

NMR and X-ray diffraction studies of amorphous and crystallized pyrolysis residues from pre-ceramic polymers

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²⁹Si MAS NMR and X-ray diffraction studies are presented of black and white pyrolysis residues obtained by initial 1100 °C pyrolyses in N₂ and NH₃ atmospheres followed by 1550 °C pyrolyses in Ar, N₂ or vacuum atmospheres of a polycarbosilane and four polysilazane precursors to SiC and Si₃N₄ ceramics. Amorphous white pyrolysis residues crystallized under the various conditions to give not only Si₃N₄ but also Si₂N₂O, SiC, SiO₂ and Si, while black amorphous pyrolysis residues crystallized to form only Si₃N₄ or SiC. In general, the crystalline ceramic products observed depended on a variety of factors, i.e. moisture sensitivity of polymer, the initial 1100 °C pyrolysis gas (N₂/NH₃), the dryness of the 1100 °C-NH₃ pyrolysis gas and the 1550 °C pyrolysis atmosphere (N₂, Ar, vacuum). An additional factor of interest affecting product distribution was the choice of crucible (alumina/graphite) employed in the 1550 °C pyrolysis. The combined studies suggest that the white amorphous pyrolysis residues are complex silicon oxycarbonitrides (Si_xN_yO_zC_a), while the amorphous black residues are silicon carbonitrides (Si_xN_yC_z).

1. Introduction

Silicon carbide (SiC) and silicon nitride (Si₃N₄) are highly valued ceramic materials due to their many desirable properties such as oxidation resistance, high hardness, low thermal expansion and high chemical stability [1, 2]. An increasing amount of research effort worldwide has been directed towards the synthesis of SiC and Si₃N₄ from pyrolysis of organosilicon precursors such as polycarbosilanes and polysilazanes. These polymers are processable in that they can be spun into fibres, or used to coat carbon fibres or other substrates. Other applications include use in ceramic matrix composites as well as in synthesis of powders and bulk shape [3]. Subsequent pyrolysis yields the desired ceramic or a mixture of a ceramic phases depending on the pyrolysis gas used [4–6]. Some polymer-derived ceramics are being manufactured on an industrial scale. For example, Nippon Carbon Co, Japan, produce SiC fibres derived from pyrolysis of oxygen-cured polycarbosilane fibre, a process pioneered by Yajima *et al.* [7].

The pre-ceramic polymers are synthesized using simple organic reagents. For example, synthesis [7] of the SiC polycarbosilane precursor (PCS) starts with (CH₃)₂SiCl₂ while the Si₃N₄ polysilazane precursors

can be made using CH₃SiHCl₂ or (C₆H₅)₂SiCl₂ as starting materials [6]. Much of the earlier work has been directed towards studying the formation, polymerization and characterization of carbosilanes and organosilazanes [8–17]. However, identification of the individual components in the mixtures of oligomeric and polymeric compounds produced, by nuclear magnetic resonance (NMR) and infrared (IR) techniques is difficult and spectroscopic characterization tends only to identify the functional groups present (e.g. Si–H, N–H, etc).

In allied studies, pre-ceramic polymers have been studied with the intention of forming ceramic coatings of SiC and Si₃N₄ from pyrolysis of thin layers on various substrates. The results of this research are the subject of separate publications [18, 19]. The substrates utilized for coating have generally limited the maximum pyrolysis temperature to 1100 °C. However, pyrolysis at 1100 °C of the polymeric mixtures obtained from the condensation reactions of chloroalkylsilanes with ammonia, for example, generally leads to amorphous ceramic chars and residues [20] whose actual structure is not accessible by X-ray diffraction (XRD) techniques. Thus “amorphous SiC” and “amorphous Si₃N₄” comprise the coatings formed at

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1100 °C and it is of interest to gain an insight into the composition of these materials. Direct examination of the coatings on substrates (by XRD, for instance) is difficult due to the amorphous nature of the coating material and thinness of the coatings. Thus, examination of residues generated by pyrolysis of bulk precursors at 1100 °C is necessary. Solid state ^{29}Si NMR is a popular and useful technique for elucidating some structural information on the amorphous residues [4, 20, 21]. The amorphous residues generated from pyrolysis of some pre-ceramic polymers often represent extremely complex systems. This is reflected in the ^{29}Si NMR bands of the residues which tend to be broad indicating the many possible chemical environments for Si thus providing information of a very general nature on the chemical structures of the powders.

This paper deals with the NMR characterization of amorphous residues derived from 1100 °C pyrolysis of a polycarbosilane and 4 polysilazane polymers in N_2 and NH_3 atmospheres. The XRD examination of these residues subsequently crystallized at 1550 °C sheds some light on their chemical complexity as shown by the NMR studies as well as the varied range of products that can result when different atmospheres, gases and crucibles are used.

2. Experimental details

2.1. Preparation of pre-ceramic polymers

Table I defines the acronyms used to refer to pre-ceramic polymers prepared in this study.

2.1.1. Polycarbosilane (PCS)

The polycarbosilane (PCS) precursor to silicon carbide was prepared following the procedure described by Yajima *et al.* [7]. Poly(dimethyl) silane (PDMS) was initially synthesized from dimethyldichlorosilane (Sigma Chemical Co) and converted to PCS by the following thermolytic process. Dry powdered PDMS (5–10 g) was placed in a silica glass sleeve which was subsequently inserted into a 100 ml capacity stainless steel bomb equipped with a pressure gauge. The bomb was pressurized with Ar to $c. 34 \times 10^5$ Pa and released three times to expel air and was then charged with $c. 6.9 \times 10^5$ Pa of Ar before sealing and heating to $c. 470^\circ\text{C}$ for 14–16 h. Over this time the internal pressure of the bomb rose to 34×10^5 – 69×10^5 Pa depending on the quantity of PDMS thermolysed.

TABLE I Definition of acronyms for pre-ceramic polymers prepared in this study

Polymer acronym	Full name
PCS	Polycarbosilane
HMCS	Hydridomethylcyclosilazane ^a
PHMCS	Poly(hydridomethylcyclosilazane) ^b
PDPS	Poly(diphenyl)silazane
PMSED	Poly(methylsilylethylenediamine)

^a Unpolymerized $\text{CH}_3\text{SiHCl}_2$ ammonolysis product.

^b Polymerized $\text{CH}_3\text{SiHCl}_2$ ammonolysis product.

After cooling, a viscous yellow semi-glassy liquid was left in the sleeve. This was dissolved in warm hexane and subsequently filtered to produce a clear yellow liquid. The hexane was then removed under reduced pressure to leave a highly viscous yellowish material which could be used directly in pyrolysis without further purification.

2.1.2. Poly(diphenyl)silazane (PDPS)

For preparation of PDPS, a solution of 30 ml of $(\text{C}_6\text{H}_5)_2\text{SiCl}_2$ (Aldrich Chemicals) in 100 ml dry diethyl ether was added dropwise over a period of 15 min to $c. 50$ ml of liquid NH_3 in a flask fitted with a condenser both of which were cooled with a mixture of dry-ice and acetone. A moderately vigorous reaction ensued in which a white solid (NH_4Cl) was produced. After addition was complete, the reaction was allowed to warm to room temperature under flowing N_2 overnight. The white gummy mass was subsequently swirled with benzene in a nitrogen dry-box and the white solid filtered off to yield a colourless solution. Removal of the benzene under reduced pressure yielded a light yellow oil (27.2 g). 26.75 g of the oil was then polymerized [11] by heating with 1.34 g of NH_4Br (5% by weight) in a two-necked flask fitted with a thermometer and vigreux column for $c. 2$ h and 15 min. Over this time a foamy, semi-rigid material was generated which was dissolved in ether and filtered through a sintered glass crucible. The filtrate was subsequently treated with gaseous NH_3 for 1 h at room temperature to remove Si–Br bonds introduced [11] by the NH_4Br . After filtration of the white solid produced, the ether was completely evaporated from the solution leaving 11.17 g of a flaky white solid which constituted PDPS.

