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Magnetic resonance characterization of solid-state intermediates in the generation of ceramics by pyrolysis of hydridopolysilazane

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Chemical intermediates produced from the pyrolysis of hydridopolysilazane (HPZ) were studied in the solid state by multinuclear nuclear magnetic resonance and electron spin resonance. When pyrolysed at temperatures of 1200 °C, uncured HPZ forms a ceramic material with a composition of $Si_{2.2}N_{2.2}C_{1.0}$. A series of HPZ-derived ceramics was produced using a number of different heat-treatment temperatures, varying between 300 and 1200 °C. Solid-state magnetic resonance data generated from this set of HPZ-derived ceramics elucidate important features of this complex transformation. Silicon atoms initially exist in two types of sites in the polymer, $>NSi(Me)_3$ and $(>N)_3SiH$ sites. Upon pyrolysis between 300 and 400 °C, the silazane cyclizes and cross-links, forming an intractable, insoluble solid. Increasing the pyrolysis temperature to between 400 and 600 °C creates a matrix that is partially inorganic; at heat-treatment temperatures in this range, many of the C–H bonds of the starting polymer are cleaved. Elevating the heat-treatment temperature to between 600 and 1200 °C generates a series of chemical structures with silicon in a tetrahedral site of the general form $SiN_{4-x}C_x$, where $x = 0, 1, 2, 3, 4$. No crystalline forms of Si_3N_4 or SiC were detected in the material prepared at even the highest heat-treatment temperature of 1200 °C.

1. Introduction

Recently, polysilazanes (polymers having a backbone with an alternating SiN sequence) have been utilized as ceramic precursors. These polymers form Si_3N_4 or a heterogeneous mixture of SiCNO ceramics when pyrolysed [1–8]. This synthesis route has proved quite successful in producing structural components (fibres with micrometre-size diameters) that are difficult or impossible to produce via traditional powder-based processing techniques. Because there is a high demand for these structural components, this has generated an intense interest in finding new polymeric ceramic precursors. However, the mechanism by which a polymer is converted to a ceramic during pyrolysis is not well understood. In order to design better synthesis and pyrolysis approaches, it is important to understand the pyrolytic conversion in detail. The pyrolytic conversion of a polysilazane to a silicon nitride ceramic is a very complicated process involving multiphase chemistry. Often it is the gas-phase products, among the many pyrolysis intermediates, that are analysed, while the solid-phase intermediates are largely ignored.

The solid-phase intermediates have often been ignored because they have not easily lent themselves to the available physical and chemical analysis techniques. The solid pyrolysis intermediates have sometimes been analysed via a combination of three techniques: X-ray crystallography, vibrational spectroscopy and solid-state magnetic resonance. Solid-state magnetic resonance has often proven to be the most informative tool of the three, because it is capable of probing both regions with long-range order (crystalline regions) and regions with only very short-range order (amorphous regions), and the resolution is often adequate for determining local chemical structure [9]. X-ray crystallography shows more promise with materials exhibiting long-range order, while vibrational spectroscopies of inorganic materials typically exhibit broad absorption bands at low wave numbers with low resolution.

The focus of this study is to elucidate the gross chemical changes occurring in the solid state during the course of the pyrolysis of hydridopolysilazane. This type of polysilazane is one of the most successful producing SiCNO ceramics in both high yield and high purity [6], and has found applications as a precursor for ceramic fibres [6], a ceramic binder [10] and as a precursor to boron- and phosphorus-doped silicon nitrides [11, 12]. However, little is known about the mechanism of conversion, except for the work of Legrow *et al.* [6]. In their paper, the analysis centred on characterizing the starting material and finished SiCNO product. The gas-phase pyrolysis products were analysed for samples of

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hydridopolysilazane fibres (HPZ which had been melt spun and cured with $HSiCl_3$), and for the most part the solid-state intermediates produced during pyrolysis were not discussed.

2. Experimental procedure

Hydridopolysilazane was synthesized by slowly adding 300 g trichlorosilane to 800 g hexamethyldisilazane, $(Me_3Si)_2NH$, at 25 °C. Because of the sensitivity of chlorosilanes to moisture, this reaction was performed under an inert atmosphere of anhydrous argon, as described previously [6]. During the addition of $HSiCl_3$, the reaction proceeded exothermically, reaching a temperature of 100 °C. The reaction mixture was then heated to a temperature of 230 °C to remove any unreacted starting materials and any low molecular weight oligomers. The resulting translucent yellow solid, hydridopolysilazane polymer (yield = 150 g), was then stored in a glovebox with an inert atmosphere of dry nitrogen before pyrolysis. In our preparation of hydridopolysilazane, no further processing was performed, i.e. no melt spinning and no curing.

Each sample was produced by pyrolysing 3–5 g polymer in a quartz combustion boat in a programmable tube furnace (Lindberg Series 54000) capable of achieving temperatures of 1200 °C. The pyrolysis chamber consisted of an air-tight quartz tube sealed at one end and open at the other. A vacuum apparatus was attached to the open end of the tube, producing a vacuum ≤ 50 mtorr (1 torr = 133.322 Pa) over each sample during the course of each pyrolysis. Starting at ambient temperature, the heating schedule consisted of five steps: (1) an initial 0.5 °C min^{-1} ramp to 250 °C, (2) a 4 h hold at 250 °C, (3) a 1 °C min^{-1} ramp to the final pyrolysis temperature (HTT), (4) a 4 h hold at the final pyrolysis temperature, and (5) pyrolysis quenching, during which the sample was allowed to cool back to ambient temperature. Prior to spectroscopic analysis, all pyrolysed samples were ground into a fine powder with an alumina mortar and pestle.

All ^{29}Si data were obtained on a modified Chemagnetics M260-S solid-state nuclear magnetic resonance (NMR) spectrometer operating at a static magnetic field strength of 6.1 T (261.6 MHz ^1H frequency) using the technique of direct polarization (i.e. Zeeman polarization of ^{29}Si by spin-lattice relaxation) and magic-angle spinning (DP-MAS). ^{29}Si chemical shifts were referenced to a solid-state calibration standard, tetrakistrimethylsilylmethane (TTMSM), which has a ^{29}Si chemical shift of − 1.65 p.p.m. [13, 14] relative to the 0 p.p.m ^{29}Si chemical shift of liquid tetramethylsilane (TMS). DP-MAS spectra were acquired using a 90° pulse width of 7 μs and a recycle delay of at least $4 \times T_1^*$ for samples with HTT < 900 °C, where T_1^* is defined as the time it takes for the longitudinal relaxation to recover to $1/e$ of its initial value under a saturation-recovery pulse sequence. T_1^* is used here because the longitudinal relaxation for almost every sample gave highly non-exponential behaviour. For samples with HTT > 900 °C the long relaxation times did not permit full magnetization recovery between acquisitions.

^{29}Si CP-MAS experiments were performed using a ^1H 90° pulse of 7μs and a spin-lock field of 35.7 kHz. Recycle delays were always greater than or equal to $5 \times {}^{H}T_1$ in order to ensure full recovery of the ^1H spin system.

All solid-state ^{15}N spectra were acquired on samples *without* isotopic enrichment on a severely modified NT-200 spectrometer operating at a static field strength of 4.7 T (^1H Larmor frequency of 200 MHz), using a probe [15] with a large sample capacity (2.5 cm^3) and an MAS rate up to 4 kHz. In each case, a ^1H $\pi/2$ pulse of 13.5 μs and a CP contact time of 1 ms were used.

