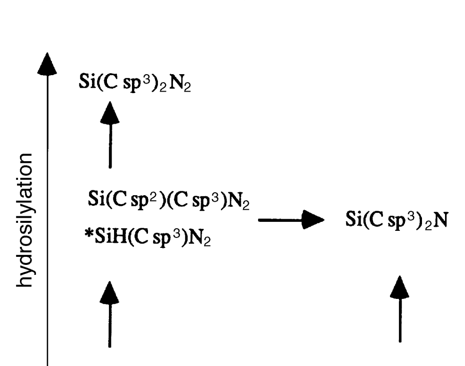

Fig. 8 Possible first coordination spheres of silicon atoms after hydrosilylation and/or vinyl polyaddition starting from the initial silicon sites (indicated with a star)

VNMS. Fig. 9A and B present the ^{29}Si MAS and CPMAS NMR spectra of VNMS pyrolysates. The main component of the spectra at 250 °C, present at δ *ca.* 0, is due to $Si(C\ sp^3)_2N_2$ sites, the component at δ *ca.* −15 to −20 corresponds to $SiH(C\ sp^3)N_2$ environments and there remain some initial sites of the type $SiH(C\ sp^2)N_2$ (δ *ca.* −30). The increase of the component at δ *ca.* −20 may correspond to the formation of $Si(C\ sp^3)N_3$ sites, which can be connected to the consumption of N—Me bonds leading to new N—Si bonds. This proposition is in agreement with ^{13}C NMR spectroscopic observations. The change is abrupt between 500 and 650 °C when a large amount of SiN_4 sites appears as a broad signal at δ *ca.* −45. This observation suggests the formation of abundant Si—N

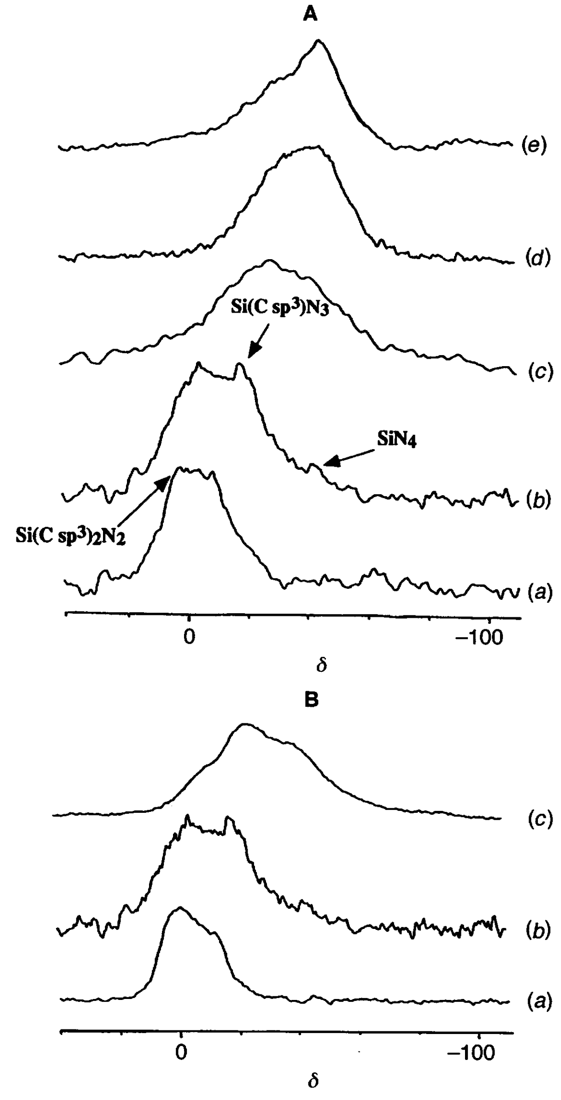

Fig. 9 NMR spectra of the VNMS residues at different pyrolysis temperatures. **A**, ^{29}Si MAS (without cross polarization): (*a*) 250 °C, (*b*) 500 °C, (*c*) 650 °C, (*d*) 850 °C, (*e*) 1400 °C, **B**, ^{29}Si CP MAS (with cross polarization): (*a*) 250 °C. (*b*) 500 °C, (*c*) 650 °C.

bonds at the expense of Si—H or, more probably Si—C bonds. The change observed in the ^{13}C NMR spectra was also very important in this temperature range. With increasing temperature, SiN_4 sites become more abundant; they are largely predominant at 1400 °C. Again, it is observed that Si—N bonds form at the expense of Si—C bonds in the silicon structure observed by ^{29}Si NMR spectroscopy.

