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Polycyclodisilazane: a new polymeric precursor for silicon nitride-based ceramics

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Several new polycyclodisilazanes with different molecular structures were synthesized and characterized using gel permeation chromatography and Fourier-transform infrared spectroscopy. All the polymers synthesized were tractable. The pyrolysis of these polymers at 900 °C in nitrogen in a thermal balance indicated that the ceramic yields were very dependent on the compositions of the precursors. The polycyclodisilazanes with reactable groups (Si–H, N–H) showed higher ceramic yields due to the cross-linked structures formed during pyrolysis. The pyrolyzed residues were crystallized by heating to >1500 °C. X-Ray diffraction of the crystallized residues showed that they were mixtures containing silicon nitride and silicon carbide. Chemical analysis of one crystallized residue which gave the highest ceramic yield showed that it contained 70 wt% Si_3N_4 and 25 wt% SiC after heat treatment at 1600 °C. The compositions of the ceramic residues produced depended on the compositions of the polymeric precursors. More silicon carbide was formed in the residues derived from the polymers with phenyl group substituents.

1 Introduction

Silicon nitride (Si_3N_4)-based ceramics are considered to be the leading candidates for a variety of high temperature applications because of their excellent strength to weight ratio, superior high-temperature properties, and resistance to thermal shock.[1,2] Si_3N_4 is usually produced by four main methods: (i) nitridation of metallic silicon ($3Si+2N_2 \rightarrow Si_3N_4$); (ii) gas-phase ammonolysis of silicon tetrachloride ($3SiCl_4+16NH_3 \rightarrow Si_3N_4+12NH_4Cl$); (iii) carbothermal reduction of silicon dioxide ($3SiO_2+6C+2N_2 \rightarrow Si_3N_4+6CO$) and (iv) thermal decomposition of silicon diimide ($3Si(NH)_2 \rightarrow Si_3N_4+NH_3$).[3]

Polysilazanes are useful precursors to various Si_3N_4-based ceramics, the exact compositions of which depend on the polymer composition and the pyrolysis conditions used.[4–23] The conversion of polymeric precursors to ceramics enables the use of processing techniques not attainable with more traditional powder forming methods, particularly in the areas of fibre and film formation and the development of fibre-reinforced ceramic matrix composites having complex shapes.[24–26] One of the limitations of this precursor based processing route is the loss of volatile organic fragments during pyrolysis, which may drastically lower the ceramic yield. This loss results from the distillation of low molecular weight oligomers and/or from depolymerization reactions.[4–8,14–17] Therefore, it is desirable for the polymeric precursors to have a branched or cyclic structure or they have to be cross-linked to form a networked structure during pyrolysis in order to obtain a high ceramic yield.[4–9,12–17,22]

The aim of this work was to investigate the effects of the composition and molecular structure of the polycyclodisilazane precursors on the preparation of Si_3N_4-based ceramics. Therefore, several polycyclodisilazanes with different molecular structures were prepared and pyrolyzed to give ceramic residues. The polymers prepared and ceramics synthesized were characterized by using several experimental techniques. The ceramics synthesized were mixtures containing Si_3N_4 and SiC and the yield was dependent on the composition and molecular structure of the polycyclodisilazane precursor. The pyrolytic yield could be increased by incorporating Si–H and N–H groups in the precursors.

2 Experimental details

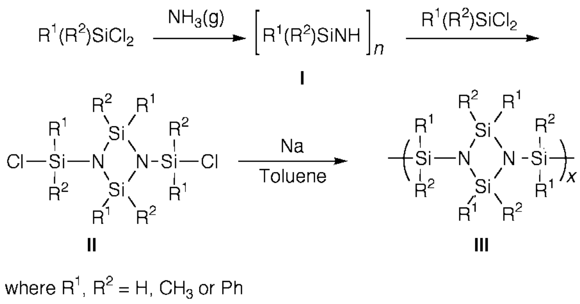
2.1 Materials

All liquid silicon compounds used in the synthesis were obtained from Aldrich Chemical Co. (Poole, UK) or from Fluorochem. Ltd. (Old Glossop, UK) and were purified by distillation. Anhydrous ammonia was used under atmospheric pressure and dried by passing through a KOH trap. Anhydrous diethyl ether and toluene were obtained from Aldrich Chemical Co. The former was used directly but the latter was dried by refluxing over sodium hydride and distilling under a nitrogen atmosphere immediately before starting the reactions. Reactions were carried out in glass equipment which was flame-dried and flushed with dry nitrogen just before use.