^{13}C CP-MAS spectra were obtained on the 6.1 T spectrometer, using a home-built probe with a MAS system based on the Chemagnetics bullet design, capable of MAS speeds of 7 kHz. ^1H $\pi/2$ pulse widths of approximately 4.5 μs and a spin-locking field of 55.5 kHz were used in each case.

^1H CRAMPS spectra were obtained at 187 MHz on a heavily modified Nicolet NT-200 NMR spectrometer that has been described previously [16]. The BR-24 multiple-pulse sequence [17] and MAS speeds of 1.5–2.0 kHz were used; typical parameter settings were ^1H $\pi/2$ pulse widths of 1.3 μs and small window values, τ, of 3.0 μs. One data acquisition point was acquired per multiple-pulse cycle, for a total of 256 points. Each of the ^1H CRAMPS spectra displayed here is the result of averaging 1024 transients.

All electron spin resonance (ESR) spectra were obtained on a Bruker Model ESP 300 X-band CW ESR spectrometer. Each spectrum was obtained with the following experimental parameters in common: (1) a modulation frequency of 100 kHz; (2) a modulation amplitude of 1 G; (3) a conversion time of 5.12 ms (time the system dwells at one field strength before a point is accumulated and the applied field is stepped to its next value); (4) an RC filter time constant of 40.76 ms; (5) an incident microwave power of approximately 200 μW with the cavity tuned for a klystron frequency of approximately 9.65 GHz; (6) a sweep width of 200 G about a centre frequency of 3440 G.

Elemental analysis for silicon, nitrogen, carbon and hydrogen was performed by Galbraith Laboratories, Knoxville, TN, USA.

3. Results and discussion

Many polysilazane pyrolysis experiments have attempted to produce materials with nominal compositions approaching that of Si_3N_4. For several applications, the desired product is a specific crystalline form of Si_3N_4, the α form. If one's goal is to achieve specificity between α, β and amorphous Si_3N_4 in the pyrolysis product, it is desirable to have a detailed chemical understanding of the pyrolysis mechanisms. This understanding can be facilitated by identifying which chemical structures are in abundance in the polymer and identifying chemical structures produced at each step in the pyrolysis. Originally, it had been proposed that the unpyrolysed polymer contained four- and

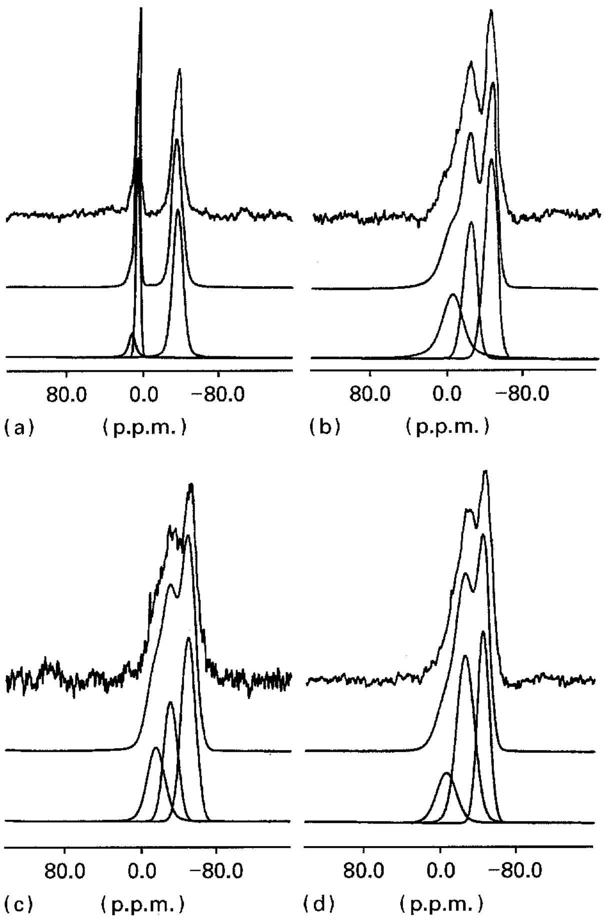

Figure 1 DP-MAS ^{29}Si NMR spectra of HPZ samples pyrolysed at (a) 300 °C, (b) 600 °C, (c) 900 °C and (d) 1200 °C. Top row, experimental DP-MAS ^{29}Si spectra; middle row, sum of deconvolutions of spectra; bottom row, deconvoluted contributions of spectra.

five-membered silazane rings [6] and that the presence of these ring systems could be responsible for the selectivity of the final pyrolysis product. Cyclic silazanes might occur in the polymer, but multinuclear NMR studies reported here indicate that they do not involve structures with $N_2Si(Me)_2$ or N_2SiH_2 incorporated into the rings.

Hydridopolysilazane polymer initially exists with silicon atoms in two different types of sites, trimethylsilyl sites, $NSi(Me)_3$, and hydridosilazane sites, N_3SiH. Both types of silicon sites are clearly evident in the ^{29}Si DP-MAS spectrum of the polymer pyrolysed at 300°C, which is shown in Fig. 1a. The resonance at 2.4 p.p.m. represents the trimethylsilyl moiety and the resonance at − 39.5 p.p.m. represents the hydridosilazane moiety. Confidence in the assignment of these two chemical shifts can be strengthened via ^{1}H–^{29}Si dipolar dephasing experiments (Fig. 2). Our application of this experiment consists of four steps, following the generation of transverse ^{29}Si magnetization: (1) gating the decoupler off for a period τ so that the ^{29}Si magnetization dephases under the dipolar Hamiltonian; (2) applying simultaneous refocusing π pulses of both ^{1}H and ^{29}Si channels; (3) allowing the system to dephase under the dipolar Hamiltonian for another period τ; and (4) finally acquiring the remaining ^{29}Si signal with high-power ^{1}H decoupling. The high-shielding ^{29}Si peak at − 39.5 p.p.m. decays to zero amplitude in less than 6 ms dipolar dephasing time, indicating that it arises solely from hydrogen-bearing silicon atoms [18] (see Fig. 2a). This finding implies that before pyrolysis the polymer has not undergone a significant degree of cross-linking to form silicon sites of the general form SiN_4, with no directly bonded hydrogen(s), according to a hypothetical scheme such as

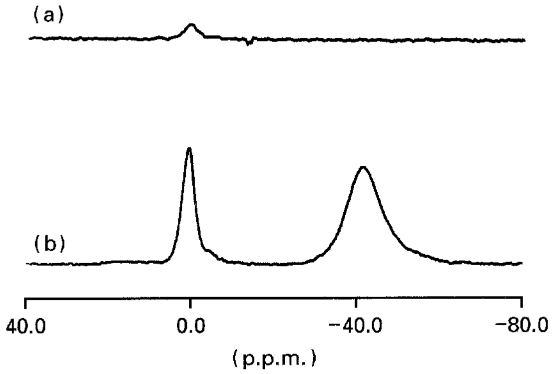

Figure 2 ^{1}H–^{29}Si dipolar-dephasing behaviour of the HPZ sample prepared at a HTT of 300 °C with a dipolar-dephasing time of (a) 6000 μs and (b) 20 μs.

$$(\geq N)_3SiH + HN(Si\leq)_2 \rightarrow (\geq N)_3SiN(Si\leq)_2 + H_2\,(g) \qquad (1)$$

The low-shielding peak at 2.4 p.p.m. does not decay to zero after 6 ms of dephasing time because the ^{1}H–^{29}Si dipolar coupling between protons and the ^{29}Si nucleus in the $Si(Me)_3$ group is exceedingly weak (see Fig. 2b) due to rapid methyl-group rotation. The strongest ^{1}H–^{29}Si dipolar couplings would arise from protons in the β position from silicon in the $Si(Me)_3$ group, i.e. where the bonding sequence between the ^{29}Si and ^{1}H proton can be represented as ${}^{\beta}$H–${}^{\alpha}$N–Si in amine moieties or ${}^{\beta}$H–${}^{\alpha}$C–Si in methyl moieties. In either case, the internuclear Si–H distance is greater than 0.2 nm [19] and the ^{1}H–^{29}Si dipolar coupling would be highly attenuated by rapid methyl-group rotation, or by rapid wagging vibrations of the amine N–H moiety. Because of the weakness of any possible couplings, the 2.4 p.p.m. resonance shows little or no decay from a dipolar mechanism.