Discussion

This discussion is divided in three parts, the first concerns the formation of the mineral network taking place below the organic–inorganic transition temperature (*ca.* 850 °C), the second one will be devoted to the evolution of the silicon-based matrix at temperatures higher than 900 °C (silicon carbonitride structure and silicon nitride phase) and the third part to the free carbon phase, its formation and its amount which is determined from the combination of quantitative NMR results and chemical analyses.

Formation of the mineral network

During the first pyrolysis step, the mineral network forms; this stage was characterized in detail by MS, TG and IR spectroscopy in the preceding paper.[21] It was shown that in the first stage, up to 400 °C, further cross-linking proceeds while a loss of low molecular mass oligomers occurs. In the second stage, from 400 to 800 °C, the mineralization step is characterized by a mass loss corresponding to the evolution of hydrocarbons and hydrogen; it is associated with the breaking of Si—H, C—H, N—H, N—C and Si—C bonds. Using ^{29}Si NMR spectroscopy, it is possible to observe the consequences of the cross-linking reactions and the gas evolution on the local transformations taking place in the solid residues. Silicon environments are very numerous below 900 °C ($SiH_pN_nC_m$ sites) and it would be hazardous to try to obtain precise values of proportions of Si sites present in the materials because of the low resolution of the resulting NMR signals. The ^{29}Si MAS NMR spectra were completely simulated but only the component present at high field (δ -45) was interpreted quantitatively. The fraction of SiN_4 sites was thus estimated from 500 to 900 °C for the three routes, it is the only signal appearing in the chemical shift range δ -45 to -50. Fig. 10 shows that at 900 °C, the fraction of SiN_4 sites reaches 54% in the VNMS route, 33% in the VS route and 23% in the VS/MS route.

In the VNMS route, it is observed that SiN_4 sites increase rapidly from 500 to 900 °C and become predominant. This can be related first to the large mass loss observed in TG (*ca.* 25%) together with the large decrease in C/Si (from 3 to 1.75) in this temperature range.[21] The decrease in C/Si is mainly due to the breaking of N—Me bonds leading to the release of CH_4 and this probably results in the formation of new N—Si bonds at the expense of Si—C and Si—H bonds. This is the first main origin of the formation of nitrogen-rich silicon sites. The second one is the expulsion of C groups from the silicon-based network to form a carbon phase, which is clearly evidenced through ^{13}C NMR studies from 650 to 850 °C. Vinyl functions first transform into C sp^3 groups essentially by polyaddition reactions. These carbon chains partly lead to the evolution of high molecular mass hydrocarbons as observed by mass spectrometry.[21] Another large number of Si—C bonds are cleaved leading to free C sp^2-type carbonaceous species and more numerous Si—N bonds in the silicon matrix. Carbon segregation thus leads to nitrogen enrichment of the silicon network.

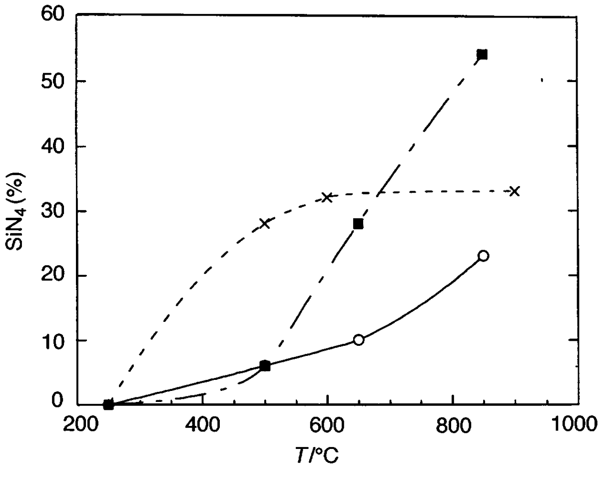

Fig. 10 Fractions of SiN_4 sites as a function of the pyrolysis temperature in the three routes. ○, VS/MS; ×, VS; ■, VNMS

In the case of the VS route, there is a first increase in the amount of SiN_4 sites up to 500–650 °C (*ca.* 30%). This phenomenon is associated with a small mass loss and a small C/Si decrease.[21] Cross-linking reactions (hydrosilylation, Vi polymerization, dehydrocoupling of Si—H and N—H bonds) have led to SiC_2N_2 and $SiCN_3$ sites. These sites can transform to N-rich sites (SiN_4) through expulsion of C groups as a solid free carbon structure. This is what is observed by ^{13}C NMR studies, showing the formation of new C sp^2 sites at 600 °C which become very abundant at 900 °C. In this case, the expulsion of carbon from the silicon-based network to give free carbon mainly explains the formation of SiN_4 sites.

