An NMR Study of the Step by Step Pyrolysis of a Polysilazane Precursor of Silicon Nitride

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Introduction

The study of organosilazane polymers has become an increasingly important area of research, since they offer alternative processing routes to the formation of silicon nitride Si_3N_4.[1] The synthesis of such polysilazanes generally involves the ammonolysis, transamination, or thermolysis of various dichlorosilanes $RR'SiCl_2$ ($R = H, CH_3, CH{=}CH_2$; $R' = CH_3$). Pyrolysis of the resulting oligomers is usually studied using coupled TGA-MS analysis. However, little could be ascertained as to the changes which the polymer underwent during the heat treatment. Since the polymer becomes insoluble at high temperatures, generally over 200 °C, solid-state magic angle spinning NMR techniques were used to characterize the ceramic residues.[2] In a recent paper,[3] a new route for the synthesis of polysilazanes from dichlorosilanes and hydrazine was reported. Pyrolysis of the resulting polymers was performed, and it was found that the combination of two chlorosilanes, $Cl_2SiMe(CH{=}CH_2)$ and $MeSiCl_3$, allowed the polymers to cross-link at the early stage of the pyrolysis, resulting in increased ceramic yields. Yet no information was forthcoming as to the changes that the polysilazanes underwent during the pyrolysis process. We have undertaken a detailed study of the pyrolysis chemistry of analogous silazanes with the objective of having a better understanding of the precursors to ceramic conversion processes. This additional information will aid in further increasing the yields and applications of the corresponding silicon nitride derivatives. We report here the systematic solid-state NMR study of the polymer and ceramic residues obtained after pyrolysis at various temperatures of the precursor resulting from the reaction of methylvinyldichlorosilane with hydrazine in the presence of triethylamine.

Experimental Section

Standard inert-atmosphere techniques were used for the preparation and manipulation of all reagents. The starting oligomer **1** was prepared as previously described.[3] Weight losses as a function of temperature were recorded on a Setaram TG 92 thermobalance. The samples were placed in an alumina crucible and heated under nitrogen. The gases evolved during the pyrolysis of the precursor were analyzed with a VG EGA 300 MM quadrupole mass spectrometer, coupled to the balance with a silica capillary heated at 80 °C. To obtain high concentrations of these gases, rapid heating rates were chosen: 300 °C/h. Mass spectra were recorded every minute. At the end of the experiment, peak intensities were converted into molecular species by taking into account for each peak the theoretical relative contributions of fragments coming from different molecules (data from tables, for 65-eV electronic ionization). The samples prepared for NMR investigation were heated at 25 °C/h and held 1 h at the desired pyrolysis temperature: 250, 300, 500, 800, 1000 °C. ^{29}Si, ^{13}C, and ^{1}H solid-state NMR spectra were recorded on a Bruker MSL 300 spectrometer, equipped with a double-bearing probe head. Single-pulse excitation at magic angle spinning was used for ^{29}Si and ^{1}H nuclei. Cross polarization at magic angle spinning was used for ^{13}C. The acquisition parameters are summarized in Table I.

Scheme I

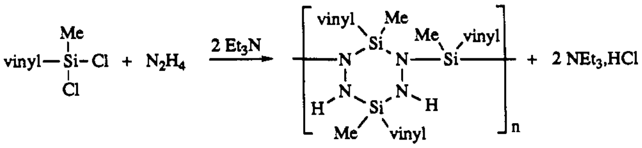

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Table I

	^{29}Si	^{1}H	^{13}C
ref ($\delta = 0$)	TMS	H_2O	TMS
spinning freq (kHz)	3-4	3-4	3-4
irradn freq (MHz)	59.6	300.1	75.5
pulse length (ns)	2	6.2	2
contact time (ms)			5
recycle delay (s)	10	1	10
no. of scans	≈7000	≈13 000	≈7000
line broadening before Fourier transformn (Hz)	30	100	30