2.1.3. Hydridomethylcyclosilazane (HMCS) and poly(hydridomethylcyclosilazane) (PHMCS)

HMCS was prepared as a yellow oil from $\text{CH}_3\text{SiHCl}_2$ (Hüls Petrarch Systems) and NH_3 following the procedure reported by Seyferth and Wiseman [22]. Separation of the HMCS from the NH_4Cl precipitate was achieved by either washing with ether and filtration or by using soxhlet extraction [23]. The latter extraction procedure produced a much clearer oil. PHMCS was prepared as a yellowish solid by dehydropolymerization of HMCS in sodium-dried THF (tetrahydrofuran) using NaNH_2 as reported previously [22].

2.1.4. Poly(methylsilylethylenediamine) (PMSED)

In this preparation, 75 ml of $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ was added to 200 ml of dry diethyl ether under N_2 . 57 ml of $\text{CH}_3\text{SiHCl}_2$ was subsequently added dropwise to this solution through an ice-water-cooled pressure-equalizing dropping funnel over a period of 30 to 45 min. A vigorous reaction ensued leading to the production of copious amounts of white fumes and

white solid. The thick yellow-white slurry resulting after addition of $\text{CH}_3\text{HSiCl}_2$ completely hardened to a light-pink/yellow solid on standing under N_2 . The solid was shaken with dry diethyl ether and filtered in a nitrogen dry box. The ether in the filtrate was removed under reduced pressure to yield 14.8 g of an initially low viscosity yellow polysilazane oil. This oil was observed to set to a dark yellow rubber and eventually solidified after 20 days standing in a sealed container.

2.2. Pyrolyses

Pyrolyses of bulk polymer samples were conducted in alumina boats in a temperature-programmed alumina tube furnace under either flowing O_2 -free N_2 (100 ml min^{-1}), technical grade NH_3 (200 ml min^{-1}) or dried technical grade NH_3 (200 ml min^{-1}). Heating rates of 120°C h^{-1} (N_2) or 300°C h^{-1} (NH_3) were used up to 1100°C where the samples were held for 2 h. Analysis supplied with the technical grade (“wet”) NH_3 showed that it contained 1250 p.p.m. water. “Dry” NH_3 was obtained by passing “wet” NH_3 through a 64 cm drying column of KOH pellets (for c. 50% of its length) and anhydrous Na_2SO_4 granules before passing into the furnace tube. For the higher temperature pyrolyses, 150–200 mg of the bulk 1100°C pyrolysis residues were heated to 1550°C in small alumina and graphite crucibles placed in a larger covered graphite pot with two holes in the lid. Firings were carried out in a graphite resistance furnace under vacuum or controlled (flowing) atmosphere conditions (using either instrument grade Ar or N_2). Samples were heated to 1550°C at $17^\circ\text{C min}^{-1}$ and soaked at this temperature for 3.5 to 4 h after which the samples were allowed to cool in the furnace. For both the 1100 and 1550°C pyrolysis experiments, weight changes were monitored for each sample and X-ray diffraction spectra of the ground powders were obtained.

Time-dependent mass spectral data were obtained by monitoring the gases evolved from 1550°C -Ar pyrolyses of 100–200 mg of residues (derived from 1100°C - NH_3 pyrolysis of PHMCS and PCS) using a Dycor mass spectrometer. The gas evolution envelope representing mass 28 species was deconvoluted using the relationship between the mass 12 (C) and mass 44 (CO_2) peaks allowing separate gas evolution curves for CO and N_2 to be determined.

2.3. Instrumentation

IR spectra were recorded using either a Perkin-Elmer 580 grating spectrophotometer or a Digilab FTF-50 FTIR spectrometer. For liquid samples, NMR spectra were obtained with a Bruker AC-300 spectrometer equipped with 5 mm dual carbon–proton and 10 mm multinuclear probes both with proton decoupling. Samples, usually dissolved in CDCl_3 or C_6D_6 , were scanned at a temperature of 30°C using tetramethylsilane (TMS) as internal (or external) reference. Solid samples were scanned on Varian XL-200 and Varian Unity 500 solid state NMR spectrometers. For ^{29}Si

MAS NMR spectra, typically 4–190 transients (acquisition time of each transient, 0.041 s) were obtained from powdered samples spun in zirconia rotors. Spinning rates of 5600–8820 Hz were employed. 90° pulse widths were of the order of 5.5 μs with delay times between successive transients of 30 or 300 s. In spectral processing, gaussian line-broadening of 200–400 Hz was normally applied. All NMR chemical shifts reported in this paper are given in p.p.m. relative to TMS.

X-ray diffraction patterns were acquired of powdered ceramic residues using a Philips PD1700 APD system employing a diffracted beam graphite monochromator, automatic divergence slit and CoK_α radiation. Thermodynamic calculations on outcomes of reactions involving ceramic species were carried out using a program package called *CSIRO Thermochemistry System Version 5.1* written by A.G. Turnbull and M. V. Wadsley of CSIRO, Australia. The relative proportions of the α - and β -phases in crystallized pyrolysis residues consisting of only α - and β - Si_3N_4 were calculated using the method reported by Gazzara and Messier [24] in which diffracted intensities are approximated by using XRD peak heights for α - and β - Si_3N_4 .

3. Results and discussion

3.1. Spectroscopic characterization of precursors

Most of the organosilicon precursor molecules under study have been subjected to extensive spectroscopic investigation by earlier authors [7, 22, 25–28]. Infrared and NMR (^1H , ^{13}C , ^{29}Si) spectra of the viscous, yellowish product obtained from thermolysing poly(dimethyl)silane confirmed it to be a polycarbosilane (PCS) similar to “PC-470” reported by Yajima and other authors [7, 25]. Infrared spectra of the PDPS pre-ceramic polymer indicated N–H groups of 3380 cm^{-1} as well as a small proportion of NH_2 groups (3560 cm^{-1}) remaining after NH_4Br -catalysed polymerization (see Section 2). Infrared and ^1H NMR spectra of HMCS and PMSED showed SiH, NH and SiCH_3 groups as expected for these molecules with some broadening (in NMR signals) observed when HMCS was polymerized to PHMCS [22, 27] and PMSED transformed (over a period of 20 days) from a viscous yellow oil to a rubber-like substance. The solidification of the PMSED polymer over time may be associated with cross-linking and elimination of ethylenediamine as has been observed by Minné and Rochow [29] for a “ladder” polymer derived from cross-linking of a polydimethylsilylethylenediamine and H_2SiCl_2 ammonolysis products which set to glassy solids in sealed containers or under N_2 [30].