In the VS/MS route, the increase in the fraction of SiN_4 is much lower up to 900 °C compared to the other two precursors. This is in accordance with the higher stability with temperature of the Si—C bond for Me groups compared to the Si—C bond obtained by hydrosilylation or polyaddition of vinyl species (stability shown by IR and ^{13}C MAS NMR studies). The formation of SiN_4 sites can be mainly related to the departure of carbon as a gaseous product; the evolution of methane is indeed observed up to 900 °C. The formation of free carbon plays a lesser role in this route, the signal corresponding to new C sp^2 environments is indeed very weak in the ^{13}C NMR spectra, in agreement with the results obtained by Raman spectroscopy.[25]

From ^{13}C and ^{29}Si NMR results, the structural state of the preceramic network can be deduced. The presence of Si—C—C—Si bridges formed at low temperature (below 600 °C) renders the matrix more stable towards redistribution around Si atoms. Note that redistribution mainly involves Si—N bonds with Si—N or Si—H ones below 900 °C. Cross-linking involving vinyl groups reduces the segment mobility and hinders exchange reactions. It was shown[21] that transamination is hindered in the VS and VNMS routes (where vinyl groups lead to a high cross-linking degree) compared to the VS/MS route; the departure of NH_3 was reported to be considerable only in the case of VS/MS polymers. At *ca.* 500 °C, considering that all vinyl groups were transformed to C sp^3 units, it is observed that VS and VS/MS intermediates contain about the same number of Si—C sp^3 bonds per silicon. Note that the ^{29}Si CPMAS NMR spectra at 500 and 600 °C of VS and VS/MS are indeed very similar, showing that the proportions of Si—C sp^3 and Si—N bonds in the silicon network are about the same in the two routes. But Si—C sp^3 bonds, appearing at low temperature by vinyl transformation are not very stable and partly disappear when the temperature is increased to 900 °C. The Si—C cleavage leads to SiN_4 sites and enrichment in N atoms of the silicon network. It was observed that the ^{29}Si MAS NMR spectra at 900 °C of VS and VS/MS are different, SiN_4 sites being more abundant in VS than in VS/MS. At 900 °C, the silicon network is mainly built of Si—N bonds but it is richer in Si—C bonds in VS/MS than in VS than in VNMS.

The combination of ^{13}C and ^{29}Si NMR results was helpful to clarify the next point: it is clear that Si—N bonds are formed at the expense of Si—C bonds, but do Si—C bonds break to form a solid carbonaceous residue or to lead to the evolution of carbon-containing gaseous products? In each route, we showed that it was possible to evaluate which phenomena predominate.

Evolution of the silicon-based network from 900 to 1400 °C

The silicon-based network is now examined in the temperature range 900–1400 °C. It is constituted of all Si atoms and N and C atoms directly bonded to Si atoms, and so it excludes the free carbon phase formed by the breaking of Si—C bonds. Up to the organic–inorganic transition temperature, deprotonation in the silicon-based network was considerable.[21] From 900 °C, it is assumed that the number of Si—H bonds is negligible. Assuming that at temperatures higher than 900 °C, C—H, N—H and N—Me bonds are also negligible, atomic compositions of the silicon matrix can be estimated. C atoms are taken into account as CSi_4 sites and N atoms as NSi_3 sites. The proportions of Si environments are obtained from deconvolution of the ^{29}Si NMR spectra considering SiC_nN_{4-n} first-coordination spheres; Fig. 11 shows the results obtained at 1400 °C. It is assumed that SiC_4 sites are negligible in these samples; this is supported by the fact that the fraction of SiC_3N sites (which would give a signal at even lower field) is found to be zero from 900 to 1400 °C. Moreover, X-ray diffraction peaks corresponding to SiC phases were never observed in those samples pyrolysed under nitrogen, even at high temperature (1450 °C).[21] The low oxygen content is neglected in these calculations, and so only Si—C and Si—N bonds are taken into account in the silicon matrix.

