Pyrolysis chemistry of polysilazane precursors to silicon carbonitride

Part 1.—Thermal degradation of the polymers

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The cross-linking reactions and the decomposition processes of three different polysilazane precursors to silicon carbonitride have been investigated systematically in the course of pyrolysis to 1400 °C. The polymer to ceramic conversion chemistry was studied for the following precursors: $(\mathrm{ViSiHNH})_n$ (VS), $(\mathrm{ViSiHNMe})_n$ (VNMS), $[(\mathrm{ViSiHNH})_{0.5}–(\mathrm{MeSiHNH})_{0.5}]_n$ (VS/MS), by means of thermogravimetry, mass spectrometry, solid-state NMR and IR spectroscopies, elemental analysis and X-ray diffraction. The influence of the structure and the polymer backbone (the nature and distribution of the functional groups) on the conversion chemistry was investigated. The occurrence of the cross-linking reactions, the ceramic yields and the abundance of the free carbon phase are related to the polymeric precursor structures.

The development of organometallic polymers as preceramic materials for the synthesis of silicon carbide (SiC), silicon nitride (Si_3N_4) and silicon carbonitride (SiCN) ceramics has recently received considerable attention.[1–11] The main advantage of the conversion from polymers to ceramics is that it is possible to prepare readily ceramic fibrous shapes which are difficult to synthesize by traditional inorganic chemical processes. These polymers may also be used as binders for sintering powders and for infiltration of porous ceramic bodies.[12–15] One of the limitations of the process is the loss of volatile organometallic species, frequently observed by pyrolysis, which may drastically lower the ceramic yield. Cross-linking of the preceramic polymers before pyrolysis is necessary to improve the ceramic yields.[16] It may be performed either chemically, in the presence of a catalyst, or thermally if the polymer is reactive enough.[17–21] The conversion of an organometallic precursor into a ceramic depends on different parameters such as the molecular structure of the polymer and the pyrolysis conditions (temperature, duration, atmosphere).[22–25] Numerous reactions occur during the thermal treatment. It is of great value to determine the nature, rate of evolution and total amounts of the major volatile products at various stages of the thermal conversion process. This type of information is needed to understand the thermal conversion process in order to control the chemical composition and microstructure of the final ceramic. Mass spectrometry (MS) in conjunction with thermogravimetry (TG) helps to provide some suggestions about the reaction mechanisms responsible for the mass losses.

This paper presents some correlations between the chemical compositions and structures of polysilazanes and their derived ceramic products, based on the results obtained using a combination of TG, MS, IR and NMR spectroscopies, elemental analysis and XRD techniques.

Experimental

Polymer preparation

The synthesis and the structural analysis of the three organometallic precursors chosen for this investigation have been described previously.[11,25,26] A summary of the synthesis and cross-linking conditions is given in Tables 1 and 2. Three functional groups (vinyl, SiH, NH) have been recognized to be effective in the construction of the polymer backbone. The possible reactions resulting from the high reactivity of these precursors are hydrosilylation, transamination, vinyl polymerization, dehydrocoupling and redistribution reactions. These reactions, which are very common in organosilicon chemistry, will be detailed later. Note that the initial C/Si ratio varied from 3 to 1.5 (see Table 5, later) in the oligosilazane compounds studied and the N/Si ratio was the same for all polymers, *i.e.* N/Si = 1.

Polymer pyrolysis

The samples were heated in an Al_2O_3 tube fitted with a programmable temperature controller and a control flowmeter in nitrogen. To obtain more details on the mechanisms of polymer pyrolysis, thermogravimetry (TG) studies (B60 Setaram, Ugine-Eyraud System, Caluire, France) were carried out under the same conditions. The gases produced during polymer pyrolysis under flowing helium were identified in a continuous process using a quadrupole mass spectrometer (MS; Quadrex 200, Leybold Heraeus, Les Ulis, France; 70 eV, electron impact). For quantitative chemical analysis (CNRS, Service Central d'Analyse) of the precursors and the pyrolysis products, the silicon content was determined by ICP (inductive coupled plasma) from an aqueous solution of sodium and/or potassium silicate resulting from the chemical attack of the sample. Carbon and hydrogen contents were established by high-temperature combustion using IR spectroscopic analysis. Similarly, the oxygen content was determined using IR spectroscopic analysis of the carbon monoxide formed after pyrolysis of the sample at *ca.* 3000 °C, whereas that of nitrogen was derived according to a thermal conductivity detection method. IR spectroscopic analyses of the cross-linked products were performed according to the conventional KBr pellet technique using an FTIR spectrometer (Nicolet 5DX, Madison, WI). The XRD patterns (Cu-Kα; PW 1130 Philips, Eindhoven) were obtained from the pyrolysis residues ground into fine powders.

Results

Thermogravimetry and ceramic yields

TG studies, at 10 °C $\min^{-1}$ under a nitrogen flow, of the three cross-linked polymers (Fig. 1) reveal that the VS precursor

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Table 1 Synthesis of the different oligosilazanes

sample	theoretical formula	synthesis[a]
VS	$(SiViH\text{-}NH)_n$	$SiViHCl_2+NH_3$, toluene
VNMS	$(SiViH\text{-}NMe)_n$	$SiViHCl_2+NMeH_2$, toluene
VS/MS	$(SiViH\text{-}NH)_x\text{–}(SiMeH\text{-}NH)_y$	0.5 $SiViHCl_2$ + 0.5 $SiMeHCl_2+NH_3$, toluene

[a] All at 0 °C.

Table 2 Cross-linking and pyrolysis of the different polymers

sample	F^a	cross-linking conditions	ceramic yield (%)
VS	3	toluene, 110 °C	87.6
VNMS	2	hexane, 70 °C with Pt^{4+} catalyst	63.6
VS/MS	2.5	heating at 120 °C without solvent or catalyst	79.8

[a] Average number of reactive functions (vinyl, SiH, NH) per silazane unit.