Results and Discussion

The starting solid oligomer **1** was prepared by reacting $Cl_2SiMe(vinyl)$ with hydrazine in dioxane in the presence of triethylamine.[3] After filtration, the solvent was evaporated under vacuum at 60 °C, giving a solid at room temperature. This solid became waxy at 50-60 °C. Its viscosity was 19 P at 100 °C and 0.45 P at 150 °C. Above 200 °C the precursor cross-linked and was transformed into an infusible and insoluble solid. From these results it was assumed (from elemental analysis) that hydrazine reacted as a trifunctional species on average.[3] A representative structure has been proposed (Scheme I). A sample of oligomer **1** was pyrolyzed at different temperatures from 250 to 1000 °C. TGA showed that the major weight loss occurred between 200 and 800 °C (ceramic yield 66.6%; see Figure 1). The gaseous product evolved between 200 and 300 °C was ammonia, between 450 and 600 °C it was mainly methane but also ethylene, propene, butene, and ammonia. Above 600 °C only evolution of methane was detected (Figure 2). Note that hydrogen evolution was also observed during the pyrolysis process. Samples of **1** pyrolyzed at 250, 300, 500, 800, and 1000 °C were analyzed by ^{29}Si (Figure 3), ^{13}C (Figure 4), and ^{1}H (Figure 5) solid-state NMR spectroscopy in addition to IR spectroscopy.

The ^{29}Si chemical shift of the starting oligomer, -9 ppm, seemed to be consistent with a structure $[(sp^2C)(sp^3C)SiN_2]_x$ with CH_3 and vinyl substituents on the silicon. The presence of methyl and

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(1) See for example: Seyferth, D.; Wiseman, G. H.; Prudhomme, C. *J. Am. Ceram. Soc.* **1983,** *66,* C-13. Seyferth, D.; Wiseman, G. H. *J. Am. Ceram. Soc.* **1984,** *67,* C-132. Arkles, B. *J. Electrochem. Soc.* **1986,** *133,* 233. Okamura, K.; Sato, M.; Hasegawa, Y. *Ceram. Int.* **1987,** *13,* 55. Brown-Wensley, K. A.; Sinclair, R. A. U.S. Patent 4537942, 1985. Rabe, J.; Bujalski, D. European Patent Application 200326, 1986. Burns, G. T.; Angelotti, T. P.; Hanneman, L. F.; Chandra, G.; Moore, J. *J. Mater. Sci.* **1987,** *22,* 2609. Legrow, G. E.; Lim, T. F.; Lipowitz, J.; Reaoch, R. S. *Ceramic Bull.* **1987,** *66,* 363. Youngdahl, K. A.; Laine, R. M.; Kennish, R. A.; Gronin, T. R.; Balavoine, G. G. A. In *Better Ceramics Through Chemistry*; Brinker, C. J., Clark, D. E.; Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh, PA, 1988; Vol. 121, pp 489-496. Pouskouleli, G. *Ceram. Int.* **1989,** *15,* 213. Peuckert, M.; Vaahs, T.; Bruck, M. *Adv. Mater.* **1990,** *2,* 398. Gordon, R. G.; Hoffman, D. M.; Riaz, U. *Chem. Mater.* **1990,** *2,* 480. Yokoyama, Y.; Nanba, T.; Yasui, I.; Kaya, H.; Maeshima, T.; Isoda, T. *J. Am. Ceram. Soc.* **1991,** *74,* 654. Narsavage, D. M.; Interrante, L. V.; Marchetti, P. S.; Maciel, G. E. *Chem. Mater.* **1991,** *3,* 721.

(2) Lipowitz, J.; Freeman, H.; Goldberg, H.; Chen, R.; Prock, E. *Mater. Res. Soc. Symp. Proc.* **1986,** *73,* 489.

(3) Colombier, C. *Proceedings of the 1st European Ceramic Society Conference,* Maastricht, The Netherlands, June 18-23, 1989.