The ^{13}C CP-MAS spectrum of the HPZ sample prepared with a heat-treatment temperature of 300°C (Fig. 3) gives a single resonance at 2.7 p.p.m. (relative to TMS) and a full-width at half-height (FWHH) of 53 Hz. This extremely small solid-state NMR linewidth and single chemical shift is a strong indication that the ^{13}C chemical environment varies very little throughout the material. Furthermore, the model compound hexamethyldisilazane gives a very similar ^{13}C chemical shift (2.9 p.p.m.) for its trimethylsilyl resonance [20]. This implies that the carbon in polysilazane after a HTT of 300°C is solely in the form of trimethylsilyl groups, and that no reactions involving C–H bond cleavage have yet taken place at this HTT; no methylene resonances are observed in the ^{13}CP–MAS spectrum of the HPZ sample prepared with HTT = 300°C.

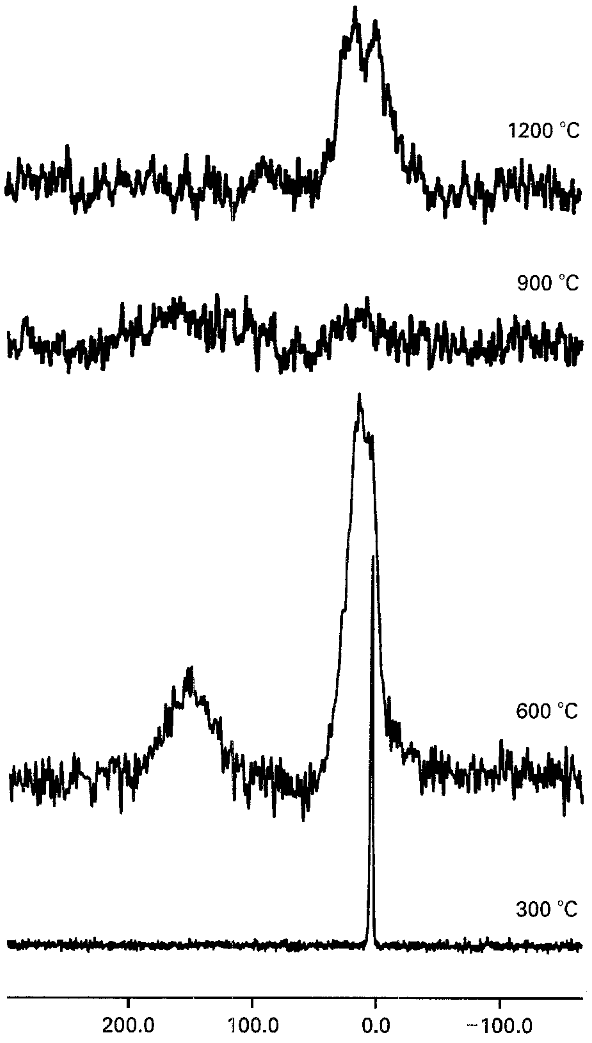

Figure 3 ^{13}C CP-MAS spectra of HPZ samples prepared with the heat-treatment temperatures shown.

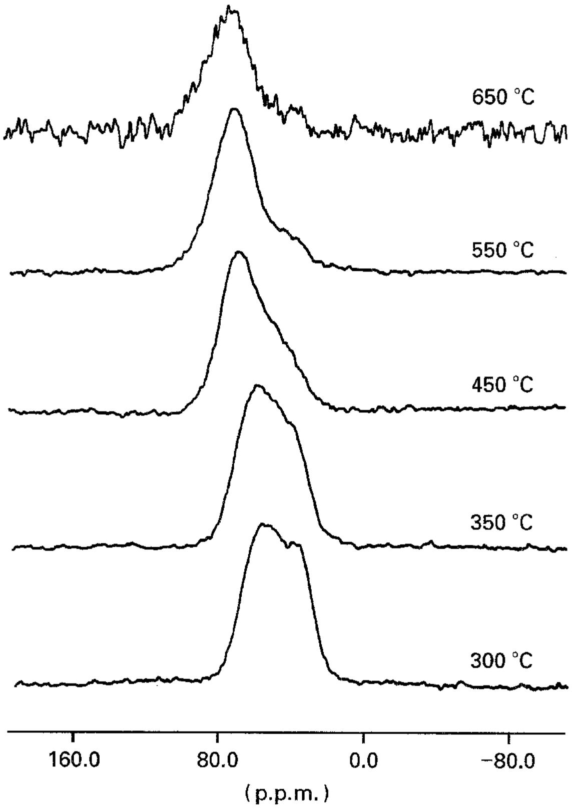

Figure 4 Natural abundance ^{15}N CP-MAS spectra of HPZ samples pyrolysed at the heat-treatment temperatures shown. The CP contact time is 1 ms for each spectrum.

Fig. 4 shows natural-abundance ^{15}N CP-MAS spectra of HPZ samples pyrolysed at various temperatures. The spectrum of the sample prepared with HTT = 300°C shows nitrogen in two forms, Si_3N and Si_2NH, at approximately 55 and 37 p.p.m. (relative to a liquid ammonia chemical shift of 0 p.p.m.). These chemical shift assignments were made partly on the basis of ^1H–^{15}N dipolar dephasing behaviour. Duff and Maciel published two examples of using the ^1H–^{15}N dipolar-dephasing method with 70 μs and 100 μs dephasing periods to distinguish between ^{15}N that is directly bonded to protons and ^{15}N that is not bonded to protons, in biuret-rich [21] and isocyanurate-rich [22] 4,4′methylenebis(phenylisocyanate)-based resins. In our application of the method to pyrolysed HPZ samples, we found that dephasing times greater than 100 μs were necessary to distinguish between Si_3N and Si_2NH resonances. After 120 μs dipolar dephasing, only the lower-shielding peak at 55 p.p.m. remained, indicating that it is weakly coupled to proton(s), while the other resonance is dipolar coupled strongly to proton(s). The relative strength of the ^1H–^{15}N dipolar coupling is corroborated by the cross-polarization dynamics in these materials. For contact times less than or equal to 60 μs, only the higher-shielding resonance gives any significant intensity.