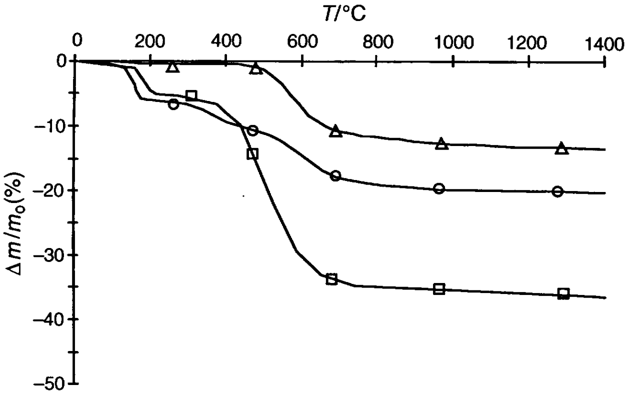


Fig. 1 TG profiles of the different precursors pyrolysed under N_2. △, VS; ○, VS/MS; □, VNMS

having the highest functionality ($F=3$) leads to the best ceramic yield (87%) at 1400 °C. Only a small mass fraction ($\Delta m/m_o=0.5\%$) is lost below 500 °C, revealing the high degree of cross-linking and the thermal reactivity of this precursor. The decomposition behaviours of the VNMS and VS/MS polymers are fairly similar. Three main regions are present in the TG curves: (1) from 100 to 300 °C, an initial 6% mass loss is observed, followed by a plateau; (2) from 300 to 450 °C, an additional 3% mass loss occurs; (3) above 450 °C, an increasing slope of the curve is observed. The mass loss is considerably greater for the VNMS polymer (29%) compared to only 11% for VS/MS and 13% for the VS polymer.

It appears that the number, the nature and the distribution of the functional groups in the polymeric structures are important factors that determine the ceramic yield. From the data in Table 3, it can also be seen that the mass loss is influenced by the pyrolysis heating rate. The lowest ceramic yield is obtained for the fastest heating rate (60 °C min^{-1}). The values indicate that the major mass loss variations occur in the low temperature range (25–250 °C). These first mass loss values appear to be of the same order of magnitude as those of the relative silicon losses ($\Delta Si/Si_p$) determined from elemental analysis. This temperature domain corresponds to the distillation of volatile silicon-containing compounds, as mentioned previously.[21]

Table 3 Mass loss of VS/MS pyrolysed under N_2 at various heating rates

heating rate/ °C min^{-1}	ceramic yield, Y(%)	first mass loss (25–250 °C) by TG	$\Delta Si/Si_p{}^a$ (%)
1	84.1	3.6	3
10	79.8	6.1	6
60	71.5	13.5	17

[a] See Table 4.

Elemental analyses

The evolutions of chemical compositions of the pyrolysed products issued from the VS, VS/MS and VNMS precursors at various temperatures are displayed in Fig. 2, 3 and 4, respectively, and suggest the following remarks: the main changes occur between 400 and 800 °C with an important loss of hydrogen and carbon; hydrogen is still present in the material even at high temperature.

The amounts of silicon present before and after the pyrolysis of 100 g of precursor are given in Table 4. Aside from possible errors in the elemental analysis, the silicon loss of 21% during the pyrolysis of VNMS is not solely due to the distillation of oligomers, in contrast to VS and VS/MS for which the silicon loss is equivalent to the first mass loss determined by TG within the temperature range 25–200 °C. For the VNMS polymer, this additional silicon loss probably occurred in the second temperature range, beyond 600 °C. Indeed, a significant mass loss is recorded by TG, showing an important modification within the polymeric backbone. As suggested previously,[17,26,27] the reactions responsible for the loss of

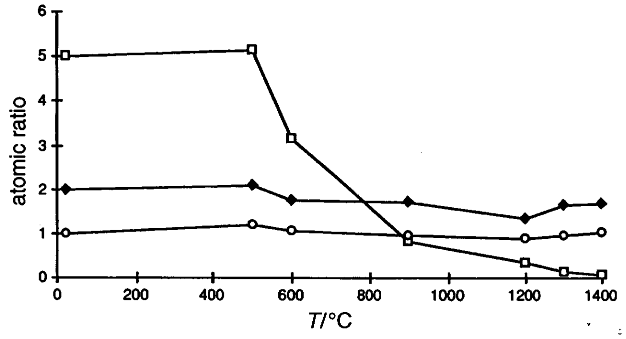


Fig. 2 Elemental analysis (atomic composition) of VS precursor and those of intermediate products isolated at different temperatures. □, H/Si, ○, N/Si; ◆, C/Si.

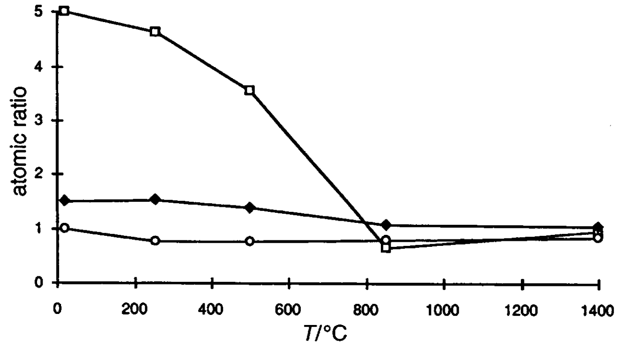


Fig. 3 Elemental analysis (atomic composition) of VS/MS precursor and those of intermediate products isolated at different temperatures. □, H/Si, ○, N/Si; ◆, C/Si.

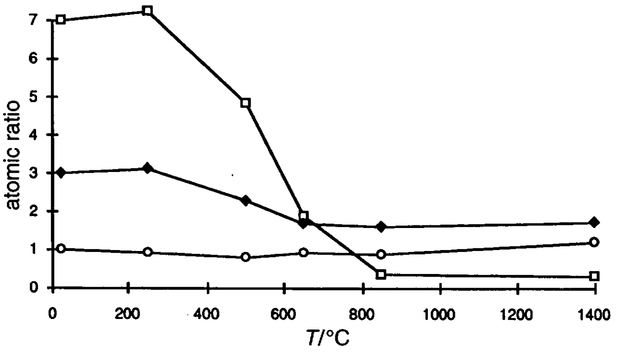


Fig. 4 Elemental analysis (atomic composition) of VNMS precursor and those of intermediate products isolated at different temperatures. □, H/Si, ○, N/Si; ◆, C/Si.

Table 4 Evolution of the silicon content of the different precursors pyrolysed under N_2 up to 1400 °C

	VS	VS/MS	VNMS
ceramic yield, Y(%)	87.6	79.8	63.6
Si_p	39.47	43.11	32.97
YSi_c	39.32	40.53	26.01
$\Delta Si/Si_p$ (%)	0.4	6.0	21.1
first mass loss (%) by TG (25–200 °C)	0.6	6.1	5.2

$\Delta Si/Si_p$ (%) $= (Si_p - YSi_c)/Si_p \times 100$, where Si_p is the silicon content in mass% (theoretical) of the starting precursor, Si_c is the silicon content in mass% of the final ceramic, Y is the ceramic yield.

organosilicon species during pyrolysis are redistribution reactions involving the exchange of Si—N and Si—H bonds and/or two Si—N bonds.

The atomic compositions of the samples heated at 1400 °C under nitrogen (determined by chemical analyses) are compared with the theoretical elemental analyses of the precursors in Table 5.