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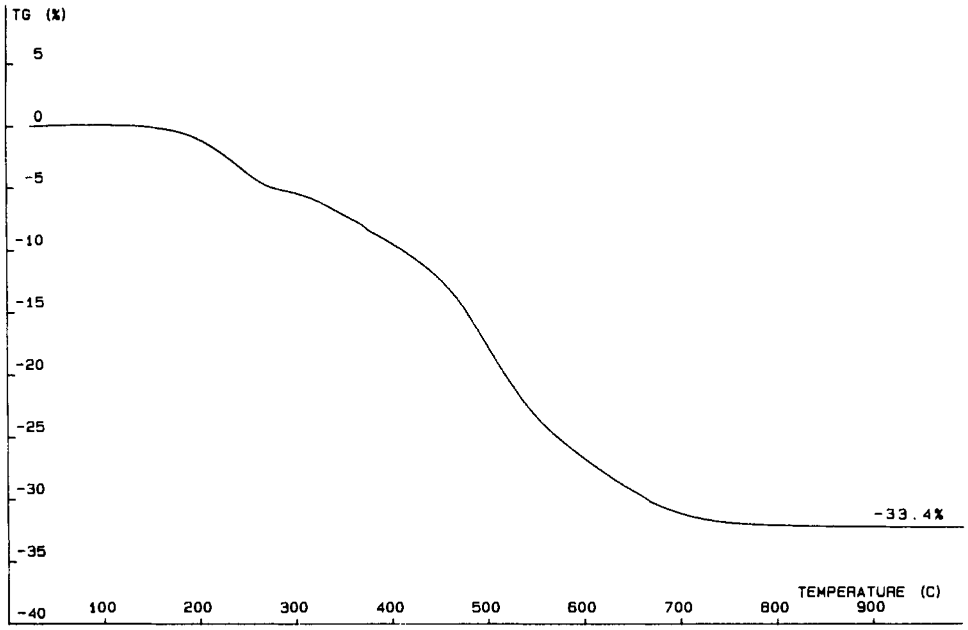

Figure 1. TGA of oligomer 1.