^{15}N proves to be a valuable probe for determining the degree of cross-linking in samples prepared at HTTs below 650 °C. At the lowest pyrolysis temperature of this study (HTT = 300 °C) the relative amounts of cross-linked nitrogen (Si_3N) to uncross-linked nitrogen (Si_2NH) are closest to being equal (see Fig. 4). As the pyrolysis temperature is increased, a greater degree of cross-linking occurs, producing a higher intensity of the lower-shielding (Si_3N) ^{15}N NMR peak relative to the higher-shielding (Si_2NH) peak. Shown below are two possible reactions that would account for this behaviour, i.e. consuming $HNSi_2$ nitrogen sites and producing Si_3N nitrogen sites in the solid phase. A combination of these reactions would also produce the two gaseous products, CH_4 and H_2, which are commonly observed in the pyrolysis of polysilazanes [6]

$$((CH_3)_2N)_3SiCH_3 + HN(Si\leqq)_2 \rightarrow ((CH_3)_2N)_3SiN(Si\leqq)_2 + CH_4(g) \quad (2)$$

$$(\geqq N)_3SiH + HN(Si\leqq)_2 \rightarrow (\geqq N)_3SiN(Si\leqq)_2 + H_2(g) \quad (3)$$

If both of the above reactions were taking place in the HPZ-derived ceramics, the ^{29}Si and ^{13}C chemical shift and dipolar-dephasing behaviours of the solid-phase reactant would not be very different from those of the solid-phase products; on the other hand, the ^{15}N

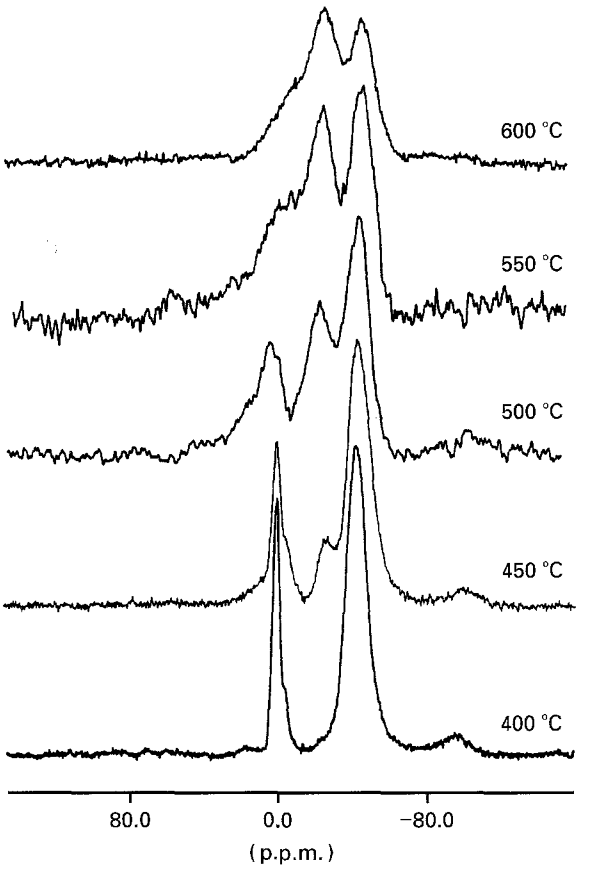

Figure 5 ^{29}Si CP-MAS spectra of HPZ samples prepared with the heat-treatment temperatures indicated.

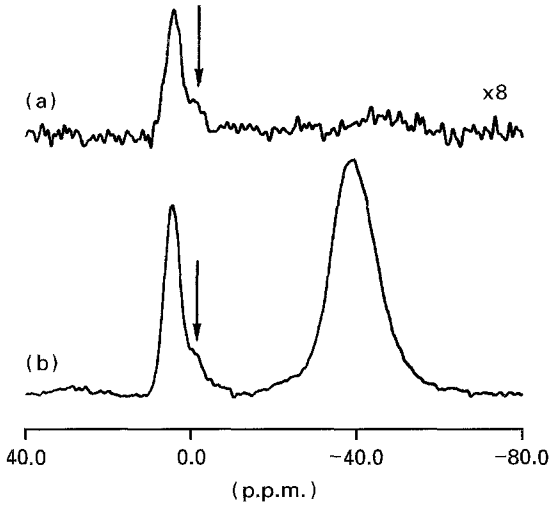

Figure 6 ^{1}H–^{29}Si dipolar-dephasing behaviour of a sample of HPZ prepared with a heat-treatment temperature of 400 °C. (a) with 6000 μs of dipolar-dephasing time and the vertical scale expanded by a factor of 8; (b) with a 20 μs dephasing period. The arrows denote where the $(\geqslant \mathrm{N})_2\mathrm{Si}(\mathrm{CH}_3)_2$ resonances should appear.

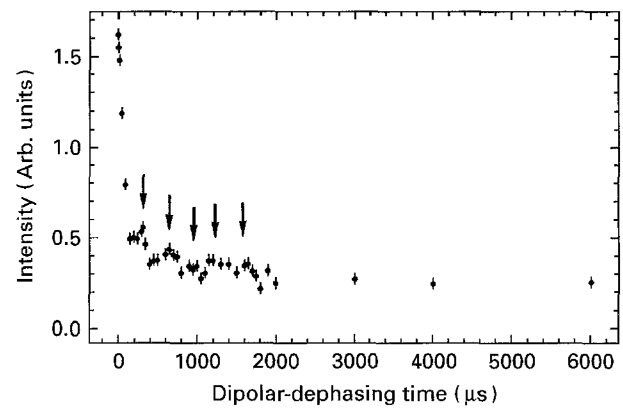

Figure 7 ^{1}H–^{29}Si dipolar-dephasing intensities of the − 47 p.p.m. peak observed for the HPZ sample prepared with a HTT = 600 °C, as a function of dipolar-dephasing time. The arrows indicate times that are integral numbers of rotor periods.

chemical shift and dipolar-dephasing behaviour of reactants and products would change drastically.

As the heat-treatment temperature is raised to 400 °C, the chemical composition of the material changes perceptibly. A new resonance appears at − 2.1 p.p.m. between the two major peaks in the ^{29}Si CP-MAS spectrum (Fig. 5). Peaks having a ^{29}Si chemical shift in this range correspond to silicon in $(\geqslant \mathrm{N})_2\mathrm{Si}(\mathrm{C}\leqslant)_2$ sites [23]. However, the ^{13}C CP-MAS spectrum of a HPZ sample prepared with a HTT of 400°C is essentially identical to that of the HPZ sample prepared with HTT = 300°C; the ^{13}C CP-MAS spectra show only a single narrow resonance at 1.7 p.p.m. The ^{29}Si and ^{13}C data taken together indicate that, even though the silicon chemical environment is altered, the carbon chemical environment remains fairly constant, i.e. carbon remains in methyl sites. Both the ^{29}Si and ^{13}C spectra imply conversion of at least a portion of the trimethylsilyl groups to dimethylsilyl groups, $(\geqslant \mathrm{N})_2\mathrm{Si}(\mathrm{CH}_3)_2$. This assignment is supported by the ^{1}H–^{29}Si dipolar-dephasing results obtained on the HPZ sample prepared with HTT = 400°C; i.e. the dephasing behaviour of both the 2.4 p.p.m. ^{29}Si resonance and − 2.1 p.p.m. ^{29}Si resonance are quite similar (Fig. 6).