2.2 Polymer synthesis

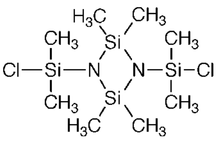
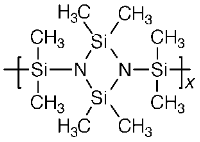
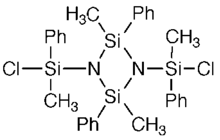
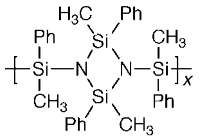
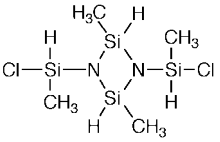
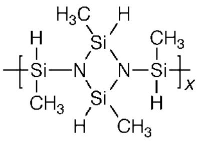
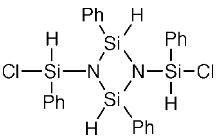
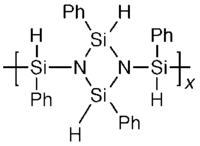
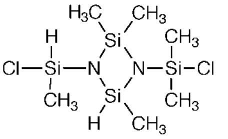
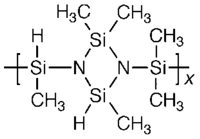
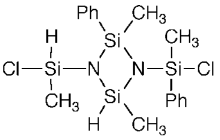
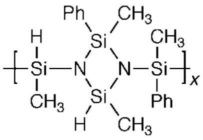
Polycyclodisilazanes in this study were synthesised as shown in reaction Scheme 1 below. The reaction sequences and nomenclature are summarized in Table 1.

The cyclic products **I** in reaction Scheme 1 were prepared by the ammonolysis reaction. In ammonolysis, bubbling ammonia gas was introduced into a molar solution of the appropriate dichlorosilanes in anhydrous diethyl ether at 0 °C. After 5 hours, the ammonium chloride produced was filtered off and the solvent was removed under vacuum to obtain a mixture of the cyclic products **I** with yields between 70 and 85 wt%.



Scheme 1

Table 1 The reaction sequences and nomenclature of tri/tetracyclosilazanes **I**, dichlorocyclodisilazanes **II** and polycyclodisilazanes **III**, see reaction Scheme 1

I	Formula of I	II	Proposed formula of II	III	Proposed formula of III
CDMZ	$[(CH_3)_2SiNH]_{3,4}$	ClDMZ		PCDMZ	
CMPZ	$[CH_3PhSiNH]_{3,4}$	ClMPZ		PCMPZ	
CMHZ	$[CH_3HSiNH]_{3,4}$	ClMHZ		PCMHZ	
CPHZ	$[PhHSiNH]_{3,4}$	ClPHZ		PCPHZ	
CDMZ	$[(CH_3)_2SiNH]_{3,4}$	ClDMMHZ		PCDMMHZ	
CDMZ	$[(CH_3)_2SiNH]_{3,4}$	ClDMPHZ		PCDMPHZ	

N,*N*′-Bis(chlorodialkylsilyl)tetraalkylcyclodisilazanes **II** were prepared by using a method described by Wannagat[27] with some modifications. As an example, *N*,*N*′-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (ClDMZ) was synthesized as follows: a mixture of 0.01 mol (2.56 g) of *n*-methylcyclosilazane and 0.01 mol (1.29 g) of dichlorodimethylsilane was heated to 175 °C for 48 hours and cooled to ambient temperature. Subsequently, 30 ml of petroleum ether (bp 40–60 °C) was added to the residue. The soluble portion was decanted away from the insoluble ammonium chloride. After removing the solvent, *N*,*N*′-bis(chlorodimethylsilyl)tetramethylcyclodisilazane (ClDMZ) was obtained (60 wt% yield).