Fig. 12 shows the evolution of the fractions of SiC_nN_{4-n} sites from 900 to 1400 °C. It is observed that a redistribution between Si—C and Si—N bonds takes place from 900 to 1400 °C. SiN_4 and SiC_2N_2 sites are favoured at the expense of $SiCN_3$ sites. A tendency to segregate a silicon nitride phase is thus observed. The linewidth of the peak due to SiN_4 environ-

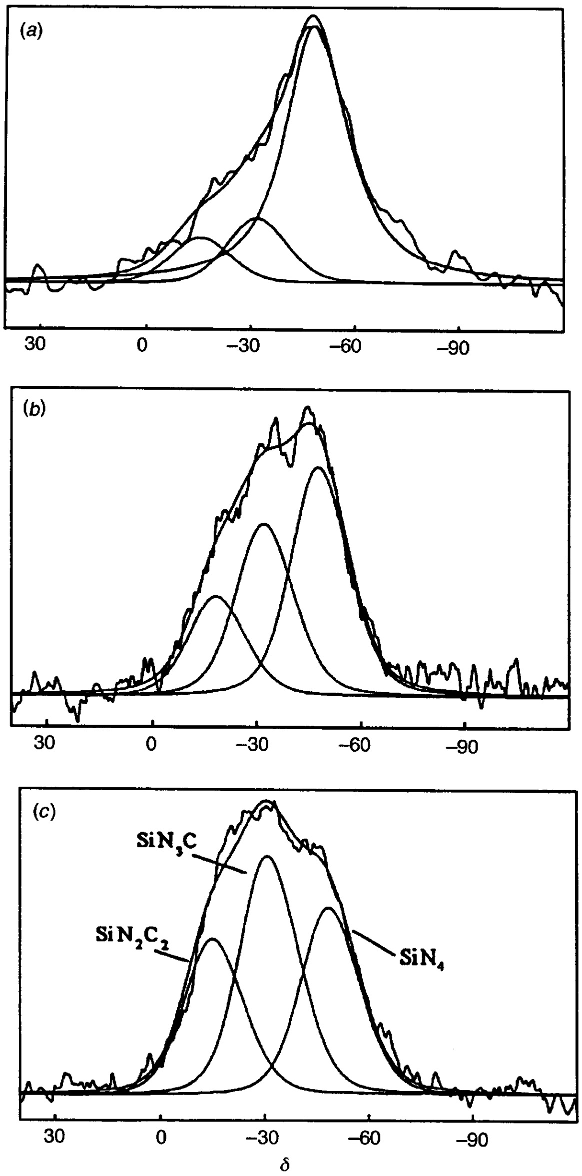

Fig. 11 ^{29}Si MAS NMR spectra of the three samples at 1400 °C: (*a*) VNMS, (*b*) VS, (*c*) VS/MS. Deconvolution into three individual peaks corresponding to SiN_4, SiN_3C and SiN_2C_2 sites.