The decay envelope of the ^{29}Si signal in the ^{1}H–^{29}Si dipolar-dephasing experiment is non-exponential for all samples, and the degree of non-exponentiality increases with increasing HTT. Fig. 7 shows that the dipolar-dephasing decay of the ^{29}Si magnetization of the sample prepared with HTT = 600°C is modulated at roughly two frequencies, one having a period equal to the rotor period and the other having a period equal to twice a rotor period. This modulation pattern of the ^{29}Si magnetization in a ^{1}H–^{29}Si dipolar-dephasing experiment has been observed before in systems exhibiting limited or no ^{1}H–^{1}H spin diffusion [24], and is a direct result of the fact that the ^{1}H concentration becomes lower as the HTT is raised, so that the protons are more dispersed in the higher HTT sample. This modulation pattern becomes more conspicuous as the HTT is raised. The most reasonable assignment for a ^{29}Si resonance with this dipolar-dephasing decay behaviour and a − 2.1 p.p.m. chemical shift is a cyclic trisilazane containing $\mathrm{Si(Me)}_2$ groups, although other cyclic silazane structures would also be possible [25]. If several different ring structures are formed, they cannot be distinguished by either dipolar-dephasing behaviour, or by ^{29}Si chemical shift differences, because of lack of sufficient resolution and similarities in dipolar-dephasing rates. Wills *et al.* [26], in their review of silazane-derived ceramics, point out that a six-membered cyclic silazane, hexamethylcyclotrisilazane, is very stable at temperatures up to about 500°C. This is in agreement with the hypothesis of Legrow *et al.* [6], that the steric effects of the bulky methylsilyl groups should make the formation of cyclic silazanes more favourable when enough thermal energy is supplied to the matrix during the early stages of the pyrolysis. Also, as the HTT is increased above 400°C, there is a reduction of relative intensity of the trimethylsilyl resonance at 2.4 p.p.m., indicating that dimethylsilyl groups in the cyclic silazanes may be derived from trimethylsilyl groups. This could be accomplished via the exchange of a methyl group with an amine group (see Reaction 2) and might be responsible for the production of methane, which is commonly observed in the gas phase when heating methyl-containing polysilazanes [6, 26, 27].

The next significant change in chemical composition as a function of increasing HTT occurs in the sample prepared with HTT = 600°C. The ^{13}C CP-MAS spectrum of this sample shows a broad peak at 140 p.p.m. (Fig. 3). The width and chemical shift of this peak are characteristic of graphite or polyaromatic compounds. The ^{29}Si DP-MAS spectra of the material formed at this heat-treatment temperature show only three broad peaks, at -5.2, -25.0 and -47.1 p.p.m. (Fig. 1b, top row). The intensity of the sharp trimethylsilyl peak at 2.4 p.p.m. has been reduced to zero, as shown in the deconvolution in Fig. 1b (bottom row). Instead we observe intensity at -5.2 p.p.m., which is the ^{29}Si chemical shift range for a cyclic tetrasilazane (e.g. $[Si(Me)_2NH]_4$) and intensity at -25.0 p.p.m., which is in the chemical shift range for amorphous silicon carbide [28–30]. However, it is probable that a mixed SiC–Si_3N_4 intermediate is formed instead of a pure silicon carbide. Gerardin *et al.* [31] have pointed out that the silicon environment giving rise to the peak at approximately -25 p.p.m. is probably silicon bonded to three nitrogens and one carbon, $\geqslant$CSi(N$<$)$_3$, rather than silicon bonded to four carbons, **Si**(C$\leqslant$)$_4$. Intensity arising from silicon in both **Si**(C$\leqslant$)$_4$ sites and ($>$N)$_3$**Si**C$\leqslant$ sites probably overlaps in the region around -25 p.p.m. Also the peak at -25 p.p.m. decays appreciably after 6 ms dipolar dephasing, indicating that it is weakly coupled to protons (Fig. 8). The third peak at -47.1 p.p.m. has the proper chemical shift and dipolar-dephasing behaviour for amorphous silicon nitride, implying that such sites have been formed in the matrix at 600 °C. As seen in Fig. 8, the -47.1 p.p.m. resonance does not decay to zero, even after a dipolar-dephasing time of 6 ms; thus the chemical environment giving rise to the -47.1 p.p.m. resonance must be at most very weakly coupled to protons, such as would be the case for silicon in a SiN_4 site in which none of the atoms in the β position are hydrogen.

No crystalline forms of Si_3N_4 are evident in the sample; instead it is predominantly amorphous [32]. The ^{29}Si linewidth of amorphous Si_3N_4 is 27 p.p.m. at 59.5 MHz [32], whereas the crystalline forms have linewidths of the order of 2–3 p.p.m. at such a frequency, depending on purity and the concentration of paramagnetic centres in the material. The linewidth of the -47.1 p.p.m. peak is thought to be predominantly caused by a variety of Si–N bond lengths, N–Si–N bond angles and J coupling, not by dipolar broadening from ^{14}N; this interpretation is consistent with theoretical calculations performed by Olivieri and Hatfield [33] for the two crystalline forms of Si_3N_4.

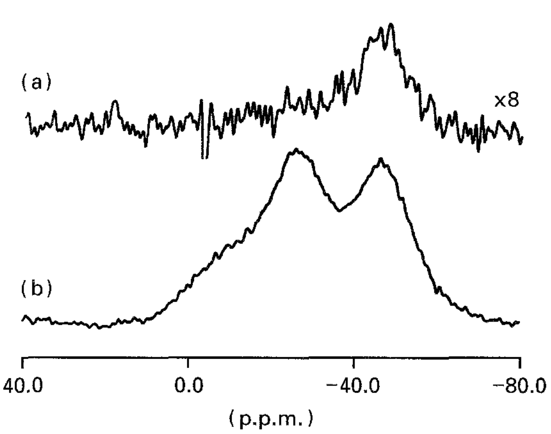

Figure 8 ^{1}H–^{29}Si dipolar-dephasing spectra of HPZ sample prepared with a heat-treatment temperature of 600 °C, (a) after 6000 μs dephasing time and the vertical scale expanded by a factor of 8; (b) after a 20 μs dephasing period.

Most of the significant chemical changes in the HPZ-derived material occur between heat-treatment temperatures of 400 and 600°C. ^{29}Si CP-MAS spectra of the materials prepared at heat-treatment temperatures in this range provide some of the best insights into the chemical composition of the matrix (see Fig. 5). These ^{29}Si CP-MAS spectra clearly display the formation of ring compounds incorporating $>$**Si**(CH$_3$)$_2$ groups at -2 to -6 p.p.m. and the creation of $\geqslant$C**Si**(N$<$)$_3$ sites evident from the resonance at approximately -25 p.p.m. in the ^{29}Si CP-MAS spectrum of the material prepared with HTT = 450 °C. Comparison of the ^{29}Si DP-MAS and CP-MAS spectra of the HTT = 600 °C sample indicates that the lower shielding resonances between -5 and -30 p.p.m. must be more strongly coupled to protons than the -47 p.p.m. resonance, because the relative intensities of the low-shielding resonances are greater in the CP-MAS spectrum relative to the -47 p.p.m. resonance than in the DP-MAS spectrum. This implies that the ^{1}H concentration is not evenly distributed throughout the matrix, but rather is in closer proximity, on average, to the ($\geqslant$C)$_3$**Si**N$<$ sites.