3.2. X-ray diffraction and solid state NMR studies of 1100°C pyrolysis residues

3.2.1. X-ray diffraction studies

Tables II to V summarize the phases formed, ceramic yield and weight loss data for the precursors pyrolysed to 1100 and 1550°C . The ceramic yields from the

TABLE II Summary of XRD, ceramic yield^a and weight loss^b data for amorphous and crystallized residues obtained from pyrolysis of PCS under various conditions

1100 °C pyrolysis gas (% ceramic yield)	1550 °C pyrolysis ^c gas	Weight loss (%)	Products
N ₂ (32)	N ₂ (G)	3.1	β-SiC (major), α-Si ₃ N ₄ (minor)
	N ₂ (A)	14.3	SiC (mixture of polytypes).
NH ₃ “wet” (38) or “dry” 24	N ₂ (G/A)	27–37	α-Si ₃ N ₄ (major), β-Si ₃ N ₄ (minor).
NH ₃ “wet” (38)	Ar (G)	50–71	Si, SiC (major), α-Si ₃ N ₄ (minor-trace), Si ₂ N ₂ O (major).
	Vacuum (G)	79.3	SiC (major), SiO ₂ (cristobalite, medium).
NH ₃ “dry” (24)	N ₂ (G)	51.9 ^d	Si ₂ N ₂ O (major), α-Si ₃ N ₄ (minor).
	Ar (A)	48–72	α-Si ₃ N ₄ (major), β-Si ₃ N ₄ (medium), SiC (medium), Si (trace).

^a Ceramic yield refers to amount of residue remaining after pyrolysis of pre-ceramic polymer in N₂ at 1100 °C for 2 h. The same applies to Tables II–V.

^b This parameter (in Tables II–V) refers to the weight loss upon heating the residue (obtained from the 1100 °C pyrolysis) to 1550 °C.

^c Samples for which results are summarized in Tables II–V were held at 1550 °C for 3.5 to 4 h. (G) and (A) refer to the crucible used in the pyrolysis (G = graphite, A = alumina).

^d This weight loss was significantly higher than the 27–37% losses recorded for those samples giving only α- and β-Si₃N₄ after crystallization at 1550 °C.

TABLE III Summary of XRD, ceramic yield and weight loss data for amorphous and crystallized residues obtained from pyrolysis of PDPS under various conditions

1100 °C pyrolysis gas (% ceramic yield)	1550 °C pyrolysis gas ^b	Weight loss (%)	Products
N ₂ (40–60)	N ₂ (G)	8.9	SiC and α-Si ₃ N ₄ (major), β-Si ₃ N ₄ (minor)
	N ₂ (G)	48.7 ^a	SiC (mixture of polytypes)
	N ₂ (A)	39.7	SiC (mixture of polytypes)
	Ar (A)	36.6	SiC (mixture of polytypes)
NH ₃ “wet” (43) and “dry” (35.9)	N ₂ (G/A)	19–37	α-Si ₃ N ₄ (major), β-Si ₃ N ₄ (minor), Si ₂ N ₂ O (major), SiO ₂ (medium) plus large amorphous component
NH ₃ “wet” (43)	Ar (A)	26.6	Si ₂ N ₂ O (major).
NH ₃ “dry” (35.9)	Ar (A)	25.4	Si ₂ N ₂ O (major), α-Si ₃ N ₄ (medium), β-Si ₃ N ₄ (trace).

^a This large weight loss was recorded for a sample which gave only SiC after crystallization at 1550 °C.

^b G = graphite, A = alumina.

TABLE IV Summary of XRD, ceramic yield and weight loss data for amorphous and crystallized residues obtained from pyrolysis of PMSED under various conditions

1100 °C pyrolysis gas (% ceramic yield)	1550 °C pyrolysis gas ^a	Weight loss (%)	Products
N ₂ (46)	N ₂ (G)	29.8	SiC and α-Si ₃ N ₄ (major phases)
	Ar (A)	84.8	SiC (mixture of polytypes)
NH ₃ “wet” (50)	N ₂ (G)	28.3	α-Si ₃ N ₄ (major), β-Si ₃ N ₄ (minor)
	Ar (A)	39.2	Si ₂ N ₂ O (major)
NH ₃ “dry” (50)	N ₂ (A)	23.5	Si ₂ N ₂ O (major), α-Si ₃ N ₄ (medium),
	Ar (A)	33.9	Si ₂ N ₂ O (major), α-Si ₃ N ₄ (major), β-Si ₃ N ₄ (trace)

^a G = graphite, A = alumina.

1100 °C pyrolyses varied from 19 to 73% with wide variation for individual polymers (e.g. see Table III for PDPS). The XRD patterns of the 1100 °C ceramic residues were extremely broad and weak in intensity indicating the amorphous character of the materials. Two types of product were obtained, a black residue obtained by pyrolysis of precursors in N₂ and an off-white or grey residue from pyrolysis in NH₃. For example, the hard, black residue obtained from 1100 °C pyrolysis of PCS in N₂ exhibited very broad XRD peaks at *d*-spacings of 0.252, 0.154 and 0.132 nm typical of amorphous SiC [31]. The black

solid derived from 1100 °C-N₂ pyrolysis of HMCS also exhibited very broad XRD patterns which consisted of two very broad peaks centred at *d*-spacings of 0.257 and 0.138 nm. These corresponded approximately to the position for the characteristic groups of peaks for crystalline Si₃N₄. However, crystallization by further heating to 1550 °C was required to provide some confirmation of this (see later). As observed by Seyferth and Wiseman [22], increasing the molecular weight by polymerization of HMCS increased the ceramic yield (in N₂) from 33.3 to 73.3% (see Table V).

TABLE V Summary of XRD, ceramic yield and weight loss data for amorphous and crystallized residues obtained from pyrolysis of HMCS (*) and PHMCS (#) under various conditions

1100 °C pyrolysis gas (% ceramic yield)	1550 °C pyrolysis gas ^a	Weight loss (%)	Products
* N ₂ (28.7)	N ₂ (G) Ar (A)	7.3 37.5	α-Si ₃ N ₄ and SiC (major phases), β-Si ₃ N ₄ (minor) SiC (mixture of polytypes)
* NH ₃ “wet” (33.3) and “dry” (19.4)	N ₂ (G/A)	17–34	α-Si ₃ N ₄ (major), β-Si ₃ N ₄ (medium/minor), Si ₂ N ₂ O (major)
* NH ₃ “wet” (33.3)	Ar (A) Vacuum (G)	44.9 87.0	Si ₂ N ₂ O (major), α-Si ₃ N ₄ (minor) β-SiC
NH ₃ “dry” (19.4)	Ar (A)	45.4	Si ₂ N ₂ O (major), α-Si ₃ N ₄ (major), β-Si ₃ N ₄ (medium)
# N ₂ (73.3)	N ₂ (G/A) Ar (A)	30.7 56.7	α-Si ₃ N ₄ and SiC (major phases), β-Si ₃ N ₄ (minor) SiC (mixture of polytypes)
# NH ₃ “wet” (64) or “dry” (66)	N ₂ (G/A)	20–47	α-Si ₃ N ₄ (major), β-Si ₃ N ₄ (minor) Si ₂ N ₂ O (major)
# NH ₃ “wet” (64)	Ar (A)	40.4	Si ₂ N ₂ O (major), α-Si ₃ N ₄ (minor), β-Si ₃ N ₄ (trace)
# NH ₃ “dry” (66)	Ar (A)	41.9	Si ₂ N ₂ O (major), α-Si ₃ N ₄ (medium), β-Si ₃ N ₄ (trace)

^a G = graphite, A = alumina.

3.2.2. Solid state NMR studies (²⁹Si)

As ²⁹Si NMR data is more instructive than ¹³C NMR data, most solid state NMR data have been derived from ²⁹Si magic angle spinning (MAS) NMR spectra of amorphous pyrolysis residues and may be compared with previously studied systems [32]. NMR spectra were recorded of residues obtained from pyrolysis at 1100 °C in: (i) N₂, (ii) “wet” NH₃ and (iii) “dry” NH₃.