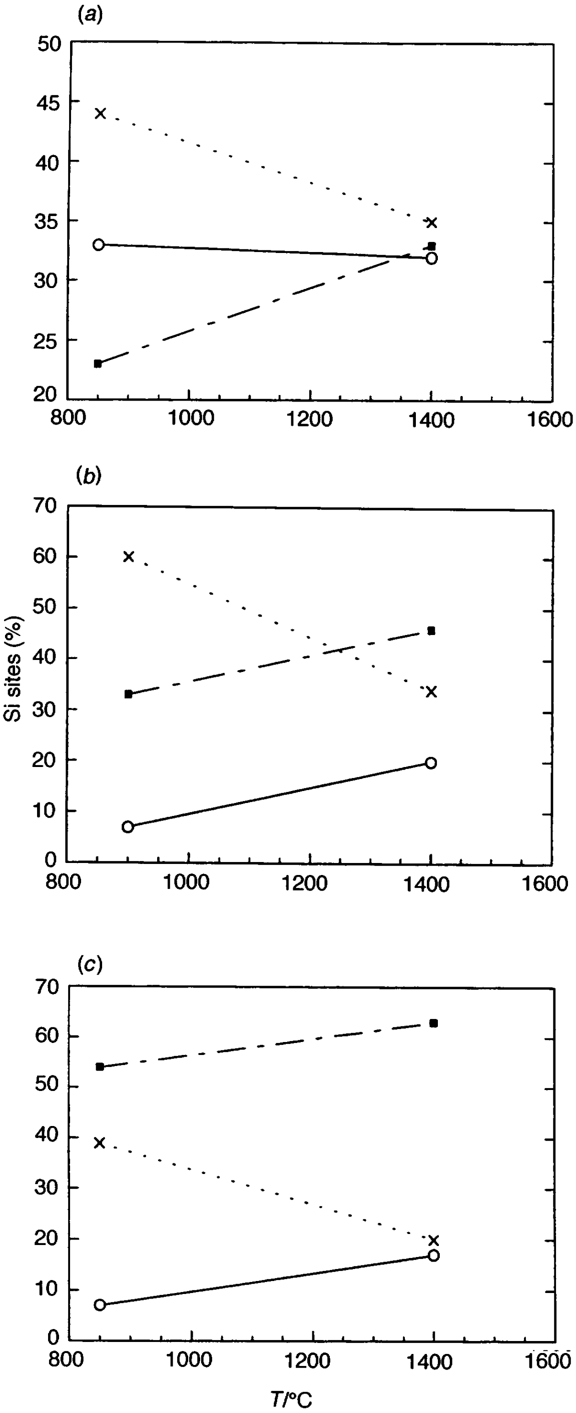

Fig. 12 Fractions of silicon sites (SiN_4, SiN_3C and SiN_2C_2) in the silicon-based networks of (*a*) VS/MS, (*b*) VS and (*c*) VNMS samples pyrolysed from 850 to 1400 °C. ○, SiN_2C_2; ×, SiN_3C; ■, SiN_4.

ments shows that, at temperatures lower than 1400 °C, the silicon nitride structure is still mainly amorphous, which agrees with XRD results.[21] With increasing temperature in the VS route, the formation of more numerous SiN_4 sites is clearly observed in the ^{29}Si NMR spectra at 1400 and 1450 °C (Fig. 2B). This agrees with the XRD results[22] which show a better crystallization of silicon nitride at 1450 °C.

Atomic compositions of the Si networks are calculated using SiC_nN_{4-n} fractions. The calculations are performed as follows: if $p = SiC_2N_2$ (%), $q = SiCN_3$ (%) and $r = SiN_4$ (%), we have: $Si(\%) = (p+q+r)/\Sigma$; $C(\%) = (2p+q)/4\Sigma$ and $N(\%) = (2p+3q+4r)/3\Sigma$ with $\Sigma = (p+q+r)+(2p+q)/4+(2p+3q+4r)/3$. The deduced C/Si and N/Si atomic ratios are indicated in Table 2. The compositions are found to be quite stable with temperature from 900 to 1400 °C, which means that carbon is not lost from the Si network in this temperature range. This observation proves that segregation of the free carbon phase takes place mainly before the organic–inorganic transition. After this transition, the main reactions are local rearrangements in the amorphous silicon matrix which permit the creation of N-rich environments in order to allow the further silicon nitride crystallization. Exchange involving Si—C and Si—N bonds is the main reaction.

The atomic compositions characterizing the silicon networks in the three samples present a similar N/Si ratio, close to unity. It is seen that C/Si ratios decrease from VS/MS to VS to VNMS, suggesting a much higher ability to retain C atoms in the silicon phase in VS/MS than in VS than in VNMS. This trend is opposite to the initial C/Si values in the precursors. Compared to the atomic compositions in the precursors, *ca.* 17% of total carbon atoms were retained in the VS/MS silicon phase compared to 10% in VS and 4% in VNMS. It is evident that an increase in the total carbon content in the precursor, whatever the polymeric backbone structure, does not lead to a proportional increase in the carbon content of the silicon-based network in the ceramic.

Let us now consider the materials pyrolysed at 1400 °C which present the formation of minor amounts of crystalline silicon nitride, and let us assume that all SiN_4 sites segregate in order to favour Si_3N_4 crystallization. In this case, it is possible to characterize the silicon carbonitride structure and calculate an estimated atomic composition of that amorphous structure. The compositions of the silicon carbonitride structure are then calculated as explained earlier, but only the strictly mixed Si sites (SiC_2N_2 and $SiCN_3$) are taken into account. The results are ($SiN_{0.85}C_{0.36}$) for VNMS, ($SiN_{0.88}C_{0.34}$) for VS and ($SiN_{0.84}C_{0.37}$) for VS/MS. Note that the compositions are very similar, close to $SiN_{0.85}C_{0.35}$ which can be also formally expressed as $0.65SiN_{1.33}+0.35SiC$. This composition is rich in nitrogen atoms, which seems to agree with the fact that the amorphous silicon carbonitride structure actually coexists with an Si_3N_4 phase in the process of crystallization. If we compare the relative abundances of the silicon nitride phase and the silicon carbonitride structure (Table 3), we observe that the amorphous silicon carbonitride structure in the three materials is more abundant in VS/MS than in VS and than in VNMS, which remains in agreement with the order of ability to retain C atoms in the Si matrix.