^{15}N CP-MAS spectra of the material prepared with HTT between 550 and 650 °C show depletion of the Si_2NH concentration relative to the Si_3N concentration (Fig. 4). Also, the ^{15}N resonance arising from the tertiary amine shifts from 55 p.p.m. to 80 p.p.m. as the HTT is raised from 300 °C to 650 °C. The breadth of the tertiary amine resonance reflects a wide distribution in the chemical environments of the Si_3N moiety and is a good indicator of how amorphous the material is when prepared at these HTTs. The large linewidths and poor resolution do not permit detailed

TABLE I Elemental composition of HPZ-derived materials as a function of the heat-treatment temprature (HTT)

HTT (°C)	Si (wt %)[a]	C (wt %)[b]	N (wt %)[c]	H (wt %)[c]	Total (wt %)
Polymer	46.99	22.72	23.14	7.86	100.7
300	46.80	21.08	23.75	7.08	98.7
400	50.72	16.22	23.47	5.56	96.0
500	49.22	13.58	27.39	3.38	94.1
600	52.25	11.67	29.16	2.21	95.3
700	54.14	10.79	29.98	0.98	94.9
800	58.49	11.66	29.86	0.68	100.7
900	59.90	11.43	29.79	< 0.5	101.12
1000	58.16	11.42	30.14	0.63	100.4
1100	56.43	11.21	30.11	< 0.5	97.8
1200	58.38	11.58	29.84	< 0.5	99.8

[a] Determined by dissolution followed by either AA or ICP spectroscopic analysis.
[b] Determined by combustion analysis or LECO furnace.
[c] Determined by combustion analysis.

assignments of individual chemical structures in the material. However, the overall lower shielding ^{15}N chemical shift of the $(\geqslant Si)_3N\leqslant$ resonance is most certainly a consequence of the approach of the chemical environment of nitrogen to that of a pure Si_3N_4; that is, the increasing number of Si–N bonds or cross-links in the polymer matrix as a function of increasing HTT means that the local chemical environments of the tertiary amine, e.g. the local bonding geometry, approach that of Si_3N_4, increasing the probability that the β substituent is another nitrogen atom and that the γ substituent is another silicon atom, etc. ^{15}N chemical shifts in the range between 72 and 47 p.p.m. are characteristic of both α and β Si_3N_4 [34], and these are the chemical shift values that are approached by the tertiary amine peak as HTT is increased. ^{15}N CP-MAS spectra with acceptable signal-to-noise ratios could not be obtained for samples prepared with HTTs greater than 650 °C because of the depletion of hydrogen in the sample (see Table I).

For a hydridopolysilzane sample pyrolysed at a HTT of 900 °C, any sharp peaks ranging from -2.4 to -6 p.p.m. are absent in the ^{29}Si DP-MAS spectrum, and the dipolar-dephasing spectra (not given here) show no significant attenuation of any of the ^{29}Si resonances after 6 ms; these observations indicate that the cyclic silazanes and organic silicon moieties are substantially depleted at these elevated temperatures (Fig. 1c). There is a slight broadening of the ^{29}Si DP-MAS resonances of the sample prepared at HTT = 900 °C. This is also the heat-treatment temperature at which maximum unpaired electron spin density occurs (see Fig. 9), indicating that thermolytic bond cleavage becomes facile at this temperature and the resulting unpaired electrons thus formed are reasonably stable in the sample prepared with HTT = 900 °C.

A substantial broadening of the ^{13}C resonances can be noticed in Fig. 3 for the HTT = 900 °C sample. The greater degree of broadening in the ^{13}C spectra relative to the ^{29}Si spectra indicate that the paramagnetic centres are, on average, more strongly coupled to nuclei in the carbon-rich regions of the material rather than in silicon-rich regions. The ^{29}Si DP-MAS spectrum of the material formed from pyrolysis of HPZ at HTT = 1200 °C shows essentially the same chemical composition as that of the HTT = 900 °C sample. However, the HTT = 1200 °C sample does not reflect the same degree of line broadening as that of the 900 °C sample. This reduction of line narrowing could be from two effects, less paramagnetic broadening and/or a higher degree of crystallinity. Attempts to probe crystallinity were made by carrying out experiments using extraordinarily long recycle delays to enhance the signal of any crystalline components, if present (Fig. 10). Several papers have reported ^{29}Si T_1 values of more than an hour for the crystalline forms of SiC [28–30] and Si_3N_4 [34]. Crystalline components in the HTT = 1200 °C sample are expected to have nearly the same relaxation behaviour as that of pure crystalline Si_3N_4, if these components are separated from the amorphous regions of the matrix, because the amorphous regions are expected to contain an overwhelming majority of the relaxation centres, i.e. paramagnetic centres. For the electron-nucleus dipolar coupling mechanism, T_1^{-1}, is proportional to the second moment, which has a $(1/r)^6$ dependence, where r is the distance between the nucleus and the unpaired electron. Fig. 10 implies that an appreciable portion of the silicon atoms of the HTT = 1200 °C sample is far removed from any paramagnetic centres, because the ^{29}Si NMR peaks narrow as the recycle delay is increased, indicating that the

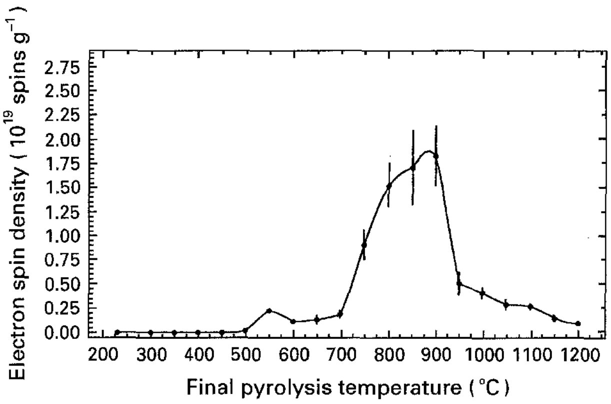

Figure 9 Unpaired electron spin density as a function of heat-treatment temperature.

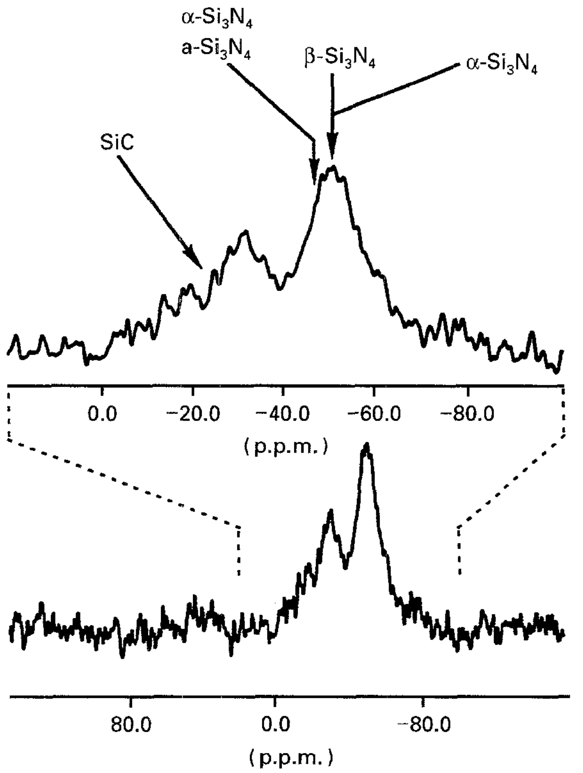

Figure 10 ^{29}Si DP-MAS spectrum of HPZ sample prepared with HTT = 1200 °C, obtained with a recycle delay of 1 h between scans, for a total of 48 scans.

slowly relaxing components arise from a portion of the sample which has a smaller distribution of bond angles and bond lengths, i.e. is more highly ordered. However, the overall ^{29}Si NMR linewidth of the sample prepared with a HTT of 1200 °C is too large to permit the distinction of any specific crystalline forms of SiC or Si_3N_4. The failure to observe any crystalline forms is consistent with the results of Legrow *et al.* [6], who observed only an amorphous matrix via X-ray scattering.