3.2.2.1. Spectra of residues generated at 1100 °C in N₂.

Fig. 1 illustrates the ²⁹Si NMR spectra of the black, amorphous residues generated from 1100 °C-N₂ pyrolysis. In general, the ²⁹Si NMR spectra of these residues gave extremely broad bands often with shoulders. With the exception of the PCS-derived residue, band maxima ranged from – 29.8 to – 50 p.p.m. The breadth of these bands (> 4000 Hz) indicated that ²⁹Si residues in a continuum of chemical environments, i.e. SiC, Si₃N₄, Si₂N₂O and, to a much lesser extent, SiO₂-type environments (see Fig. 1) thus revealing the chemical complexity of the residues. The residues from HMCS and PHMCS exhibited very similar spectra (see Fig. 1). The spectrum of the residue from solidified PMSED pyrolysed in N₂ differed significantly from the other spectra in that a broad peak centred at – 105.0 p.p.m. indicating some SiO₂-type character was observed.

The ²⁹Si spectrum of the black residue generated from pyrolysis of PCS exhibited a relatively narrower, slightly skewed peak at – 14.5 p.p.m. (see Fig. 1). A ¹³C spectrum of the same residue featured a peak at 21.1 p.p.m. These resonance positions are practically identical in position to those reported for amorphous SiC in NICALON SiC fibres [32]. However, in contrast to the NICALON fibres, little or no Si–O content was detected by ²⁹Si NMR in the amorphous PCS-derived SiC since an oxygen curing step was not employed. Oxygen curing used in the production of NICALON SiC fibres gives rise to a continuum of SiC₄ and SiC_{4-x}O_x species in the fibres [33–35] which

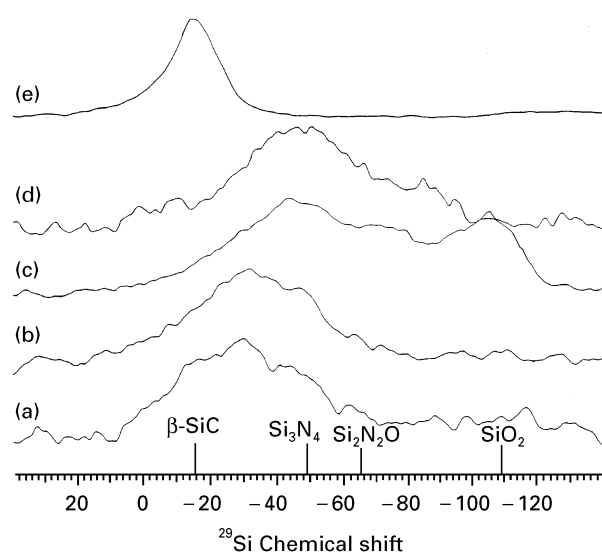


Figure 1 ²⁹Si MAS NMR spectrum of the black residues generated from 1100 °C-N₂ pyrolysis of (a) HMCS, (b) PHMCS, (c) PMSED, (d) PDPS and (e) PCS. Possible candidate species are listed.

were assigned to peaks appearing at *c.* – 75 and – 112 p.p.m. in the reported ²⁹Si MAS NMR spectrum.

3.2.2.2. Spectra of residues generated at 1100 °C in “wet” NH₃.

Fig. 2 illustrates the ²⁹Si NMR spectra of amorphous white residues obtained after 1100 °C-“wet” NH₃ pyrolysis. The spectra usually exhibited two distinct peaks with variable relative intensities. The first of these peaks occurred between – 45.0 and – 53.7 p.p.m. (see Fig. 2). Peaks in this position are typical of Si₃N₄-type species [33] and have been observed in previous studies of pyrolysis of other hydridopolysilazane and polycarbosilane polymers in NH₃ [20]. The second peak occurred between – 87.9 and – 99.9 p.p.m. (see Fig. 2). Typically, ²⁹Si chemical shifts of the silica polymorphs range from – 107.0 to – 121.0 p.p.m. [36], while the ²⁹Si chemical shift of silicon oxynitride (Si₂N₂O) is reported at

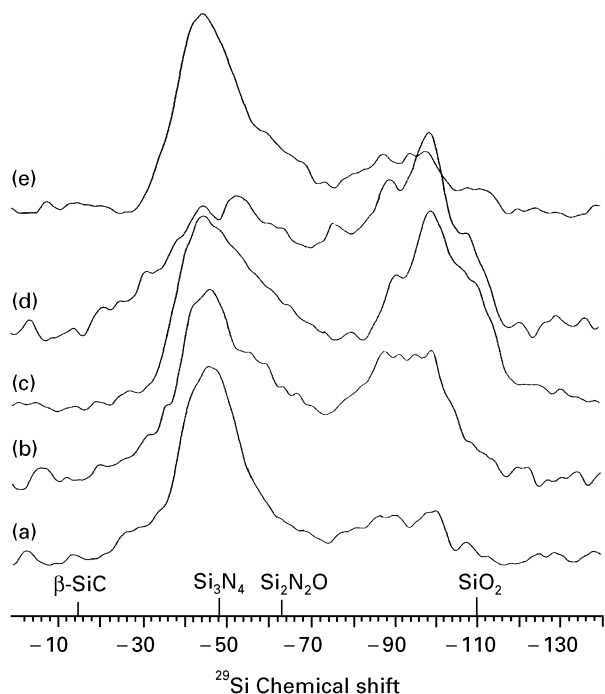


Figure 2 ^{29}Si MAS NMR spectrum of the off-white residue generated from 1100°C -“wet” NH_3 pyrolysis of (a) HMCS, (b) PHMCS, (c) PMSED, (d) PDPS and (e) PCS.

– 63 p.p.m. [37]. It appears that the residues generated from pyrolysis in “wet” NH_3 may contain two general types of Si–O species: (a) $\text{Si}_2\text{N}_2\text{O}$ -type species giving rise to the broad peaks, which although centred at *c.* – 45 p.p.m. overlap into the – 63 p.p.m. region where $\text{Si}_2\text{N}_2\text{O}$ species occur and (b) Si–O species of predominantly SiO_2 -type character which give the peaks at – 87.9 to – 99.9 p.p.m. The ^{29}Si chemical shift for such species is less than the shifts observed for silica polymorphs possibly because of the influence of (or interaction with) neighbouring Si–N species in the pyrolysis residue. It was discovered that the “ SiO_2 -type” character of the pyrolysis residues (typified by the – 87.9 to 99.9 p.p.m. peaks) was caused largely by the moisture content (1250 p.p.m.) in the “wet” NH_3 pyrolysis gas.