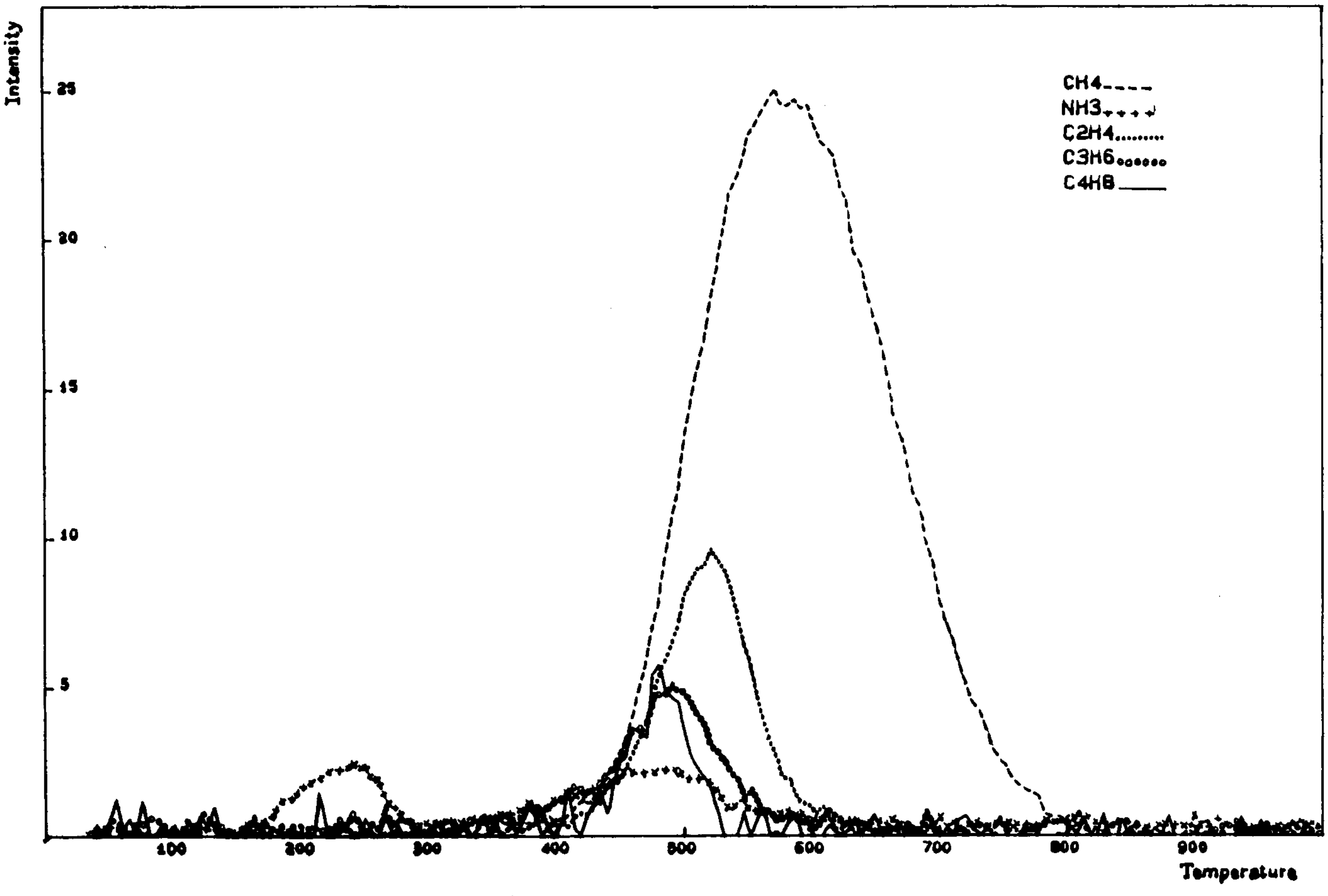

Figure 2. Pyrolysis of oligomer 1: gas analysis by TGA/MS coupling.

vinyl groups is corroborated by ^{13}C NMR spectra which exhibited peaks at 135 (vinyl groups) and –1.97 (methyl groups) ppm (Figure 4). The use of the solid-state ^{29}Si NMR technique allowed us to observe between 250 and 1000 °C the following features: (i) appearance of a peak at –5 ppm (250 and 300 °C), (ii) appearance of another signal centered at –21 ppm (500 °C) besides those at –5 ppm, (iii) at 800 °C a broad peak at –29 ppm which was also present at 1000 °C. At 1000 °C the ^{29}Si NMR spectra displayed a signal at –47 ppm (expected range for a silicon nitride ceramic).[4]

The evolution –9 → –5 → –21 → –29 → –47 ppm could be explained as follows.

The first step transformation "–9 → –5" is the polyaddition of vinyl groups which is completed by 500 °C, as indicated by ^{13}C

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(4) Carunder, K. R.; Carter, R. O., III; Milberg, M. E.; Crosbie, G. M. *Anal. Chem.* **1987**, *59*, 2794.