It is shown that the N/Si ratios of the VS and VNMS samples did not decrease from the precursors (N/Si ≈ 1) to the final ceramics, indicating that the transamination reactions are negligible.[11,28,29] The distillation of organosilicon species and exchange reactions should not modify the N/Si ratio. In contrast, a decrease in the nitrogen content of VS/MS is consistent with the release of a large amount of NH_3 issued from transamination reactions, as will be confirmed later in this paper by the mass spectrometry results.

A comparison between the C/Si ratios in the precursors and in the final ceramics shows that the presence in VNMS of a methyl group on the nitrogen atom (NMe) instead of a hydrogen atom (NH) in the oligosilazane does not lead to a significant increase in the final carbon content: C/Si = 1.75 compared to C/Si = 1.59 for pyrolysed VS. This result reflects the high lability of methyl groups bonded to nitrogen atoms. The partial replacement of vinyl groups by non-reactive methyl groups bonded to silicon atoms leads to a small decrease in the total carbon content: C/Si = 1.59 for pyrolysed VS compared to C/Si = 1.08 for pyrolysed VS/MS. This is equivalent to a total C loss of 20% for VS compared to 27% for VS/MS and suggests that C atoms from vinyl groups are less readily evolved as gaseous products than Me groups.

The compositions of the residues at 1400 °C, assuming that only equilibrium phases, SiO_2, SiC, Si_3N_4 and free carbon, are present in the final ceramics are reported in Table 5. These data show that the pyrolysis of polysilazane precursors leads to ceramic residues containing high free carbon levels. It can already be noticed that this calculation leads to a larger amount of free carbon in VNMS than in VS than in VS/MS. These results will be confirmed and detailed by quantitative NMR measurements in Part 2.[30]

Note that elemental analysis of ceramic products is difficult and poses problems attributed on the one hand to a possible incomplete combustion of the compounds and, on the other hand, the pyrolysis products are porous, absorb moisture and volatiles very readily, leading sometimes to misleading results.

IR spectroscopy

The IR spectra of unpyrolysed polymers and those of solid samples isolated at intermediate temperatures during the decomposition of polymers VS, VS/MS and VNMS are displayed in Fig. 5, 6 and 7, respectively.

VS. Fig. 5 displays the IR spectra of the VS precursor and of samples obtained at different temperatures. When the pyrolysis temperature is increased, a decrease in the intensity is observed as well as a broadening of the absorption bands. The spectrum of the sample pyrolysed at 250 °C indicates a decrease in the band intensities of vinyl groups at 3047, 1592 and 1406 cm^{-1}. The Si—H stretching band at 2135 cm^{-1} is less modified. At 500 °C, the absorption bands arising from N—H (3400, 1170 cm^{-1}), Si—H (2130 cm^{-1}) and vinyl groups (3050,

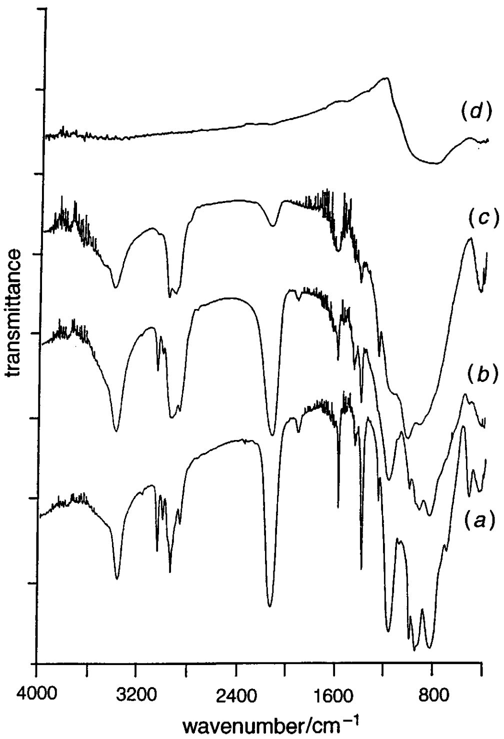


Fig. 5 Evolution of the FTIR spectra of VS under N_2 at various temperatures. (a) Precursor; (b) 250 °C; (c) 500 °C; (d) 1400 °C.

Table 5 Atomic compositions of the oligosilazanes and ceramic compositions after pyrolysis under N_2 at 1400 °C

sample	N/Si (initial)	N/Si (final)	C/Si (initial)	C/Si (final)	theoretical formula
VS	1	0.98	2	1.59	55.6 Si_3N_4, 15.2 SiC, 2.9 SiO_2, 26.3 C
VS/MS	1	0.86	1.5	1.08	54.3 Si_3N_4, 20.2 SiC, 8.5 SiO_2, 17.0 C
VNMS	1	1.19	3	1.75	61.4 Si_3N_4, 1.1 SiC, 7.1 SiO_2, 30.4 C

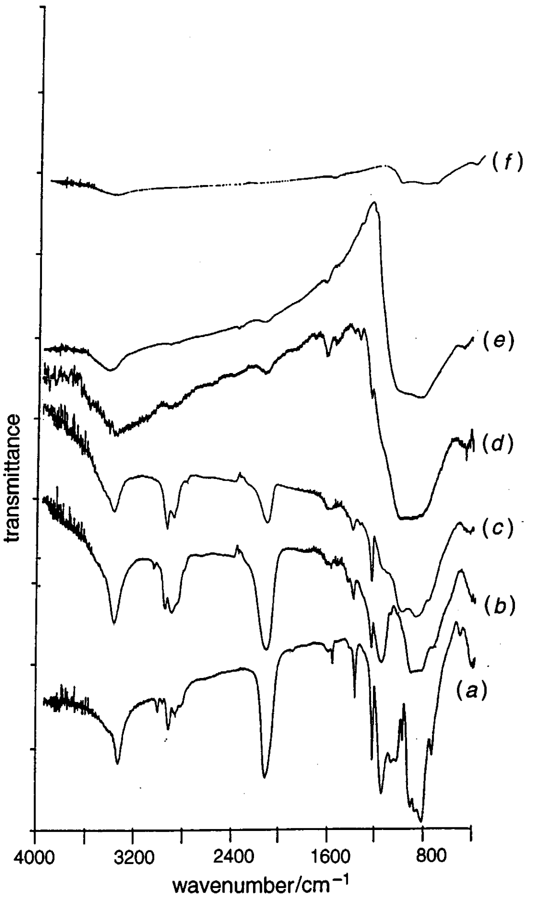


Fig. 6 Evolution of the FTIR spectra of VS/MS under N_2 at various temperatures. (*a*) Precursor; (*b*) 250 °C; (*c*) 500 °C; (*d*) 650 °C; (*e*) 850 °C; (*f*) 1400 °C.