Table 2 N/Si and C/Si atomic ratios in the silicon-based matrices at 900 and 1400 °C, determined by NMR

	silicon matrix at 900 °C		silicon matrix at 1400 °C	
sample	N/Si	C/Si	N/Si	C/Si
VNMS	1.11	0.13	1.15	0.13
VS	1.09	0.19	1.09	0.19
VS/MS	0.97	0.27	1.00	0.25

Table 3 Estimated proportions of silicon nitride and silicon carbonitride structures in the silicon-based networks at 1400 °C

sample	silicon nitride + silicon carbonitride
VNMS	$0.64\ SiN_{4/3}+0.36\ SiN_{0.85}C_{0.36}$
VS	$0.44\ SiN_{4/3}+0.56\ SiN_{0.88}C_{0.34}$
VS/MS	$0.32\ SiN_{4/3}+0.68\ SiN_{0.84}C_{0.37}$

It is also interesting to compare the composition of the silicon carbonitride structure of these materials to the composition of another silicon carbonitride structure obtained in a material which leads to the major crystallization of SiC and not Si_3N_4 at high temperature. From carbosilazane precursors prepared from thermolysis of $(SiMe_2)_n$–$(NHSiMeHNH)_m$ copolymers,[27,28] silicon carbonitride ceramics with SiC crystals were obtained at 1400 °C.[16] Following a similar strategy to characterize these ceramics,[16,23] it was shown that the main Si sites present in that silicon network were SiC_4, SiC_3N and SiC_2N_2 from 900 to 1400 °C. Again, if we assumed that all SiC_4 sites are only part of the SiC crystalline phase at 1400 °C, it was possible to estimate an atomic composition characterizing the amorphous silicon carbonitride structure that coexists with the SiC crystals. The whole silicon phase was found to have the composition $SiC_{0.71}N_{0.40}$, and the silicon carbonitride structure (excluding in this case SiC_4 sites) to have the composition $SiC_{0.61}N_{0.52}$, which can be formally written as $0.6SiC+0.4SiN_{1.33}$. Note that the atomic composition of the amorphous silicon carbonitride structure is rich in carbon atoms in this case and thus seems to be related directly to the nature of the coexisting crystallizing phase, which is thermodynamically expected. Note that carbon atoms initially present as Si—Me groups in this route lead to a stable incorporation of carbon in the silicon carbonitride structure and to $<5\%$ of free carbon.

The free carbon phase

It was reported, in Part 1,[21] that the global N/Si and C/Si atomic ratios in the pyrolysed materials were almost constant from 900 to 1400 °C; the corresponding values obtained from chemical analyses at 1400 °C are indicated in Table 1. We have just shown that these ratios calculated now for the silicon-based network from ^{29}Si NMR results were also constant from 900 to 1400 °C (Table 2). Both results suggest that carbon atoms have left the Si network mainly before the mineral transition at 900 °C to form a free carbon phase. This combination of quantitative analyses obtained from ^{29}Si MAS NMR studies and chemical analyses is in accordance with the qualitative ^{13}C MAS and CPMAS NMR spectra. It was shown that changes in C chemical environments were considerable before 900 °C: a large increase in the fraction of new C sp^2 sites was observed from 600 to 900 °C at the expense of C sp^3 atoms bonded to Si atoms. The new C sp^2 sites were attributed to protonated cyclic precursors of a graphite-type structure formed by Si—C bond cleavages; the protons play the role of poisons in the growth of graphitic carbon cages. These results were supported by TEM data from Delverdier.[29] When free carbon appears, it is present as small aromatic carbon units. The first primary aromatic entities, called basic structural units (BSU), are embedded in the amorphous silicon carbonitride phase. When the temperature increases, the BSUs rearrange into carbon stacks giving rise to more or less complete cages formed from graphite planes.

The abundances of the free carbon phases in the different routes can be estimated from the fractions of C atoms which are no longer bonded to Si atoms. These values can be obtained from the comparison of the C/Si ratios in the global materials obtained by chemical analyses (CA) and in the Si networks obtained by NMR studies (Tables 1 and 2). The percentages of atoms in the free carbon phase are calculated as follows: free $C(\%)=[(C/Si)_{CA}-(C/Si)_{NMR}]/[1+(C/Si)_{CA}+(N/Si)_{CA}]$. The results are as follows: 41% (VNMS), 39% (VS) and 28% (VS/MS), which correspond to the following fractions of total C atoms: 93% for VNMS, 87% for VS and 76% for VS/MS. It is shown that the abundance of free carbon is inversely related to the abundance of the amorphous silicon carbonitride structure. This observation is true for pyrolytic residues at 850 °C and holds up to 1400 °C. The relative abundances of the three different structures present in the materials at 1400 °C are summarized in Table 4.