3.2.2.3. *Spectra of residues generated at 1100°C in “dry” NH_3 .* Fig. 3 illustrates the ^{29}Si NMR spectra of the white amorphous residues obtained from 1100°C -“dry” NH_3 pyrolysis. It is apparent that by drying, the “wet” NH_3 through a $\text{KOH}/\text{Na}_2\text{SO}_4$ column before its entry into the furnace tube, a significant reduction in the SiO_2 -associated peaks at – 87.9 to – 99.9 p.p.m. in the ^{29}Si MAS NMR spectra can be obtained. This was most dramatic for the residue from PHMCS which exhibited no SiO_2 -associated peaks in the ^{29}Si MAS NMR spectrum (see Fig. 3b), Pyrolytic residues obtained from heating PCS, PDPS, and PMSED in “dry” NH_3 still exhibited SiO_2 -associated peaks but at a significantly lower level. In the case of the pyrolytic residue from PDPS, an asymmetric peak was observed in the ^{29}Si NMR, the tail of which was skewed to the – 88 to – 100 p.p.m. region suggesting SiO_2 -type species were present. The HMCS residue

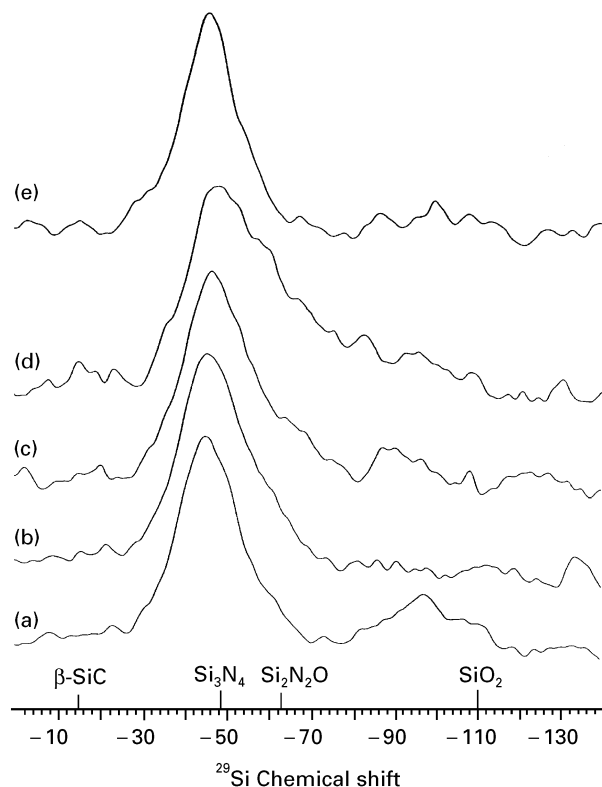


Figure 3 ^{29}Si MAS NMR spectrum of the off-white residue generated from 1100°C -“dry” NH_3 pyrolysis of (a) HMCS, (b) PHMCS, (c) PMSED, (d) PDPS and (e) PCS.

was unusual in that there was little difference between the ^{29}Si NMR spectra of the residues generated from pyrolysing HMCS in “wet” and “dry” NH_3 . Since some pyrolytic residues exhibit SiO_2 character by NMR even when “dry” NH_3 has been used in the pyrolysis, it must be assumed that the original pre-ceramic polymer itself contained some Si–O character. Many of the organosilicon polymers do exhibit varying degrees of susceptibility of Si–N bonds to hydrolysis on exposure to moisture. Indeed, as shown later, despite the predominance of the Si_3N_4 -associated (– 45 p.p.m.) peak in ^{29}Si NMR spectra of the amorphous residues, many of the white residues pyrolysed to higher temperatures exhibited $\text{Si}_2\text{N}_2\text{O}$ as a major phase.

Another factor which may possibly influence the presence of Si–O character is the previous observation [19] that amorphous Si_3N_4 powders generated by polymer pyrolysis in NH_3 tend to be air and moisture sensitive. However, this uptake of oxygen was observed to occur slowly over a period of months whereas the powders in the present study, were examined by NMR within one or two weeks of their preparation.

In previous studies [21, 38], the crystallization of residues obtained by pyrolysing pre-ceramic polymers in either N_2 or NH_3 was not observed to occur until at least 1500°C . Since the ^{29}Si NMR peaks were broad, it was difficult to identify discrete chemical species in the residues. Further heating of all pyrolytic residues to *c.* 1550°C in a graphite furnace was thus carried out in different furnace atmospheres. Crystallization or partial crystallization of the residues was, therefore,

achieved so allowing identification of ceramic components by XRD.

3.3. X-ray diffraction studies of residues heated to 1550 °C

Both the phases formed and the weight loss data collated from 1550 °C pyrolysis of the amorphous black and white residues obtained from initial 1100 °C pyrolyses in N₂ and NH₃ are summarized in Tables II to V.

3.3.1. 1550 °C pyrolyses of white amorphous powders obtained from initial 1100 °C pyrolyses of pre-ceramic polymers in "wet" and "dry" NH₃

3.3.1.1. *Pyrolysis in N₂*. For most precursors studied, pyrolysis in N₂ gave variable results (see Table II–V). The crystalline products from individual samples could vary from pure Si₃N₄ (see Table VI) to mixtures of Si₃N₄ with Si₂N₂O and occasionally SiO₂. Weight losses varied from sample to sample as well as from precursor to precursor, although they did not exceed 52%. Volatilization of SiO, N₂ or CO are probably the main contributors to the weight loss. Indeed, whisker formation observed around the tops of the crucibles after 1550 °C-N₂ firings was an indication of SiO volatilization. SiO volatilization appears to be an important feature in 1550 °C-N₂ pyrolyses of PCS- and PMSED-derived amorphous residues which showed particularly heavy whisker deposits.

The use of graphite or alumina crucibles was also found to influence the crystalline materials produced from pyrolysis in N₂ at 1550 °C. Interaction of the Si–O containing species in the residue with graphite probably leads (in an N₂ atmosphere) to CO and Si₃N₄. Alumina crucibles, on the other hand, are more chemically inert so that the level of Si₂N₂O present in residues after 1550 °C pyrolysis might be expected to be relatively higher (see later for equations).

When the residue from PHMCS was pyrolysed at 1550 °C in graphite and alumina crucibles placed side-by-side in the same furnace firing, relatively higher levels of Si₃N₄ intermixed with Si₂N₂O were detected in the graphite crucible. A similar trend was observed for PMSED (Table IV).

PCS (Table II) usually gave only Si₃N₄ when pyrolysed in N₂ in either graphite or alumina crucibles,

even when the original residue had been previously pyrolysed in "wet" or "dry" NH₃ to 1100 °C. When pure Si₃N₄ was formed, weight losses tended to fall within the 27–37% range (see Table II). However, for one sample where Si₂N₂O was the major product (with α-Si₃N₄ as a minor product), a significantly higher weight loss of 51.9% was obtained implying the probable loss of N₂ (see Table II). Pyrolysis products from PDPS, HMCS and PHMCS (Tables III and V) gave extremely variable product distributions. The predominance of Si₂N₂O in some products was not strictly dependent on the use of "wet" or "dry" NH₃ in the initial 1100 °C pyrolysis. This implies that Si–O character is already present in the original precursor molecule prior to the initial 1100 °C-NH₃ pyrolysis, owing to inevitable moisture uptake on handling and sample preparation. Thermodynamic calculations indicate that a mixture of SiO₂ and Si₃N₄ is unstable with respect to Si₂N₂O above 800 °C. SiO₂-type species have been observed in the ²⁹Si MAS NMR spectra of the amorphous white residues (see Figs 2 and 3). Thus it is reasonable to say that reaction of the SiO₂ and Si₃N₄ entities within the pyrolytic residues at 1100–1550 °C results in Si₂N₂O being formed.