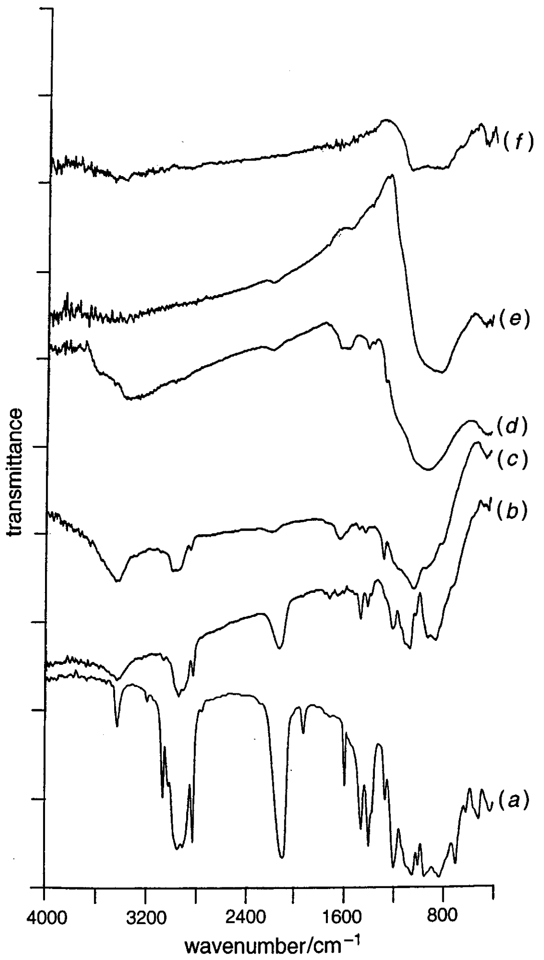


Fig. 7 Evolution of the FTIR spectra of VNMS under N_2 at various temperatures. (*a*) Precursor; (*b*) 250 °C; (*c*) 500 °C; (*d*) 650 °C; (*e*) 850 °C; (*f*) 1400 °C.

1594, 1404 cm^{-1}) are reduced considerably. As the temperature increases, the residual Si—H, N—H and C—H bonds are eliminated. The spectra show only broad absorption bands arising from Si—N and Si—C bonds in the 1200–600 cm^{-1} range.

VS/MS. On heating the cross-linked precursor from 25 to 250 °C (Fig. 6), there is a decrease in the intensity of the asymmetric $CH{=}CH_2$ stretch at 3048 cm^{-1} and those of Si–vinyl deformation (1408 cm^{-1}) and C=C stretch (1595 cm^{-1}). A broadening and a slight decrease in the Si—H band (2122 cm^{-1}), as well as a broadening of the N—H deformation band (1179 cm^{-1}) are observed. At 500 °C, the Si—H band has decreased but remains intense, whereas the bands arising from the vinylic groups have disappeared almost completely. The intensity of the band attributed to the $Si{-}CH_2{-}Si$ deformation (1046 cm^{-1}) increases with increasing temperature, suggesting the insertion of methylene groups into the silicon network. The band at 1179 cm^{-1} of the N—H deformation decreases significantly in intensity. Note that the $Si{-}CH_3$ deformation band at 1260 cm^{-1} is still present. This suggests that $Si{-}CH_3$ groups are more stable than Si–vinyl groups up to 500 °C. Above 500 °C, the IR spectra indicate that most of the Si—H, N—H and C—H functionalities are lost. By 1200 °C, only bands between 1200 and 600 cm^{-1} characteristic of Si—C and Si—N bonds are present.

VNMS. As shown in Fig. 7, the IR absorption peaks at 3400 and 1200 cm^{-1} arising from N—H bonds indicate the presence of this group in the structure of polymers. With increasing temperature to 250 °C, the intensities of the IR absorption bands assigned to vinyl groups (3047, 1591 and 1402 cm^{-1}) decrease significantly. At the same time, the Si—H stretch (2100 cm^{-1}) and $N{-}CH_3$ (1460 cm^{-1}) deformation decrease. The spectrum of the sample at 500 °C shows a weak and broadened Si—H stretching band (2160 cm^{-1}). It is interesting to note that a broadened peak centred near 1600 cm^{-1} appears; this suggests that a new structure with unsaturated carbon is formed. Above 500 °C, there remains only a very broad absorption band between 1200 and 600 cm^{-1}, attributed to Si—C and Si—N bonds.

Mass spectrometry analysis

Correlations between MS results and TG profiles help to provide some suggestions about the mass loss mechanisms.

The TG–MS analyses under helium of the three precursors VS, VS/MS and VNMS are given in Fig. 8, 9 and 10(*a*)–(*c*) respectively.

VS. The TG–MS curve (Fig. 8) shows a very small mass loss (0.5%) up to 400 °C. This mass loss is probably due to the distillation of low molecular mass compounds which condense rapidly at low temperatures in the gas line. Thus, they could not be observed by MS. From 200 to 300 °C some traces of NH_3 (at $m/z=17$) were detected, indicating a low degree of transamination. Hydrogen starts to evolve only above 300 °C. In the 400–1200 °C range, the mass loss increases considerably (13%). This domain is characterized by the main evolution of methane ($m/z=15$), ethane, ethene ($m/z=26$, 27, 28) and hydrogen ($m/z=2$).

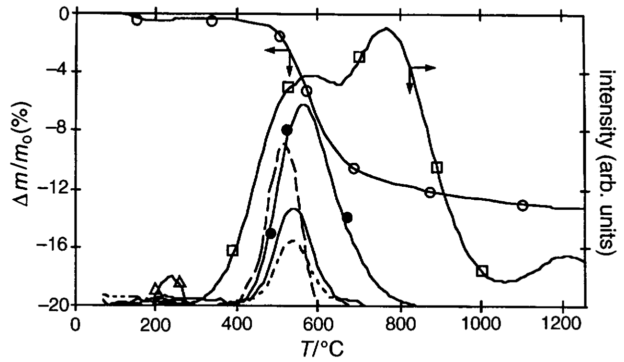


Fig. 8 TG–MS analyses of VS pyrolysed under a helium flow. ○, TG; $m/z=2$ (□), 15 (●), 17 (△), 26 (– –), 27 (——), 28 (- - - -).