Polycyclodisilazanes **III** were prepared *via* the alkali dechlorination reaction carried out under a nitrogen atmosphere where the synthesized *N*,*N*′-bis(chlorodialkylsilyl)tetraalkylcyclodisilazanes were used as starting monomers. As an example, poly[*N*,*N*′-bis(dimethylsilyl)tetramethylcyclodisilazane] was synthesized as follows: 30 ml of freshly dried toluene was charged into a 50 ml two-necked round-bottomed flask equipped with a reflux condenser and nitrogen inlet. Freshly cut sodium ($[Na]_0/[Si–Cl]_0 = 1.1$) was placed in the flask and the mixture was heated to reflux and stirred for 30 min, producing a fine dispersion. Then, 1.0 g (0.003 mol) of *N*,*N*′-bis(chlorodimethylsilyl)tetramethylcyclodisilazane in 2 ml toluene was added dropwise (with stirring) to the dispersion. The heating was shut off during monomer addition to maintain the reaction under gentle boiling. Then, the mixture was stirred and refluxed overnight under nitrogen. After cooling to ambient temperature, unreacted sodium and precipitated sodium chloride were filtered out. The solvent and any unreacted monomers in the filtrate were removed by vacuum distillation to obtain a very viscous liquid, poly[*N*,*N*′-bis(dimethylylsilyl)tetramethylcyclodisilazane], with a yield of 54 wt%.

2.3 Pyrolysis

The polymers were placed in an alumina boat and pyrolyzed in a tube furnace (Lenton Thermal Designs Ltd., Market Harborough, UK) in the presence of flowing nitrogen (flow rate approximately 250 ml min^{-1}). The furnace tube was at 120 °C when the polymers were inserted (to minimize any effects of moisture) and heating to 900 °C was carried out at 2 °C min^{-1} followed by soaking at this temperature for 2 hours. Subsequently, the furnace was switched off and allowed to cool to ambient temperature.

2.4 Crystallization

The residues after pyrolysis were heated in the tube furnace in the presence of flowing nitrogen (flow rate approximately 250 ml min^{-1}) to different temperatures (up to 1700 °C) at 2 °C min^{-1} followed by soaking at this temperature for 3 hours and subsequently cooled to ambient temperature at 2 °C min^{-1}.

2.5 Characterization

Fourier-transform infrared (FT-IR) spectra of the cyclosilazanes, dichlorocyclodisilazanes and synthesized polymer samples were obtained using a Nicolet 710 FT-IR at a resolution of 4 cm^{-1} in the wavenumber range of 4000–400 cm^{-1} using standard procedures. The molecular weights of the polymers were determined at RAPRA Technology Ltd., Shrewsbury, Shropshire, UK, by gel permeation chromatography calibrated by polystyrene standards and with tetrahydrofuran as the eluent.

A Fisons Instruments MD 800 gas chromatography–mass spectrometry (GC–MS) unit was used to analyze the mixture of the cyclic products **I** of CDMZ and CMHZ obtained from the ammonolysis reaction. In this analysis, the temperature was programmed to increase at 10 °C min^{-1} over the range 50–250 °C and held at 250 °C for 10 min. The results were recorded and processed with a VG ORGANIC MS Data system (Fisons Instruments MD 800).

The pyrolytic yield from each cyclosilazane, dichlorocyclodisilazane and polycyclodisilazane polymer was measured by thermogravimetry. Samples were heated up to 900 °C in flowing nitrogen (flow rate of 0.5 ml min^{-1}) at 10 °C min^{-1} using a Perkin-Elmer TGA 7 thermal balance. The process of polymer conversion to ceramic, in the temperature range 25 to 800 °C, was investigated further by heating samples to different temperatures at 10 °C min^{-1} in flowing nitrogen (flow rate of 0.5 ml min^{-1}). The residues obtained at different temperatures were characterized subsequently by FT-IR using a procedure identical to that described above.