The abundance of free carbon can be related directly to the nature and amount of cross-linking reactions occurring below 900 °C. The combined results suggest that Vi polyaddition mainly leads to carbon structures with very little carbon insertion into the Si network. Polyaddition creates new C—C bonds and the formation of polymeric carbon chains $(CH_2)_n$ with $n \geqslant 3$ gives Si—C sp^3 bonds with very low stability. Hydrosilylation is the main reaction that creates new Si—C bonds at low temperature leading to stable carbosilane bridges from vinyl groups. Hydrosilylation leads to Si—C—C—Si chains or Si—C—Si bridges. As the temperature increases, Si—C—C—Si chains can rearrange into Si—C—Si carbosilane units. Stable carbon incorporation into the silicon network can thus occur. In the VS route, Vi polyaddition in preference to hydrosilylation consumes Vi groups, and it is even more true in VNMS, for which hydrosilylation is certainly hindered by the presence of N—Me groups;[21] this leads to high free carbon contents. Vi groups are not readily evolved as gaseous products, they lead to high final carbon contents in the ceramics and that carbon is very slightly incorporated in the silicon matrix when polyaddition is preferred to hydrosilylation. In the VS/MS route, the methyl groups give rise preferentially to either gaseous products such as methane or to stable Si—CH_2—Si carbosilane bridges which progressively deprotonate into $CHSi_3$ and finally transform into CSi_4 environments. These processes lead to a low free carbon content but to a reasonable amount of silicon carbonitride structure. It is possible to summarize schematically the evolutions of carbon atoms from the precursors to the ceramic materials obtained by pyrolysis at 1400 °C for the three routes (Table 5). Three possible final carbon states are considered: gaseous products, carbon in a free carbon phase and carbon as CSi_4 sites in a silicon-based structure. This Table is very informative about the transformations of the carbon-containing substituents in the precursors. It appears that NMe groups lead to a completely inefficient carbon insertion in the solid material. Tables 3 and 5 may be very helpful in the design of the backbone of polymeric precursors if one knows the approximate proportions of phases in the ceramics desired for specific properties.

Table 4 Atomic fractions of the three structures constituting the ceramics at 1400 °C

sample	Si_3N_4 (atom%)	SiN_xC_y (atom%)	C (atom%)
VNMS	38	21	41
VS	28	33	39
VS/MS	25	47	28

Table 5 Estimated distributions of carbon atoms in the three possible final states: carbon incorporated in the silicon carbonitride structure, carbon in free carbon and carbon in gaseous products

	no. of C atoms per Si			
sample	initial	Si carbonitride	free carbon	gaseous products
VNMS	3	0.13	1.62	1.25
VS	2	0.19	1.40	0.41
VS/MS	1.5	0.25	0.81	0.44

Conclusions

The present study shows that solid-state NMR permits the elucidation of different aspects of the pyrolytic conversion of polysilazane precursors into silicon carbonitride ceramics.

The assignment of the signals corresponding to SiC_nN_{4-n} ($n=0, 1, 2, 3, 4$) sites allows us to follow the different reactions of cleavage or formation of bonds in the silicon-based matrix. The quantification of these sites leads to a more precise description of the structural evolution with temperature of the different phases forming the material, namely the silicon-based network and the free carbon phase, which at high temperature separate in three distinct structures: the crystallizing silicon nitride phase, the amorphous silicon carbonitride structure and free graphitic carbon.

From the combination of quantitative NMR results and chemical analyses, the following points are clearly shown. Below the organic–inorganic transition temperature the carbon groups leave the silicon network to segregate as a free carbon structure. The carbon-bearing functions, *i.e.* the Si—Me, Si—Vi and N—Me groups, are compared by evaluating in the three routes the different relative amounts of the three final carbon states, which are gaseous products, carbon incorporated in the silicon matrix and free carbon. Another major point is that the chemical composition of the amorphous silicon carbonitride structure can be estimated; in the present cases, it is close to $SiN_{0.85}C_{0.35}$. It is shown that that composition is essentially related to the nature of the coexisting phase which is crystallizing (Si_3N_4 or SiC). Also, the proportions of all the coexisting phases in the ceramics can be deduced.