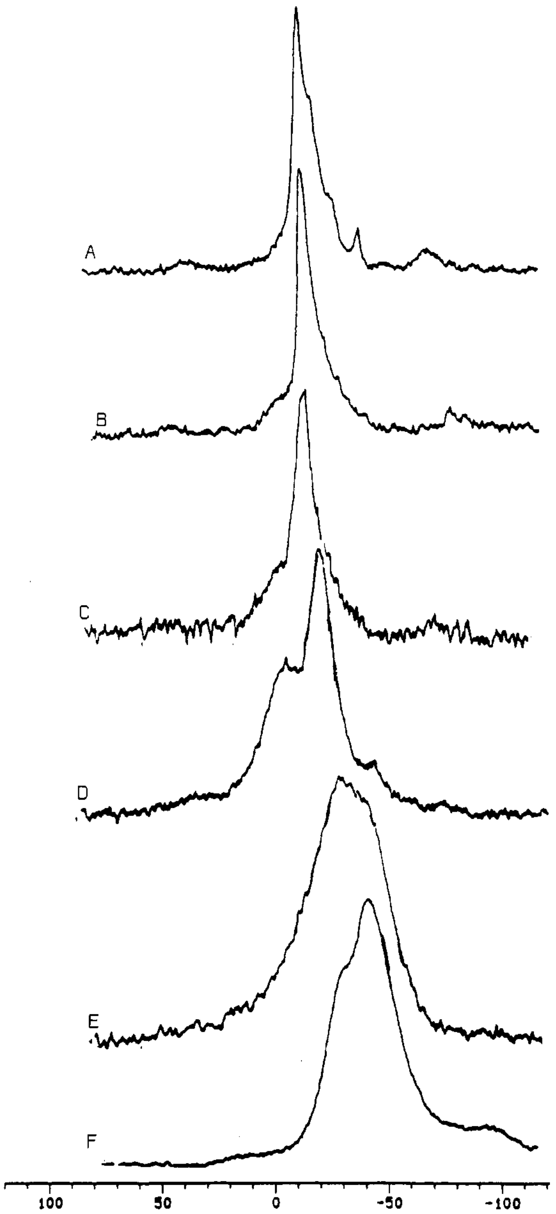

Figure 3. ^{29}Si solid-state NMR spectra of **1**: (A) room temperature; (B) 250 °C; (C) 300 °C; (D) 500 °C; (E) 800 °C; (F) 1000 °C.