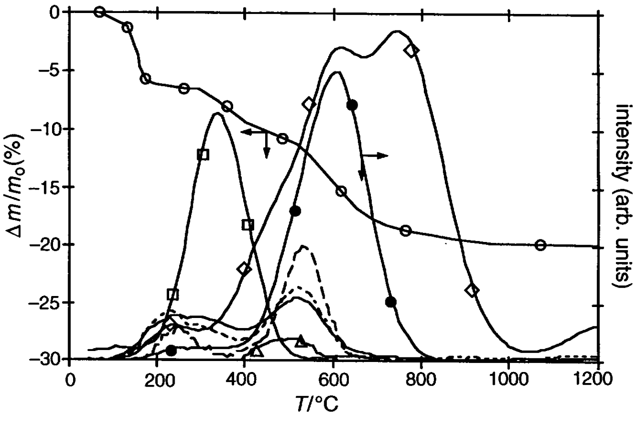
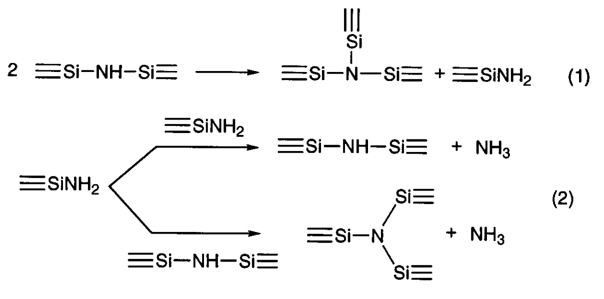


Fig. 9 TG–MS analyses of VS/MS pyrolysed under a helium flow. ○, TG; $m/z=2$ (◇), 15 (●), 17 (□), 26 (– –), 27 (——), 28 (- - - -), 41 (△).

VS/MS. The TG–MS analysis of VS/MS is displayed in Fig. 9. On heating from room temperature to 200 °C, a mass loss of 6% is observed, corresponding to the distillation of low molecular mass oligomers (not detected by MS). Between 200 and 400 °C, a second mass loss (3%) is observed and at the same time a large release of ammonia at $m/z=17$ is detected by MS, which indicates the occurrence of transamination reactions [eqn. (1), (2)].



A lesser release of hydrogen ($m/z=2$), which indicates dehydrogenation reactions, is also detected. In this temperature range, the plateau observed by TG can be explained by reactions which do not lead to the release of a gas, such as the hydrosilylation reaction *via* vinyl and Si—H groups and/or polymerization reactions *via* vinyl polyaddition. These reactions will be discussed later. Likewise, some volatile species with smaller fractions are also detected [methane ($m/z=15$), ethane, ethene ($m/z=26$, 27, 28)]. Above 400 °C, the main gases produced are methane, hydrogen and, to a lesser extent, ethene and propene ($m/z=41$). At higher temperature, only hydrogen is detected.

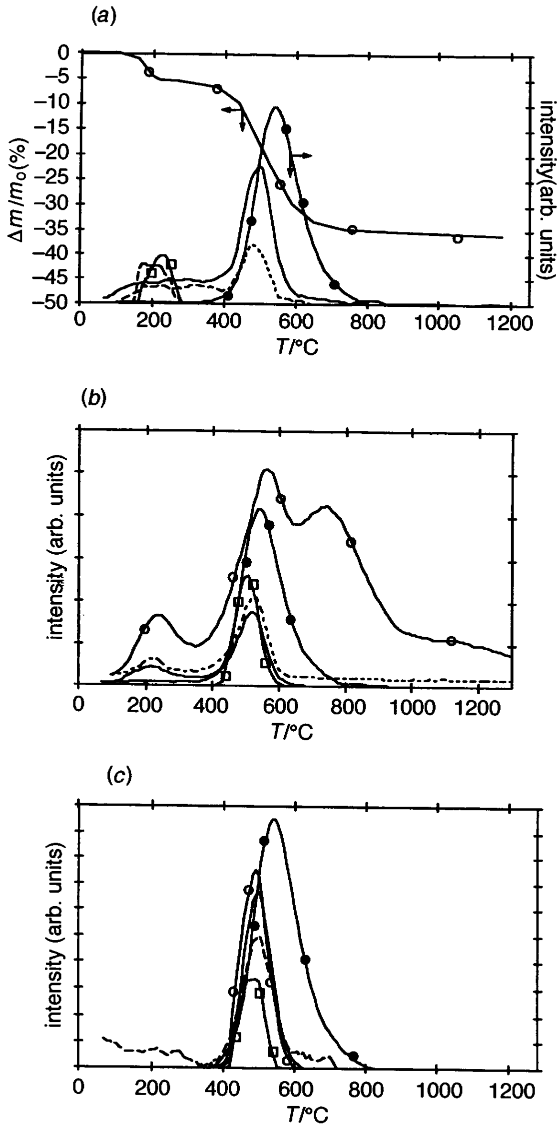


Fig. 10 TG–MS analyses of VNMS pyrolysed under a helium flow. (*a*) ○, TG; $m/z=15$ (●), 30 (——), 31 (- - - -), 85 (□), 86 (– –). (*b*) $m/z=2$ (○), 15 (●), 27 (——), 28 (- - - -), 41 (□). (*c*) $m/z=15$ (●), 42 (——), 43 (○), 44 (- - - -), 56 (□).

VNMS. The TG–MS analysis of VNMS is shown in Fig. 10(*a*)–(*c*). Because of the escape of numerous different fractions in this case, the TG–MS results are displayed on three separate graphs in order to show a clearer presentation of the evolution curves. From 80 to 400 °C the loss observed by TG corresponds to the escape of $(HSiViNHMe)^+$ at $m/z=85$ and $(SiViHNHMe)^+$ at $m/z=86$, arising from $SiViH_2NHMe$ and probably other oligomers which condense in the cold parts of the apparatus. In parallel the *N*-methylamine at $m/z=30$, 31 is detected, arising from transamination of the SiNMeH groups corresponding to the ends of the chains of linear oligomers present in the product as observed by IR analysis. Small amounts of hydrogen ($m/z=2$), ethane and ethene at $m/z=27$, 28 are also detected. In the 400–800 °C range, the mass loss increases sharply (25%). The main gases detected by MS are hydrocarbons such as methane ($m/z=15$), ethylene, ethane ($m/z=27$, 28) and a significant amount of propene ($m/z=41$, 42), butane and butene ($m/z=56$, 41). Under the same experimental conditions and with the same initial mass of product, the intensities of the signals at $m/z=41$ and 56 are higher for VNMS than for the other polymers. A second gaseous evolution at $m/z=30$, 31 with a maximal release speed at 500 °C is observed. It is difficult to assign this peak in the same way as in the first temperature range, *i.e.* to the *N*-methylamine arising from transamination of the ends of the chains, owing to the small number of N—H bonds present in

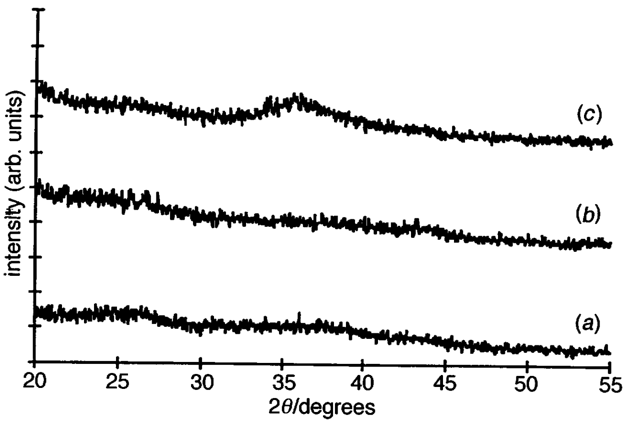


Fig. 11 XRD patterns of the residues resulting from the pyrolysis at 1400 °C of the three precursors. (*a*) VS; (*b*) VNMS; (*c*) VS/MS.