In the instances where the crystalline products were only Si₃N₄ (from 1100 °C-NH₃ residues), the relative ratios of α- and β-Si₃N₄ in the product were calculated using the method reported by Gazzara and Messier [24]. Table VI summarizes the results of these calculations for various samples and precursors. α-Si₃N₄ was the dominant phase in most samples. The % β-Si₃N₄ in each sample varied from 0 to 20%. However, as shown in Table VI, the relative ratios of α- and β-Si₃N₄ are not reproducible for residues derived from PCS and PDPS between different furnace firings. Consistent ratios were only observed for two separate PCS samples pyrolysed in the same furnace run (see Table VI). It was difficult to check the reproducibility of relative α- and β-Si₃N₄ ratios for the PMSED, HMCS and PHMCS precursors since 1550 °C-N₂ pyrolyses most frequently gave Si₂N₂O mixed with the Si₃N₄ which renders the Gazzara–Messier calculation invalid. However, a visual examination of the XRD spectra containing the mixtures of Si₂N₂O and Si₃N₄ revealed that the relative levels of α- and β-Si₃N₄ were also variable in these spectra.

Pure samples of the α-Si₃N₄ phase can be produced (see Table VI). The residues derived from PCS and PHMCS give phase purities similar to those specified

TABLE VI Relative ratios of α- and β-Si₃N₄ in crystallized precursor residues which were composed of Si₃N₄ only

Precursor	Pyrolysis history (G = graphite crucible, A = alumina crucible)	% α-Si ₃ N ₄	% β-Si ₃ N ₄
PCS	1100 °C "wet" NH ₃ , 1550 °C N ₂ (G)	82.4	17.6
	1100 °C "dry" NH ₃ , 1550 °C N ₂ (G)	~ 100	~ 0
	1100 °C "dry" NH ₃ , 1550 °C N ₂ (A)	~ 100	~ 0
PDPS	1100 °C "wet" NH ₃ , 1550 °C N ₂ (G)	93.3	6.7
	1100 °C "dry" NH ₃ , 1550 °C N ₂ (A)	80.5	19.5
PMSED	1100 °C "wet" NH ₃ , 1550 °C N ₂ (G)	80	20
HMCS	1100 °C "wet" NH ₃ , 1550 °C N ₂ (G)	96.2	3.8
PHMCS	1100 °C "wet" NH ₃ , 1550 °C N ₂ (G)	98.6	1.4

for commercial grades of α - Si_3N_4 such as Starck LC-10 which is 95% pure. It has been suggested that the α - β conversion of Si_3N_4 proceeds via the formation of a glassy phase [39]. Thus in this study, the α - β ratio for the various crystallized precursor residues is determined by the unique composition of the glassy phase forming during the 1550 °C pyrolysis of the amorphous residue, particularly its Si-O character [40].

3.3.1.2. Pyrolysis in Ar. Ar, as opposed to N_2 , is a non-reactive gas at 1550 °C and thus provides information on how the pyrolysis residues transform without interference from the furnace atmosphere at temperatures > 1100 °C. Perhaps a consequence of the inert atmosphere was the consistent weight losses obtained for individual precursor samples between different furnace firings. For example, the weight losses for the chemically related HMCS and PHMCS were usually reproducible at 40–45% (see Table V). While there were variations in weight losses for the PCS-derived residue these losses were always high (>50%).

In the majority of cases where 1550 °C-Ar pyrolyses of white amorphous powders were carried out in alumina crucibles (see Tables II–V), $\text{Si}_2\text{N}_2\text{O}$ was the dominant product, intermixed with varying quantities of α - and β - Si_3N_4 . For some precursors initially pyrolysed to 1100 °C in “wet” NH_3 (PMSED, PDPS), further pyrolysis in Ar to 1550 °C gave solely $\text{Si}_2\text{N}_2\text{O}$ although in some instances, broad underlying peaks indicated that some amorphous component was still present in the samples. The production of XRD pure $\text{Si}_2\text{N}_2\text{O}$ is significant as this material is usually difficult to obtain free of other crystalline contaminants. However, when “dry” rather than “wet” NH_3 was employed for the initial pyrolysis of the PDPS, PMSED, HMCS and PHMCS precursors, the level of Si_3N_4 observed in XRD spectra usually increased noticeably (Tables III–V). The mode of formation of $\text{Si}_2\text{N}_2\text{O}$ in 1550 °C-Ar firings could be similar to that proposed in the 1550 °C- N_2 firings i.e. via interaction of SiO_2 -type species with Si_3N_4 (see above).

Distinct crucible effects were also observed in the 1550 °C-Ar pyrolyses. Samples of white amorphous powder derived from 1100 °C pyrolyses of PCS and PHMCS in “dry” NH_3 were heated to 1550 °C (in Ar) side-by-side in alumina crucibles as well as in graphite crucibles of different sizes to investigate the crucible effect. The results of these furnace firings are illustrated in Figs 4 and 5. The PHMCS-derived residue formed solely $\text{Si}_2\text{N}_2\text{O}$ when pyrolysed in an alumina crucible (Fig. 4a). However, samples fired in the graphite crucibles (Fig. 4b and c) showed noticeable levels of Si_3N_4 along with $\text{Si}_2\text{N}_2\text{O}$. The level of Si_3N_4 observed increased with graphite crucible size for a constant weight of sample and β - Si_3N_4 is in fact a major phase in Fig. 4c. It is probable that the larger crucible size allows less restriction on gas flow around the sample. These observations indicate that the graphite crucible is actively reducing the $\text{Si}_2\text{N}_2\text{O}$ in the PHMCS-derived residue.

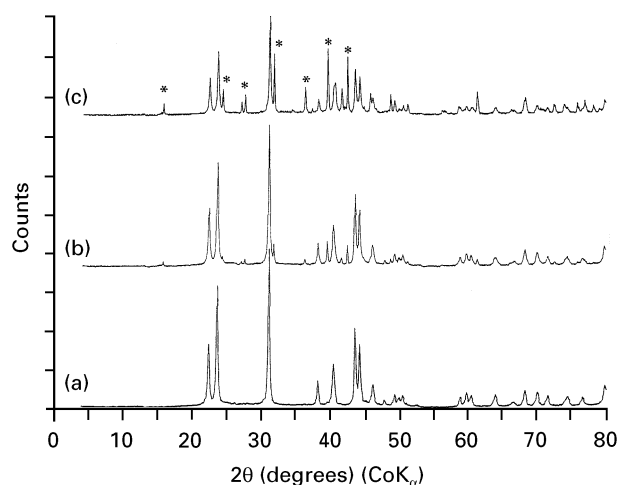


Figure 4 X-ray diffraction patterns showing the effect of crucible choice on product distributions obtained from the 1550 °C pyrolysis (in Ar) of the white amorphous residue obtained from initial pyrolysis of PHMCS in “dry” NH_3 at 1100 °C: (a) alumina crucible (residue weight loss, 18.9%), (b) small graphite crucible (residue weight loss, 32.7%) and (c) large graphite crucible (residue weight loss, 44.0%). Peaks associated with the Si_3N_4 phase are marked with asterisks (*).

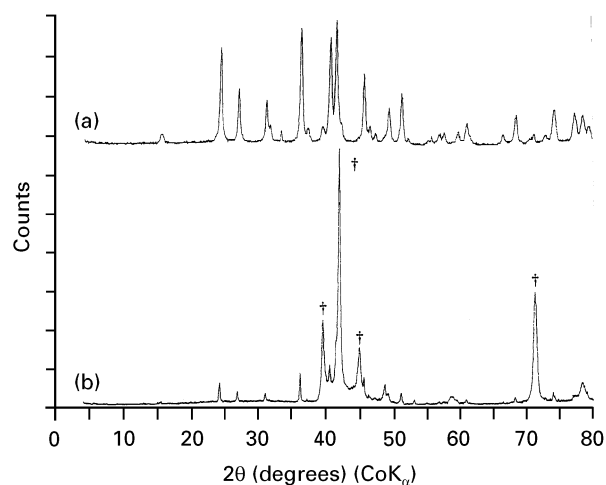
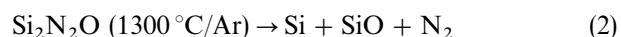
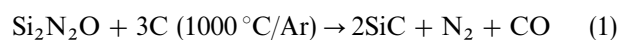


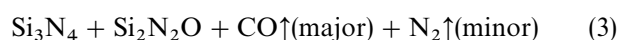
Figure 5 X-ray diffraction patterns showing the effect of crucible choice on product distributions obtained from the 1550 °C pyrolysis (in Ar) of the white amorphous residue obtained from initial pyrolysis of PCS in “dry” NH_3 at 1100 °C: (a) alumina crucible (residue weight loss, 48.9%) and (b) small graphite crucible (residue weight loss, 56.9%). Peaks associated with the SiC phase are marked with daggers (†).