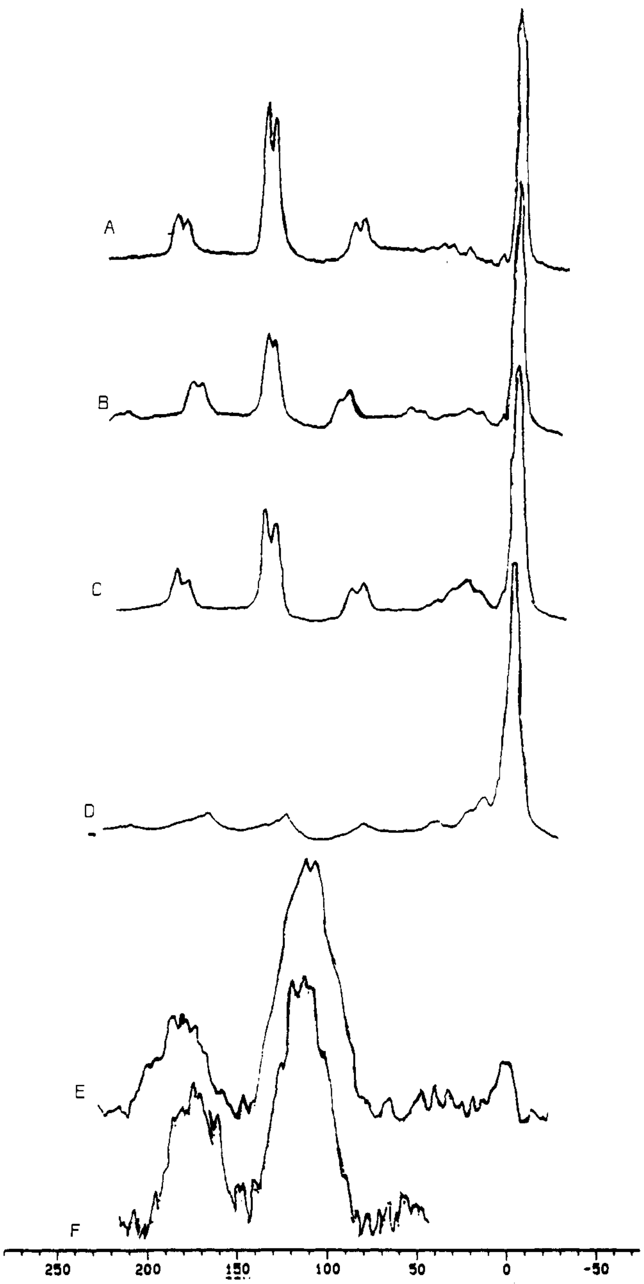

Figure 4. ^{13}C solid-state NMR spectra of **1**: (A) room temperature; (B) 250 °C; (C) 300 °C; (D) 500 °C; (E) 800 °C; (F) 1000 °C. Cross polarization was used.

solid-state NMR (Figure 4).

$$N_2Si(Me)CH{=}CH_2 \rightarrow [N_2Si(Me)CHCH_2]_n$$

A similar deshielding effect was observed in the literature upon moving from (sp^{2}C)(sp^{3}C)SiN$_2$ (^{29}Si δ from −14 to −17 ppm) to (sp^{3}C)(sp^{3}C)SiN$_2$ (^{29}Si δ from −4 to −8 ppm).[5] Moreover, a similar ^{29}Si chemical shift (−6 ppm) was assigned to a $[SiN_2C_2]_n$ species.[6] The IR spectra showed that the characteristic $\nu_{C=C}$ (stretching) and $\nu_{vinyl\ CH_2}$ (deformation), respectively, at 1592 and 1403 cm^{-1} disappeared between 300 and 500 °C.

The second or concomitant step "−5 → −21" is the formation of polymers possessing Si–H bonds. Indeed, IR spectra of the sample obtained after pyrolysis at 500 °C showed a band at 2193 cm^{-1} which has been attributed to SiH.[7] This band was very weak at 300 °C but intense at 500 °C. Such a formation of SiH has already been observed when a polymer derived from the tetraaminosilane Si(NHEt)$_4$ was heated at 800 °C. In this case, such a bond arose from cleavage of a silicon–nitrogen bond. In our case, a silicon–carbon bond cleavage is proposed on the basis of the gaseous products (mainly methane) evolved between 500 and 800 °C. Only a small amount of ammonia was detected between 400 and 550 °C.

The following step (δ(^{29}Si) from −21 to −29 ppm) is likely the transformation C–Si(H)N$_2$ → C–SiN$_3$, i.e. the dehydrocoupling leading to Si–N bond formation from SiH and NH bonds. Indeed, the Si–H vibration exhibited in the IR spectra at 800 °C is extremely weak. Such a hypothesis seemed to be corroborated by examination of some ^{29}Si NMR values reported in the literature. A similar shielding effect has been observed upon moving from (sp^{3}C)Si(H)N$_2$ (δ(^{29}Si) from −24 to −31 ppm) to (sp^{3}C)SiN$_3$ (δ(^{29}Si) from −33 to −35 ppm).[5]

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(5) Kwet Yive, N. S. C.; Corriu, R.; Leclercq, D.; Mutin, P. H.; Vioux, A. *New J. Chem.* **1991**, *15*, 85 and references therein.

(6) Gerardin, C.; Taulelle, F.; Livage, J. *J. Chim. Phys.* **1992**, *89*, 461.