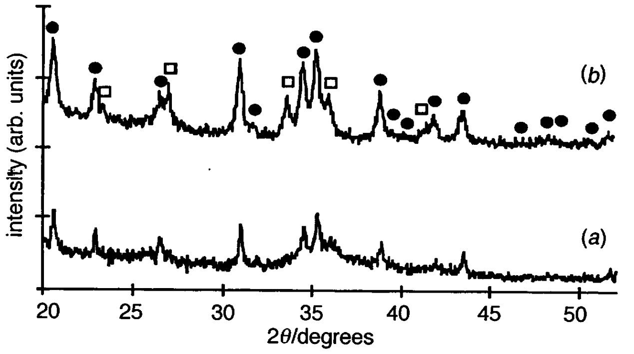
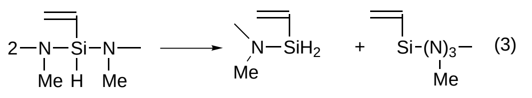
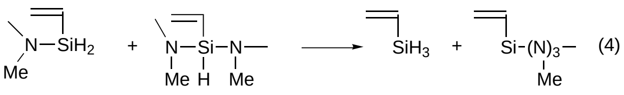


Fig. 12 Comparison of XRD patterns of pyrolysed products under nitrogen at 1450 °C, 48 h. (*a*) VS/MS; (*b*) VNMS. ●, α-Si_3N_4; □, β-Si_3N_4.

the product. The most rational hypothesis for the formation of such fragments is redistribution involving exchange of Si—N and Si—H bonds which may lead to the volatile silane $CH_2{=}CHSiH_3$ [eqn. (3), (4)] with abundant ions SiH_2^+ at $m/z = 30$ and SiH_3^+ at $m/z = 31$.



$$2\,{-}\underset{\text{Me}}{\text{N}}{-}\underset{\text{H}}{\overset{=\!\urcorner}{\text{Si}}}{-}\underset{\text{Me}}{\text{N}}{-} \longrightarrow \diagdown\!\underset{\text{Me}}{\text{N}}{-}\overset{=\!\urcorner}{\text{SiH}_2} + \overset{=\!\urcorner}{\text{Si}}\text{-(N)}_3\underset{\text{Me}}{-} \quad (3)$$



$$\diagdown\!\underset{\text{Me}}{\text{N}}{-}\overset{=\!\urcorner}{\text{SiH}_2} + \diagdown\!\underset{\text{Me}}{\text{N}}{-}\underset{\text{H}}{\overset{=\!\urcorner}{\text{Si}}}{-}\underset{\text{Me}}{\text{N}}{-} \longrightarrow \overset{=\!\urcorner}{\text{SiH}_3} + \overset{=\!\urcorner}{\text{Si}}\text{-(N)}_3\underset{\text{Me}}{-} \quad (4)$$

Note that this redistribution reaction leads to the formation of trisilylated nitrogen atoms, NSi_3.

The departure of these silanes would explain the loss of silicon observed by chemical analysis (Table 4).

Beyond 800 °C, the release of hydrogen continues.

X-Ray diffraction analysis

As shown in Fig. 11, the diffraction patterns of the three polymers pyrolysed under nitrogen up to 1400 °C do not exhibit any significant diffraction peaks. Thus, these products consist of amorphous structures. The development of crystallinity was observed in samples fired at higher temperature^{27} (Fig. 12). Note that no SiC phase was observed by XRD.

Discussion

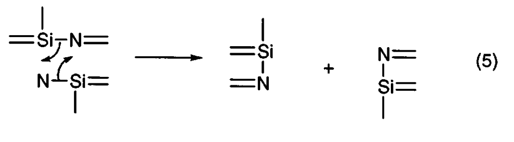
From the data obtained using different analysis techniques, the pyrolysis process of the organometallic precursors may be considered to take place in three consecutive stages: (1) in the first stage (up to 400 °C), further cross-linking proceeds by various reactions. Likewise, the loss of low molecular mass oligomers occurs; (2) in the second stage (400–800 °C) the Si—C, Si—H and C—H bonds are broken and small molecules, mostly hydrocarbons and hydrogen, are evolved. This step is commonly called a mineralization step and consists of the organic–inorganic transition; (3) at temperatures higher than 800 °C, a mineral ceramic material is obtained consisting of free carbon and an amorphous SiC_xN_y silicon network. As the temperature reaches 1450 °C, crystallization is induced.

Cross-linking

The difference in ceramic yields between the three samples stems primarily from the difference in the degrees of cross-linking occurring during the first step up to 400 °C. On the basis of the IR spectroscopic data, the chemical analysis of the intermediate product at 250 °C and the amount of silicon lost during pyrolysis which is equivalent to the first mass loss, there is a clear similarity between the composition of the volatile organosilicon species and the starting precursor. Many kinds of reactions can account for the departure of volatile products. At the beginning, the escape of organosilicon species can be explained on the one hand by the distillation of low molecular mass oligomers when cross-linking is inadequate and, on the other hand, by depolymerization reactions such as exchange of Si—N bonds or Si—N and Si—H bonds, or Si—N and N—H bonds.

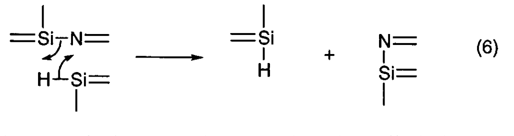
Exchange of Si—N bonds according to eqn. (5) would lead to the formation of silazane oligomers having the same structural units as the precursor, whereas the exchange between Si—N and Si—H bonds [eqn. (6)] would lead to volatile silanes as suggested in the case of the thermolysis of the VNMS precursor [eqn. (3), (4)].

Exchange of Si—N bonds:



(5)

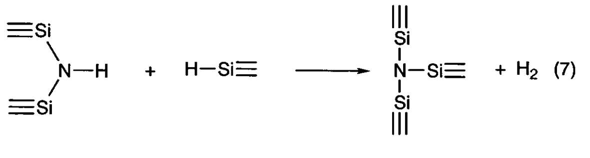
Exchange of Si—N and Si—H bonds:



(6)

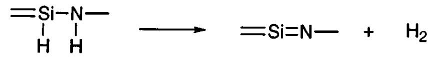
The exchange of Si—N and N—H bonds, called the transamination–condensation reaction [eqn. (1), (2)] involves the formation of new Si—N bonds and the release of NH_3. Note that the escape of NH_3, detected by MS analysis, indicates that the transamination reaction occurs between 200 and 500 °C whatever the precursor. The presence of methyl groups on the nitrogen atoms ($N{-}CH_3$) instead of NH groups prevents the transamination reaction, as in the case of the VNMS precursor. In this case, the *N*-methylamine observed by MS corresponds only to transamination of the ends of chains.