Characterization of the paramagnetic centres themselves could help in elucidating the pyrolysis chemistry of HPZ. Accordingly, ESR spectra were obtained on samples prepared with HTTs ranging from 300 to 1200 °C. Fig. 11 shows most of those ESR spectra. The first appearance of unpaired electrons in the ceramic matrix can be detected in the ESR spectrum of the sample prepared with HTT = 500 °C. For this heat-treatment temperature and for HTT = 550° C the ESR spectrum consists of two lines, one with a g value of 2.0020 and the other with a g value of 2.0140. From several published studies of radicals produced in the pyrolysis of organic materials [29, 35–38], we know that small graphitic domains, or polyaromatics, should form at approximately 500 °C. Following the analogy of pyrolysed organic materials, the unpaired electron spin density should increase in samples heated to higher HTTs, until a maximum unpaired electron spin density is reached at approximately 800 °C [36, 37]. A roughly similar behaviour is observed here in HPZ-derived ceramics. This could be the result of domain formation of polyaromatic compounds within the material during pyrolysis. However, the maximum spin density occurs in the HTT = 900 °C sample, in contrast to the maximum at roughly 800 °C observed in organic materials. The maximum occurs at a different temperature in pyrolysed HPZ because of the presence of radicals other than those associated with graphite, e.g. dangling-bond free radicals with the unpaired electron situated on the silicon atom in a matrix of the SiC [39–41] or Si_3N_4 [42–44] type. As can be seen in Fig. 11, none of the ESR spectra show any hyperfine coupling. Previous ESR studies [38–43] have demonstrated that neither SiC nor Si_3N_4 manifest hyperfine couplings in their pure forms. Also, the g values of paramagnetic centres in SiC, Si_3N_4 and graphite matrices are all approximately 2.002 ± 0.002 and therefore probably could not be distinguished from one another in the ESR spectra obtained in this study.

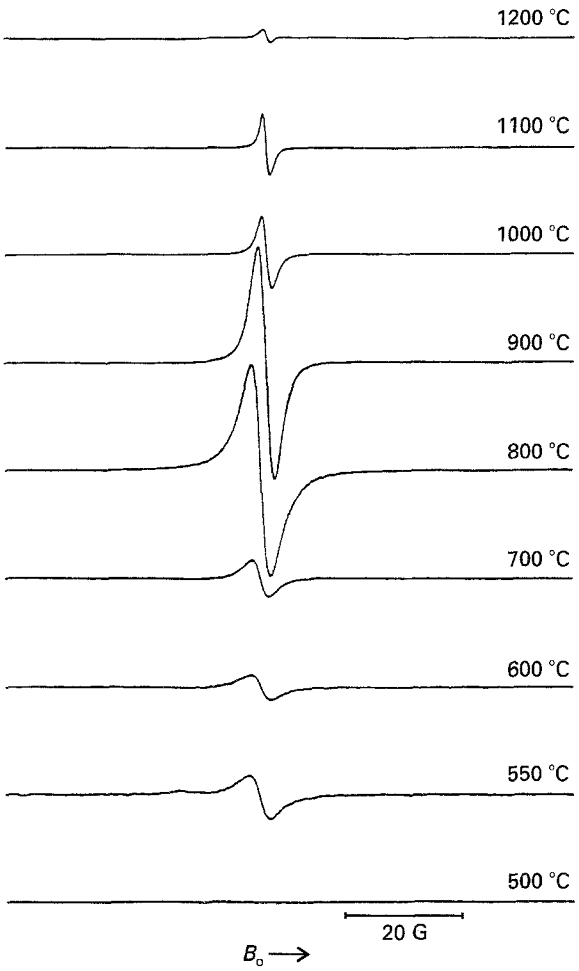

Figure 11 X-band ESR spectra of HPZ samples prepared with HTTs indicated.

Another interesting feature of the ESR spectra is that for samples prepared with HTT = 1000, 1100 and 1200 °C, the lineshapes show asymmetry, with the magnitude of the intensity of the lower-field peak (positive peak) being greater than that of the higher-field peak (negative peak). This lineshape approaches that of a Dysonian lineshape, characteristic of conductors [46, 47], and could indicate that conductive components exist in the HPZ material prepared with HTT greater than 1000 °C. The only known conductive material in the HPZ-derived ceramics that could give rise to a Dysonian ESR lineshape is graphite.

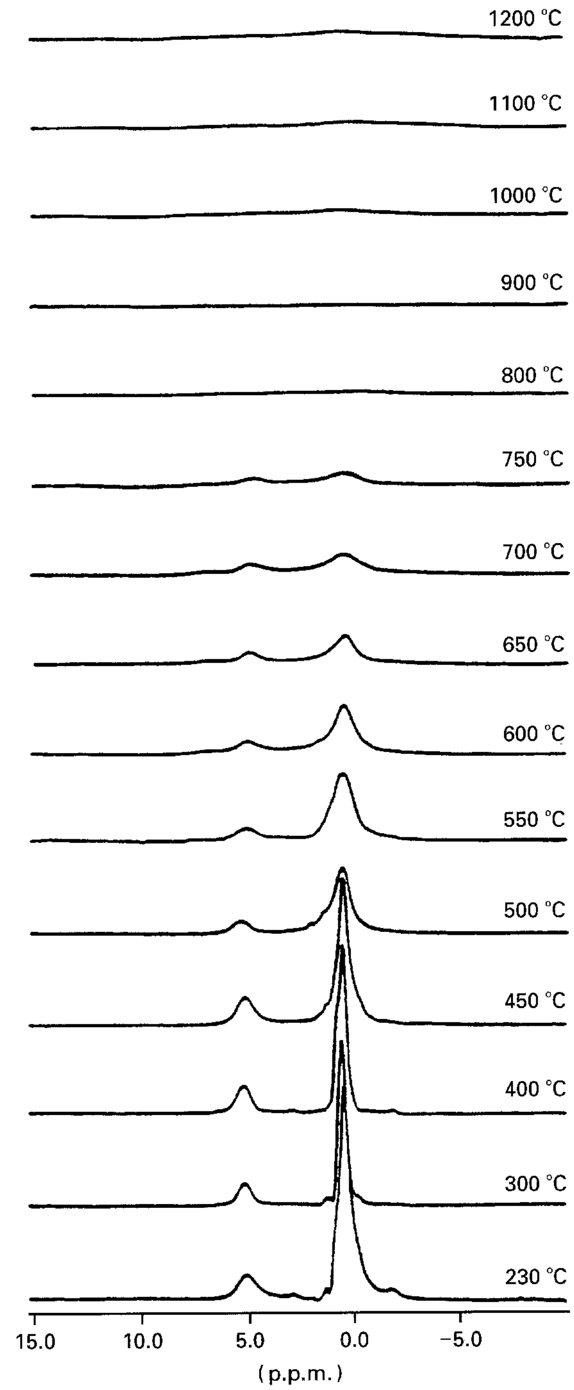

Figure 12 ^{1}H CRAMPS spectra of HPZ samples pyrolysed at the heat-treatment temperatures indicated. Each spectrum represents 1024 repetitions. Vertical scaling kept constant.