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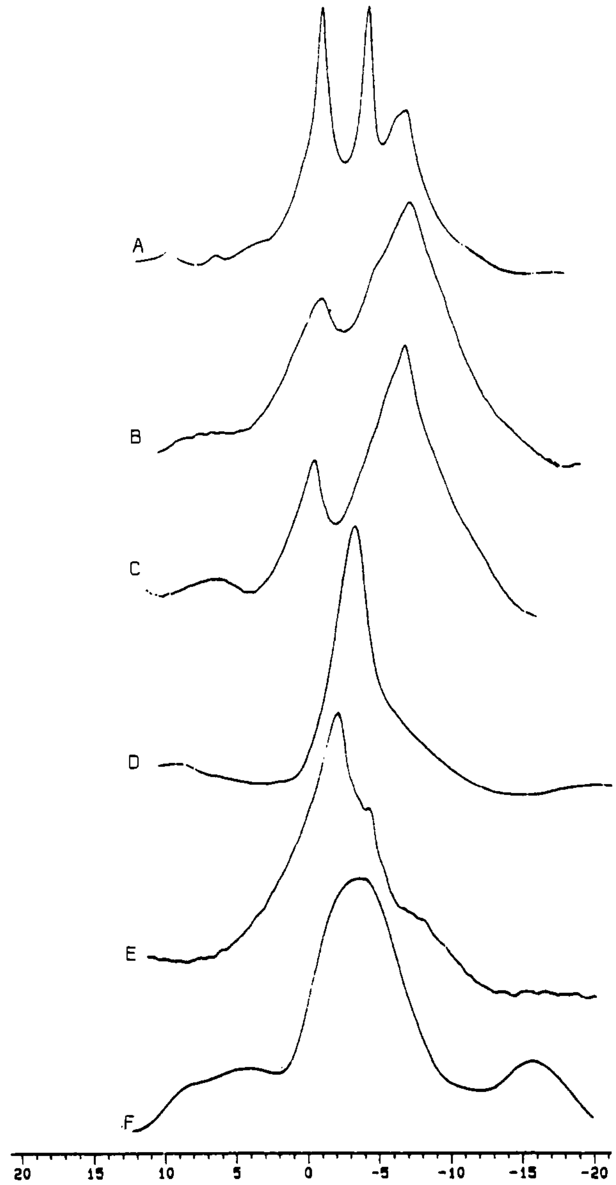

Figure 5. ^{1}H solid-state NMR spectra of **1**: (A) room temperature; (B) 250 °C; (C) 300 °C; (D) 500 °C; (E) 800 °C; (F) 1000 °C.

The next main transformation at high temperature (>800 °C) (see Figure 3) is the cleavage of the last Si–C bonds, i.e. the formation of "ceramic" silicon nitride from $CSiN_3$. This reaction led also to graphite. The ^{13}C solid-state NMR spectrum of the sample heated at 800 or 1000 °C showed the presence of two broad signals centered at 175 and 111 ppm assignable to graphite. Indeed, these values are close to those found in early publications:[8] the low-shielding peaks are assigned to aromatic type environments, and the high-shielding signals are assigned to carbon in a tetrahedral bonding arrangement. Up to 1000 °C no signal for β-silicon carbide in the ^{13}C NMR spectrum (normally single peak between 18 and 24 ppm depending of the crystalline size)[9] was observed. After the sample was heated at 1400 °C, X-ray powder diffraction showed that β-SiC was formed. The formation of β-SiC can be explained either by the $(SiCN_3)_x$ species which are still present at 1000 °C (shoulder at +29 ppm in ^{29}Si solid-state NMR) or more conveniently by the recombination of Si_3N_4 with carbon. Indeed, the formation of β-silicon carbide from the combination of α-silicon nitride and carbon at 1500 °C has already been observed.[8,10]

Conclusion

^{29}Si solid-state NMR spectroscopy seemed to be one of the best techniques to follow the transformation of polysilazane subjected to pyrolysis. The silicon atom environment progressively changed from $N_2Si(Csp^2)(Csp^3)$ to $N_2Si(Csp^3)_2$, $N_2SiH(Csp^3)$, $N_3Si(Csp^3)$, and finally C_xSiN_{4-x}.

Such an evolution is somewhat different from that observed during the pyrolysis of hydrogenovinylsilazanes obtained from aminonolysis of dichlorovinylsilane.[6] ^{13}C solid-state NMR as well as IR, although not so useful, gave additional information corroborating ^{29}Si NMR observations. Taking into account these results, work to elucidate structures of other oligomer precursors of silicon nitride is in progress.

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