As mentioned already, the transamination reaction allows the formation of trisilylated nitrogen atoms (NSi_3). Such NSi_3 sites can also result from dehydrogenation reactions between Si—H and N—H bonds [eqn. (7)] and thus can explain the release of hydrogen observed by MS during the thermolysis of the polymers below 400 °C.



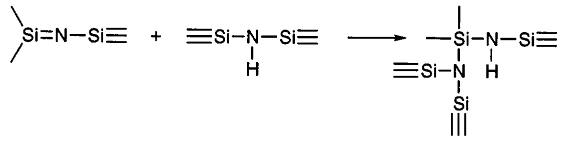
$$\begin{array}{l}\equiv\text{Si}\\ \;\diagdown\\ \;\;\text{N—H}\\ \;\diagup\\ \equiv\text{Si}\end{array} + \text{H—Si}\equiv \longrightarrow \begin{array}{c}\equiv\\ \text{Si}\\ |\\ \text{N—Si}\equiv\\ |\\ \text{Si}\\ \equiv\end{array} + \text{H}_2 \quad (7)$$

Dehydrogenation of Si—H and N—H contiguous bonds can also explain the departure of hydrogen through an intermediate silylimine as suggested previously.[17,28] Then, the silylimine reacts by insertion into N—H and/or Si—H bonds following reactions (8), (9) and (10), leading to the formation of NSi_3 sites.



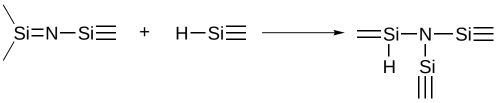
$$=\underset{H}{Si}-\underset{H}{N}- \longrightarrow =Si=N- + H_2 \quad (8)$$

Insertion into N—H bond:

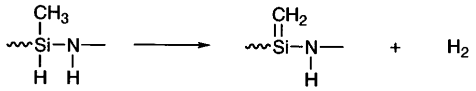


$$\rangle Si=N-Si\equiv + \equiv Si-\underset{H}{N}-Si\equiv \longrightarrow -\overset{|}{\underset{\equiv Si-\underset{\underset{\equiv}{Si}}{N}}{Si}}-\underset{H}{N}-Si\equiv \quad (9)$$

Insertion into Si—H bond:



$$\rangle Si=N-Si\equiv + H-Si\equiv \longrightarrow =\underset{H}{Si}-\underset{\underset{\equiv}{Si}}{N}-Si\equiv \quad (10)$$

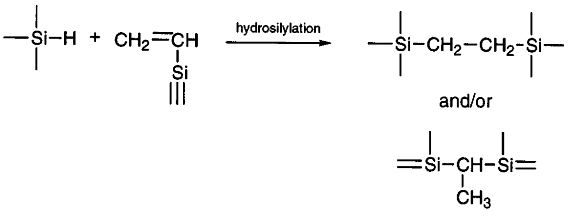


$$\sim\overset{CH_3}{\underset{H}{Si}}-\underset{H}{N}- \longrightarrow \sim\overset{CH_2}{\overset{\|}{Si}}-\underset{H}{N}- + H_2 \quad (11)$$

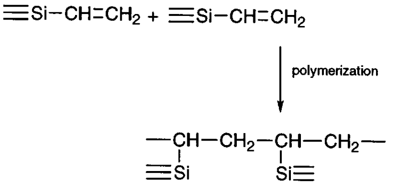
Hydrogen was also postulated to arise from reaction (11), producing silene species[30,31] which could insert into Si—H bonds to form new $\equiv Si-CH_2-Si\equiv$ bridges. Thus, carbon atoms can be incorporated into the silicon network.

This reaction is consistent with our ^{29}Si NMR observations, detailed in the following paper.[30] It is shown that the silicon carbonitride SiC_nN_{4-n} sites are more numerous in VS/MS than in VS and VNMS ceramic products.

In addition, the higher mass retention of VS relative to those of VS/MS and VNMS precursors during thermolysis is attributed to the greater degree of branching and cross-linking issued from the conversion of vinyl groups to saturated hydrocarbon functionalities according to eqn. (12) and (13).

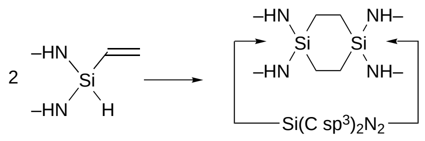


$$-\overset{|}{\underset{|}{Si}}-H + CH_2=\underset{\underset{\equiv}{Si}}{CH} \xrightarrow{\text{hydrosilylation}} -\overset{|}{\underset{|}{Si}}-CH_2-CH_2-\overset{|}{\underset{|}{Si}}- \text{ and/or } =\overset{|}{Si}-\underset{CH_3}{CH}-\overset{|}{Si}= \quad (12)$$

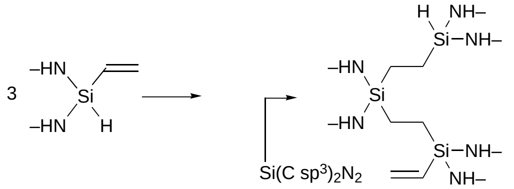


$$\equiv Si-CH=CH_2 + \equiv Si-CH=CH_2 \xrightarrow{\text{polymerization}} -\underset{\equiv Si}{CH}-CH_2-\underset{Si\equiv}{CH}-CH_2- \quad (13)$$

This is supported, on the one hand, by the IR study which indicates the formation of more saturated CH_2 groups (2900 cm^{-1}) and a decrease in the number of vinyl groups (3048, 1595 and 1408 cm^{-1}) and Si—H bonds (2120 cm^{-1}) and, on the other hand, by the ^{13}C CPMAS NMR characterization which reveals that substantial amounts of vinyl groups were consumed (resonance centred at δ 135) in favour of essentially aliphatic carbon atoms (resonance centred at δ 10–30) below 500 °C in the three routes. The ^{29}Si MAS NMR spectra detailed in Part 2 confirm these results;[30] the silicon environments are described as a distribution of $Si(C\ sp^3)(C\ sp^2)N_2$, $Si(C\ sp^3)HN_2$ which can be formed by simple hydrosilylation or vinyl polymerization, whereas $Si(C\ sp^3)_2N_2$ sites can be formed from duplicate hydrosilylation as shown in reactions (14) and (15).