A thermodynamic analysis reveals that the reduction of $\text{Si}_2\text{N}_2\text{O}$ to Si_3N_4 is not favoured. Over the temperature range 1000–1120 °C, $\text{Si}_2\text{N}_2\text{O}$ is expected to react with carbon (C) to give SiC, N_2 and CO (Equation 1). Above 1120 °C, disproportionation is favoured giving Si, SiO and N_2 (Equation 2).



Equations 3 and 4 are proposed for describing the 1550 °C-Ar pyrolyses of the PHMCS-derived residue in graphite and alumina crucibles. In these equations, the white amorphous residue derived from

1100 °C-NH₃ pyrolysis of PHMCS is represented as a polymeric species consisting of a silicon, oxygen, nitrogen and carbon backbone (i.e. Si_xN_yO_zC_a). This species, unlike crystalline Si₂N₂O *per se*, is capable of being reduced to Si₃N₄ during firing in a graphite crucible. The oxygen and nitrogen content Si_xN_yO_zC_a is inferred from ²⁹Si NMR and the products observed after crystallization in various atmospheres and crucibles. Carbon content and the relative amounts of CO and N₂ evolved during pyrolysis were deduced from mass spectral data from the 1550 °C-Ar pyrolysis (see later).



These equations were corroborated by weight losses recorded for the side-by-side crucible experiment. Weight losses increase concomitantly with the level of Si₃N₄ observed in the spectra, i.e. on passing to graphite crucibles (see caption for Fig. 4). Thus this implies the crucible itself becomes reduced in weight by the loss of CO as well as the residue which loses N₂ in addition to CO. The side-by-side 1550 °C pyrolysis involving the PCS-derived white amorphous residue gave quite different results. In alumina, the residue produces predominantly α-Si₃N₄ and a trace of Si metal (see Fig. 5a). However, in graphite (see Fig. 5b), a mixture of two polytypes of SiC results with α-Si₃N₄ being a minor component of the product mix. Weight losses are high and roughly the same for all three samples (48–57%) in keeping with the trend observed from other 1550 °C-Ar pyrolysis experiments involving the PCS-derived white amorphous residue (see Table II). Thus the PCS-derived residue is also reacting with the graphite crucible during pyrolysis. The following equation is a thermodynamically favoured pathway for the transformation of Si₃N₄ into SiC.



PCS appears different from the other amorphous residues in that it has exhibited Si₂N₂O formation less frequently in XRD spectra of products after crystallization in Ar at 1550 °C (see Table II). XRD-phase pure α-Si₃N₄ has in fact been obtained on one occasion from the PCS-derived residue after firing in Ar at 1550 °C. This suggests that the amorphous white PCS-derived residue is predominantly of Si–N character which would lend credence to the validity of Equation 5 in explaining how this residue gives SiC upon being fired in a graphite crucible. Large weight losses recorded for the PCS-derived residues (40–72%) after 1550 °C-Ar pyrolysis could represent N₂ removal (see later). Despite the 1100 °C-NH₃ treatment, carbon in the PCS-derived amorphous white residue can be inferred because SiC was observed after a 1550 °C-Ar firing in an alumina crucible. Oxygen content (as Si–O) in the residue, although not altogether absent, is

likely to be removed by formation of CO during the 1550 °C-Ar pyrolysis (see later). In addition, elemental Si has been observed after 1550 °C-Ar firings in both graphite and alumina crucibles. From the earlier thermodynamic analysis describing thermal disproportionation (see Equation 2), Si₂N₂O or a closely related species in the PCS-derived amorphous residue is a strong candidate as the source compound for the observed elemental Si.

3.3.1.3. Time-dependent mass spectrometry of 1550 °C-Ar pyrolysis effluent gases. Time-dependent mass spectrometry was used to monitor the effluent gases from 1550 °C-Ar pyrolyses of 1100 °C-NH₃ residues from PHMCS and PCS in graphite and alumina crucibles. In all 1550 °C-Ar pyrolyses carried out, gaseous species of mass 28 (representing either CO or N₂) were evolved. Small quantities of H₂ and CO₂ were also detected. Deconvolution of the mass 28 envelope into the separate CO and N₂ contributions revealed the effect of the crucibles on the 1550 °C-Ar pyrolysis. The results are demonstrated graphically in Fig. 6 for 1550 °C-Ar pyrolyses of the PCS-derived residue in graphite and alumina crucibles. In alumina crucibles (Fig. 6a), N₂ was the predominant gaseous species being evolved. CO was also evolved but at a relatively lower level.

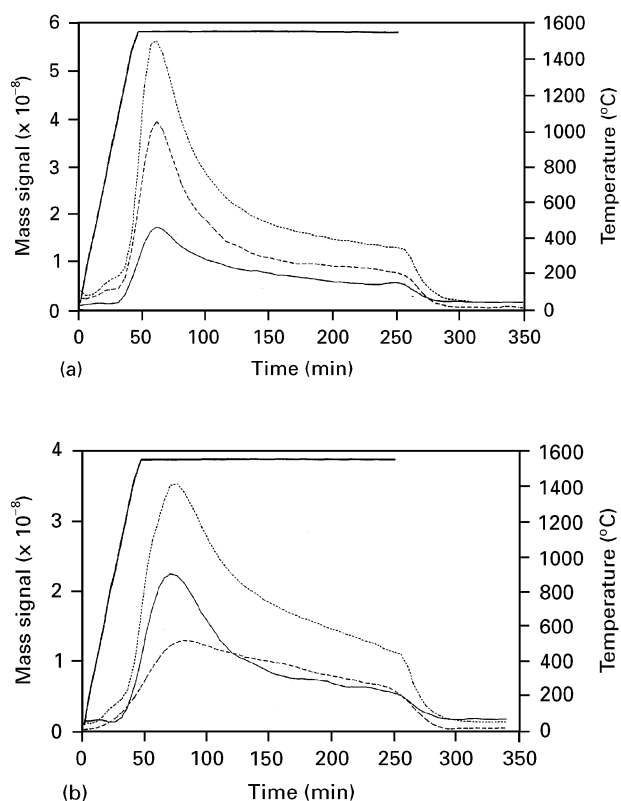


Figure 6 Time dependent mass-spectral data obtained of the effluent gases (mass 28) from 1550 °C-Ar pyrolyses of the residue produced by initial 1100 °C-NH₃ pyrolysis of PCS in graphite and alumina crucibles. The mass 28 envelope has been deconvoluted into the separate CO and N₂ contributions for when the PCS-derived residue has been pyrolysed in (a) alumina crucible and (b) a graphite crucible. Key: Mass 28; — CO; ---- N₂; — temperature.