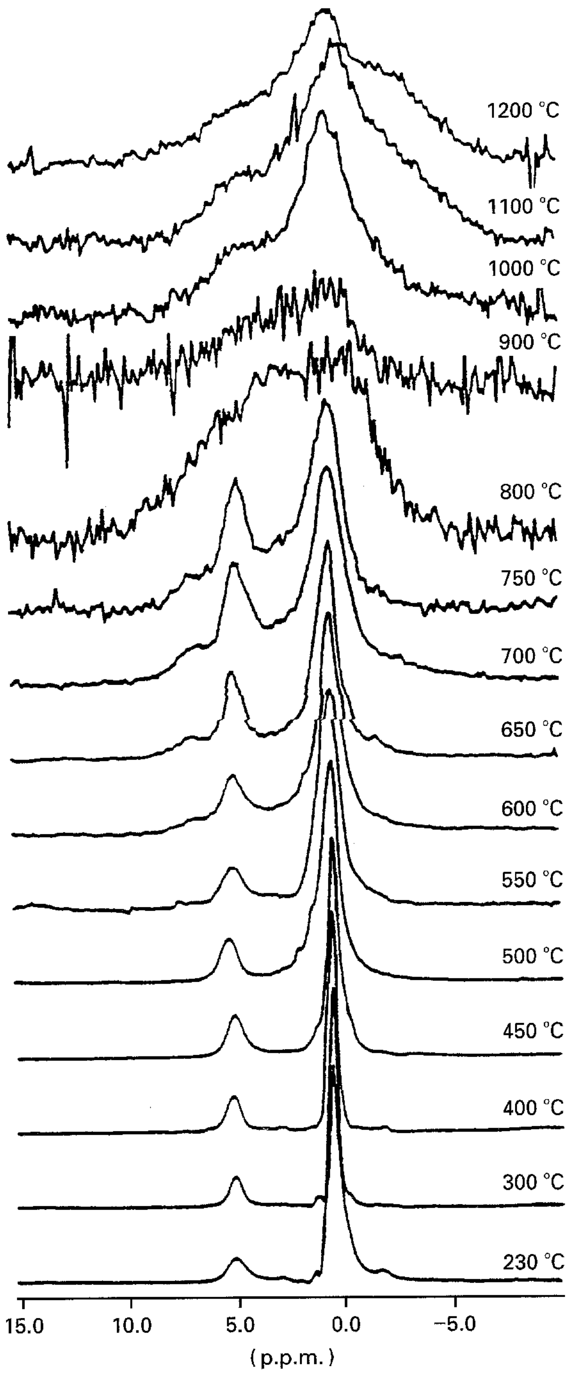

Figure 13 Same as Fig. 11, but each spectrum scaled to the same maximum peak amplitude.

Therefore, it appears that graphite, once formed, is not depleted in the material prepared with a HTT of 1200 °C. Graphite can react with Si_3N_4 at temperatures exceeding 1000 °C and convert it to SiC [48], hence, the ceramics exhibit some chemical heterogeneity even after being heated at 1200 °C.

Many of the solid-state reactions [27] that are proposed to occur in HPZ during pyrolysis consume hydrogen-containing species and result in a set of inorganic compounds. The most important hypothesized reactions taking place in the solid matrix are those that lead to an increased number of Si–N bonds; see Reaction 2. Because of the importance of this pathway, it is important to characterize the hydrogen-containing species in HPZ as a function of pyrolysis temperature.

Figs 12 and 13 show a series of ^{1}H CRAMPS spectra obtained on HPZ samples pyrolysed at different HTTs. All of the spectra show at least two peaks, a higher shielding peak at approximately 0 p.p.m. and a lower shielding peak at 5 p.p.m. On the basis of chemical shifts of model compounds in solution-state NMR, these peaks can be assigned to trimethylsilyl groups, $-Si(CH_3)_3$, and hydridosilyl ($\geq$Si–H) sites [49]. The fact that both of these types of moieties are present in the material, even after heating at 1200 °C, indicates that some portions of the sample are not highly chemically reactive, again reflecting the heterogeneous nature of the pyrolysis product. In samples prepared at HTTs higher than 800 °C, a significant amount of line broadening occurs from the presence of paramagnetic centres and a significant loss of ^{1}H NMR signal can be observed for samples with HTTs exceeding 800 °C. This decrease in the overall ^{1}H intensity is not evenly distributed throughout the spectrum. The methyl proton peak (near 0 p.p.m.) appears to be either depleted or broadened to a much greater extent than the SiH proton resonance. This implies that organic portions of the sample (portions containing CH_3 groups) are either depleted preferentially or are nearer to the free radicals. In samples prepared at heat-treatment temperatures exceeding 600 °C, a lower shielding peak appears at approximately 7 p.p.m. This new resonance is assigned to protons on aromatic structures, and its appearance coincides with the formation of graphite implied by the ^{13}C CP-MAS NMR and ESR results.

One resonance that is not detected in any of the ^{1}H CRAMPS spectra is the proton resonance of amine ($\geq$N–H) species. In the solid state the ^{1}H–^{14}N dipolar coupling cannot be averaged completely by MAS, because the ^{14}N nucleus has a substantial nuclear electric quadrupole interaction. Furthermore, the magnitude of this dipolar coupling, approximately 7.5 kHz, if r_{NH} equals 0.105 nm, is so large that its residual under MAS often obscures any ^{1}H signal arising from hydrogen directly bound to a nitrogen. Using the amine resonance of 1, 1, 3, 3, 5, 5-hexamethylcyclotrisilazane as a model compound [50] and the theory of Hexem *et al.* [51], the amine proton linewidth was simulated theoretically. We obtained a linewidth of approximately 1 kHz ($\sim$5 p.p.m.) at a static magnetic field of 187 MHz, if the multiple-pulse scaling of the heteronuclear dipole coupling is taken into account [52]. The observed linewidth should be larger than 5 p.p.m., because other line-broadening mechanisms should be present in the HPZ-derived ceramics, e.g. chemical dispersion, paramagnetic broadening or bulk susceptibility effects.

4. Conclusion

The entire chemical scheme for the conversion of HPZ polymer to Si–C–N–O ceramic can be summarized as follows. The original polymer contains $\geq$Si–H and –Si$(CH_3)_3$ groups, and does not appear to have a large degree of cyclization until it has been pyrolysed at a temperature of at least 400 °C. In samples prepared at HTTs between 400 and 500 °C, the matrix forms cyclic silazanes, with dimethylsilyl groups incorporated into the rings, and inorganic moieties of the general form N_xSiC_{4-x}, where $x = 0$–4. At HTT = 500 °C the matrix can stabilize free radicals and the ESR data indicate that the free radicals formed are, at least in part, contained in a graphite matrix. The ^{1}H CRAMPS and ^{13}C CP-MAS spectra confirm the conclusion that aromatic compounds have been formed in the matrix at 500 °C. ^{15}N CP-MAS data provide an excellent probe of the degree of cross-linking of the polymer, the distribution of $(\geq Si)_3N$ nitrogen environments, and the inorganic nature of the matrix as a function of HTT. In samples prepared at HTTs exceeding 800 °C, ^{1}H CRAMPS data indicate that very little organic material is left in the matrix and ^{29}Si DP-MAS chemical shift assignments indicate that the material consists predominantly of SiC, Si_3N_4 and a mixed species that can be described as silicon bonded to three carbon atoms and one nitrogen atom. The sample prepared at the highest heat-treatment temperature, 1200 °C does not explicitly show any crystallinity in the long-delay ^{29}Si DP-MAS spectrum; however, the ^{29}Si spectrum does indicate that a significant portion of the matrix is far removed from paramagnetic centres. The ESR lineshapes indicate that some conductive material is formed at the highest HTT, albeit a minor amount.

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