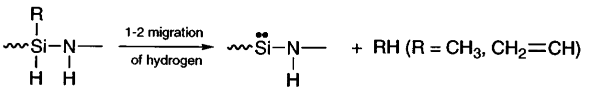
(14)



(15)

Thus the resulting preceramic network is more stable towards redistribution/exchange of bonds than the Si—N skeleton, and this seems to be an important inhibiting factor in the depolymerization reactions. The small mass loss, the results of elemental analysis and the few traces of ammonia observed by MS during the thermolysis of VS reinforce this suggestion.

In the cases of VNMS and VS/MS, the departure of gaseous hydrocarbons (ethane, methane) detected by MS analysis in this temperature range ($T < 400$ °C) could be assigned to 1–2 migration of hydrogen with formation of silylene species[29] according to reaction (16) rather than *via* the formation of radical groups $R^{\cdot}$ and $H^{\cdot}$.



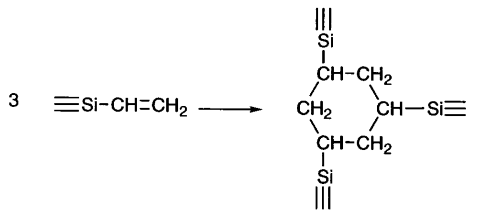
$$\sim\overset{R}{\underset{H}{Si}}-\underset{H}{N}- \xrightarrow[\text{of hydrogen}]{\text{1-2 migration}} \sim\ddot{Si}-\underset{H}{N}- + RH\ (R = CH_3, CH_2{=}CH) \quad (16)$$

These silylene species could then, in turn, insert into other Si—H, C—H or N—H bonds producing Si—Si bridges (less probable), $Si-CH_2-Si$ or $-Si-(N)_3=$bridges respectively.

The combined results for the samples heated to 400 °C show that a lower cross-linking degree corresponds to more numerous redistribution reactions. The various losses are consistent with the occurrence of exchange reactions (transamination, exchange of Si—N bonds with Si—H or Si—N ones) which are facilitated in VS/MS compared to VS. It is clear that the presence of Si—Me groups alternating with Si—Vi ones in the precursor backbone limits the occurrence of cross-linking reactions involving Vi groups (hydrosilylation, Vi polyaddition) and thus gives less rigidity to the silicon network below 400 °C. These conclusions are in agreement with the results previously reported by Choong Kwet Yive *et al.*[26]

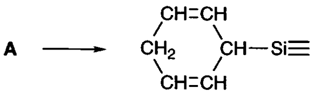
Mineralization step

A considerable change occurs within the temperature range 400–800 °C. The mass loss observed, whatever the starting precursor, is mainly assigned to an evolution of hydrocarbons and hydrogen resulting from broken Si—C and N—C bonds and also Si—H, C—H and N—H bonds. A detailed study of these decomposition reactions, which involve radical mechanisms, has been published previously.[25] A comparison between the evolution during pyrolysis of the three precursors indicates a significant difference in where the carbon atoms bind to the Si skeleton atoms. Indeed, the high molecular mass hydrocarbons detected by MS analysis, such as propene, butane and butene, are only obtained in the case of the VNMS precursor. This can be explained by the presence of the methyl group on nitrogen atoms which limits cross-linking processes such as the hydrosilation reaction. This reaction is limited because of the steric hindrance due to methyl groups. Consequently, the degree of polymerization *via* polyaddition of vinyl groups [reaction (13)] increases, which produces bridged or ring-type hydrocarbon products as shown schematically in eqn. (17) and (18).



(17)

A



(18)

These six-membered rings formed with C atoms may be precursors for the free carbon phase. Such structures lead to a low carbon content in the silicon network. This agrees with the low fraction of silicon carbonitride sites observed in the ^{29}Si NMR spectra of VNMS heated at 600 °C and the appearance of C sp^2 sites shown by ^{13}C CPMAS NMR results. The limitation of the hydrosilylation reaction due to the presence of NMe groups would explain the higher free carbon content in VNMS compared to VS, if we accept that Me groups bonded to N atoms are evolved as a gaseous product. The occurrence and abundance of free carbon in the three materials will also be discussed in the following paper.[30]

Crystallization

From 800 °C, after the organic-to-inorganic transformation, the three different materials are constituted of several structures (free carbon, silicon carbonitride, silicon nitride) as suggested by the nature of local environments which are observed by NMR (detailed in Part 2).[30] The only change in chemical composition is the decrease in H/Si ratio with increasing temperature, which is confirmed by the release of hydrogen. XRD studies of the residues issued from pyrolysis under nitrogen at 1400 °C for 1 h indicated the completely amorphous structure of the silicon carbonitride ceramics (Fig. 11). With increased temperature and holding time (pyrolysis at 1450 °C for 48 h), the development of a crystalline phase corresponding to α-Si_3N_4 was observed (Fig. 12). Compared to other routes, the VNMS-derived product seems to be more crystallized in α- and β-Si_3N_4 phases. The high free carbon content, lost by the silicon network, does not prevent the crystallization of Si_3N_4 phases.

Note that, beyond 1400 °C, the stability and the crystallisation of the SiCN phase depends on the nature of the pyrolysis atmosphere. As shown in previous work,[27] the decomposition under argon of the amorphous Si—N—C material yields a pyrolytic residue almost totally free of nitrogen but enriched by an SiC phase, involving the formation of gaseous species (N_2, Si) and also oxygen-based species[31] (SiO, CO). Oxygen contamination mainly comes from exposure to the air during handling. In contrast, during the heat treatment under nitrogen the decomposition of the Si—N—C structure leads to Si_3N_4 and free carbon. Si_3N_4 formation can also result from a reaction involving SiO and nitrogen according to the following equation:[31] $3SiO + 2N_2 \rightarrow Si_3N_4 + 3/2\ O_2$.

It seems that the decomposition of the Si—N—C(O) phase is temporarily impeded under a nitrogen atmosphere in comparison with argon. This nitriding process will be discussed in detail in a future paper.[32]

Conclusion

The combination of different analysis techniques has led to the following conclusions: there exist strong relationships between the structure of the polysilazane precursor and the ceramic yields and the global atomic compositions of the final ceramics. The results reveal phase separation during the pyrolysis process, the formation of a structure with an Si—N—C backbone and the separation of free carbon. The stability of Si—C bonds and the stable incorporation of carbon into the Si—N—C network during pyrolysis appear to depend strongly on the substituents on the Si and N atoms in the precursor backbone. The differences between the thermochemical evolutions of the three preceramic polymers will be clarified further in the following paper on the basis of quantitative ^{29}Si MAS NMR studies which examine Si—(C,N) bonds directly.

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