References

1 R. M. Laine, Y. D. Blum, D. Tse and R. Glaser, *Inorganic and Organometallic Polymers; ACS Symp. Ser. 360*, ed. M. Zeldin, K. J. Wynne and H. R. Allcock, ACS, Washington, DC, 1988, p. 124.
2 D. Seyferth, in *Silicon-based Polymer Science. A Comprehensive Resource; Adv. Chem. Ser. 224*, ed. J. M. Zeigler and F. W. Fearon, ACS, Washington, DC, 1990, p. 565.
3 K. J. Wynne and R. W. Rice, *Annu. Rev. Mater. Sci.*, 1980, **14**, 297.
4 M. Peuckert, T. Vaahs and M. Bück, *Adv. Mater.*, 1990, **2**, 398.
5 D. Seyferth and G. H. Wiseman, *J. Am. Ceram. Soc.*, 1984, **67**, C132.
6 Y. D. Blum, K. B. Schwartz and R. M. Laine, *J. Mater. Sci.*, 1989, **24**, 1707.
7 K. B. Schwartz and Y. D. Blum, *Mater. Res. Soc. Symp. Proc.*, 1988, **121**, 483.
8 N. S. Choong Kwet Yive, R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *Chem. Mater.*, 1992, **4**, 141.
9 R. J. P. Corriu, D. Leclercq, P. H. Mutin and A. Vioux, *Chem. Mater.*, 1992, **4**, 711.
10 A. Lavedrine, D. Bahloul, P. Goursat, N. S. Choong Kwet Yive, R. Corriu, D. Leclercq, H. Mutin and A. Vioux, *J. Eur. Ceram. Soc.*, 1991, **8**, 221.
11 G. T. Burns, T. P. Angelotti, L. F. Hanneman, G. Chandra and J. A. Moore, *J. Mater. Sci.*, 1987, **22**, 2609.
12 H. N. Han, D. A. Lindquist, J. S. Haggerty and D. Seyferth, *Chem. Mater.*, 1992, **4**, 705.
13 C. Gérardin, F. Taulelle and J. Livage, *J. Chim. Phys.*, 1992, **89**, 461.
14 C. Gérardin, M. Henry and F. Taulelle, *Mater. Res. Soc. Symp. Proc.*, 1992, **271**, 777.
15 C. Gérardin, F. Taulelle and J. Livage, *Mater. Res. Soc. Symp. Proc.*, 1993, **287**, 233.
16 D. Mocaer, R. Pailler, R. Naslain, C. Richard, J. P. Pillot, J. Dunoguès, C. Gérardin and F. Taulelle, *J. Mater. Sci.*, 1993, **28**, 2615.
17 W. R. Schmidt, P. S. Marchetti, L. V. Interrante, W. J. Hurley, R. H. Lewis, R. H. Doremus and G. E. Maciel, *Chem. Mater.*, 1992, **4**, 937.
18 R. H. Lewis and J. E. Maciel, *J. Mater. Sci.*, 1995, **30**, 5020.
19 E. Bacque, C. Richard, J. P. Pillot, M. Birot, J. Dunoguès, M.

Pétraud, C. Gérardin and F. Taulelle, *J. Inorg. Organomet. Polym.*, 1995, **5**, 169.
20 G. E. Legrow, T. F. Lim, J. Lipowitz and R. S. Reaoch, *Am. Ceram. Soc. Bull.*, 1987, **66**, 363.
21 D. Bahloul, M. Pereira and C. Gérardin, *J. Mater. Chem.*, preceding paper.
22 D. Bahloul, M. Pereira and P. Goursat, *J. Am. Ceram. Soc.*, 1993, **76**, 1156.
23 C. Gérardin, PhD dissertation, Université P. et M. Curie, Paris, 1991.
24 M. Henry, C. Gérardin and F. Taulelle, *Mater. Res. Soc. Symp. Proc.*, 1992, **271**, 243.
25 D. Bahloul, M. Pereira, T. Merle, P. Goursat, C. Gerardin and F. Taulelle, *3rd Int. Conf. Ceramic–Ceramic Composites*, October 1994, Mons, Belgium.
26 A. Lavedrine, PhD Thesis, University of Limoges, 1992.
27 E. Bacque, J. P. Pillot, J. Dunogues and P. Olry, *Eur. Pat.*, 296028, 1988.
28 E. Bacque, J. Dunogues, C. Biran, P. Olry and J. P. Pillot, *Fr. Pat.*, 2589037, 1986.
29 O. Delverdier, PhD Thesis, University of Pau, 1991.

Paper 6/03181A; *Received 7th May*, 1996