In contrast, CO is the predominant gaseous species evolved for 1550 °C-Ar pyrolyses in graphite crucibles (Fig. 6b) which confirms the involvement of the crucible in the pyrolysis. Very similar results were observed for the PHMCS-derived residue.

The results for PHMCS in fact lend support to Equations 3 and 4 describing the proposed transformation of $\text{Si}_x\text{N}_y\text{O}_z\text{C}_a$ during 1550 °C-Ar pyrolysis. In addition, the observation of CO evolution from PHMCS-derived residues during 1550 °C-Ar pyrolyses in alumina crucibles indicated that C was present in the amorphous white residue justifying its representation as $\text{Si}_x\text{N}_y\text{O}_z\text{C}_a$. The detection of some surface C in “ $\text{Si}_3\text{N}_4/\text{Si}_2\text{N}_2\text{O}$ ” coatings by X-ray photoelectron spectroscopy (XPS) [18] and electron spin resonance (ESR) active C in amorphous white PDPS-derived bulk residues [41] confirms that a small amount of C remains in all amorphous white residues derived from 1100 °C-NH₃ pyrolysis of pre-ceramic polymers.

All mass 28 envelopes detected (i.e. from runs involving both PHMCS and PCS-derived residues) peaked between 50 and 100 min after the 1550 °C heating program was initiated (see Fig. 6). In addition, the mass 28 envelopes (for both PHMCS and PCS-derived residues) exhibited long asymmetric tails after showing a peak in gas evolution. The mass signal giving rise to the asymmetric tails terminated abruptly at the conclusion of the 1550 °C heating program (see Fig. 6). This strongly suggests that the residues were still reacting and evolving gases right up to the point of the termination of the 1550 °C heating program. This was confirmed by determining the half-life for gas mixing within the furnace for the specific argon flow gas conditions used, which was found by experiment to be only 7 min.

3.3.1.4. Pyrolysis in vacuum. All white residues pyrolysed in vacuum to 1550 °C gave extremely high (> 70%) weight losses (see Table II) which makes this method of pyrolysis less desirable. The powders generated from pyrolysis of PDPS and PMSED volatilized completely in vacuum at 1550 °C while the white residue from HMCS lost 87% of its original weight. The residue remaining was black and XRD analysis indicated β -SiC. The underside of the graphite furnace cover was covered in a silvery grey metallic-looking material, the identity of which was not clear from XRD spectra, although it is believed to be elemental Si (with a trace of SiC). The degree of volatility of samples can be qualitatively correlated with the amount of Si-O character deduced from ²⁹Si MAS NMR of the original amorphous residues indicating that Si-O character will determine volatility. The white residue obtained from pyrolysis of HMCS generally exhibited less than 100% volatility which is probably attributable to the lower SiO character possessed by this residue as found in the ²⁹Si NMR spectrum. The crystalline products derived from the 1550 °C vacuum pyrolysis of the PCS-derived amorphous white residue were similar to that obtained from HMCS, i.e. SiC, although a mixture rather than a single polytype of

SiC was detected. In addition, SiO₂ in the form of cristobalite was detected. Given the results from the Ar pyrolysis of residues in graphite crucibles, it is likely that the PCS-derived amorphous white residue is interacting with the graphite as described earlier to give SiC as a major product. The same applies to the HMCS-derived white residue.

3.3.2. 1550 °C pyrolyses of black amorphous powders obtained from 1100 °C-N₂ pyrolyses of pre-ceramic polymers

Tables II-V summarize the X-ray diffraction results.

3.3.2.1. Pyrolysis in N₂. Residues from 1100 °C pyrolysis of pre-ceramic polymers with alternating Si-N bonds in their polymeric structure (e.g. HMCS, PHMCS, PDPS and PMSED) usually crystallized at 1550 °C to produce a mixture consisting of significant amounts of SiC and α -Si₃N₄ and trace amounts of β -Si₃N₄. For PDPS (Table III) and HMCS (Table V) rather low weight losses of 8.9 and 7.3%, respectively, were noted. However, for PDPS, one sample subjected to 1550 °C-N₂ pyrolysis exhibited a much higher weight loss of 48.7% and gave SiC as the sole crystalline product. This signifies that approximately half the weight of the PDPS-derived residue has Si-N character as indicated by the ²⁹Si MAS NMR signal in the region expected for Si₃N₄. This is probably lost at N₂ during the pyrolysis.

PCS, in contrast to the other precursors, does not possess any Si-N bonds and is relied upon commercially [7] to yield SiC (fibres) upon pyrolysis in N₂. The PCS-derived black residue obtained from 1100 °C pyrolysis in N₂ predictably yielded SiC as a major product at 1550 °C (weight loss, 3.1%). This correlates well with the ²⁹Si MAS NMR spectrum of the PCS-derived residue after pyrolysis at 1100 °C which showed a single peak assigned to amorphous SiC. The PCS precursor shows the importance of the 1100 °C pyrolysis gas with earlier PCS-derived white residues giving predominantly Si₃N₄ after pyrolysis to 1550 °C.

3.3.2.2. Pyrolysis in Ar. All black residues pyrolysed to 1550 °C in Ar generally gave the same product, i.e. a mixture of two polytypes of SiC. Weight losses for each black amorphous residue fired varied over a wide range from 14.3% (for the PCS-derived black residue) to 84.75% for the black residue generated by initial pyrolysis of PMSED in N₂ to 1100 °C. For the PMSED residue, the ²⁹Si NMR spectrum revealed a significant peak at -105.0 p.p.m. indicating Si-O content which may explain the unusually high volatility. Care was taken to remove O₂ in the initial 1100 °C pyrolysis so it is very likely that the Si-O character was already present in the polymer before it was pyrolysed. All residues heated in Ar gave consistently higher weight losses than when they were pyrolysed in N₂ (see Tables II-V). This may reflect losses of N₂ and CO from the residue upon heating.

4. Conclusions

Pyrolysis of a polycarbosilane and 4 polysilazane polymers in flowing NH_3 or N_2 at 1100°C produce amorphous grey-white and black residues, respectively. NMR and XRD studies reveal that the amorphous white residues are complex products consisting of a Si-C-N-O polymer backbone. These silicon oxycarbonitride residues lose mainly CO and N_2 upon further heating to 1550°C yielding crystalline products. The level of $\text{Si}_2\text{N}_2\text{O}$ and Si_3N_4 in residues subjected to 1550°C pyrolyses depends on a variety of factors such as the furnace atmosphere, the dryness of the NH_3 used in the initial 1100°C - NH_3 pyrolyses as well as the choice of crucible. The initial state of the organosilicon precursor before pyrolysis is also important owing to their moisture sensitivity so that the introduction of Si-O character during handling in ambient conditions is inevitable.

In contrast, NMR and XRD studies indicate that amorphous black residues generated from 1100°C - N_2 pyrolyses of precursors consist of a Si-N-C backbone. In some cases, moisture sensitivity of the precursor polymer will lead to a Si-N-C-O polymer backbone after 1100°C - N_2 pyrolysis as observed for PMSED. In general, the silicon carbonitrides also lose CO and N_2 during crystallization at 1550°C forming significant amounts of SiC and/or Si_3N_4 depending on the choice of furnace atmosphere and starting precursor.

This study provides important insights into the chemical characteristics of the original amorphous residues which are believed to comprise the coating material formed on fibres and planar substrates reported in earlier studies. The crucible dependence of products generated from 1550°C pyrolyses of amorphous residues is of valuable significance in efforts to achieve deliberate control of crystalline products produced from pre-ceramic polymer pyrolyses.

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