X-Ray diffraction (XRD) was carried out on a standard Si_3N_4 powder (supplied by the AME Division of Morgan Matroc, UK) and the SiC–Si_3N_4 ceramic residues after heating to various final temperatures ($\geqslant$1200 °C) in nitrogen. Samples for X-ray diffractometry were ground using an agate pestle and mortar. A modified Philips X-ray diffractometer with filtered Cu-Kα radiation of wavelength 0.15418 nm was used (a graphite monochrometer removes Kβ radiation). The voltage and current settings of the diffractometer were 40 kV and 30 mA, respectively. The scan range was from 10° to 90° with a step size of 0.05° and a scan speed of 0.025° s^{-1}. The samples were mounted on a glass slide using a double-sided tape.

Chemical analysis of PCMHZ was carried out at Ceramic Research, Stoke-on-Trent, Staffordshire, UK. Carbon was determined using a LECO CS125 instrument and accelerated oxidation where the C was converted to CO_2 which was analyzed by infra-red detection. Nitrogen and oxygen were analyzed by heating a sample in an electrode EF-500 furnace followed by thermal conductivity measurement and infrared detection, respectively.

3 Results and discussion

3.1 Synthesis and characterization of the polycyclodisilazanes

The polycyclodisilazanes were prepared by stepwise reactions as shown in Scheme 1. In the ammonolysis of dichlorodiorganosilanes R_2SiCl_2 (R = alkyl and/or aryl), cyclic products $(R_2SiNH)_n$ are usually formed.[5–10,20,28–31] In the cases of dichloromethylsilane ($Me(H)SiCl_2$) and dichlorodimethylsilane (Me_2SiCl_2), GC–MS results showed that tri- and tetra-cyclosilazanes were the main cyclic products. For example, as shown in Fig. 1, two major peaks were observed for CMHZ, indicating the presence of these two compounds as the main products. Typically the peak at the lower retention time (15.25 min) was 90.9 wt% of the total product and the second peak at 22.81 min was 8.5 wt%. The corresponding molecular weights were found by mass spectrometry to be 240 and 342 and were identified as $(Me(H)SiNH)_4$ (molecular weight = 236) and $(Me(H)SiNH)_6$ (molecular weight = 354), respectively. Other peaks at the retention times of 12.35 min and 29.18 min are associated with $(Me(H)SiNH)_3$ and $(Me(H)SiNH)_7$ and only accounted for 0.5 and 0.4 wt% of the products, respectively. Therefore, over 90% of the cyclic products are trimethylcyclotrisilazane and tetramethylcyclotetrasilazane. The GC–MS results for CDMZ also showed that the major cyclic products upon ammonolysis of dichlorodimethylsilane were tri- and tetra-cyclosilazanes accounting for over 98 wt%: 53.0 wt% $(Me_2SiNH)_3$ and 45.5 wt% $(Me_2SiNH)_4$. Similar results have been obtained by other researchers too.[8,20,30,31]

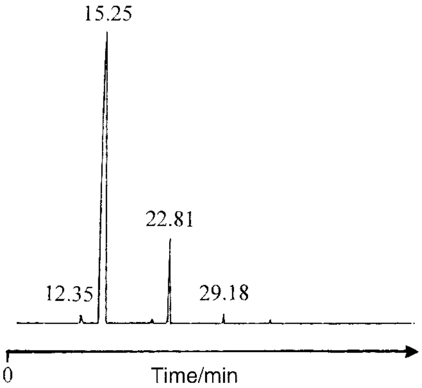


Fig. 1 GC–MS trace of CMHZ.

The FT-IR spectrum of the ammonolysis products (CPHZ) of dichlorophenylsilane, as an example, is shown in Fig. 2a. The spectrum exhibits C–H stretching in the phenyl group at 3066, 3051 and 3003 cm^{-1}. A strong peak at 1425 cm^{-1} and three weak peaks at 1949, 1887 and 1815 cm^{-1} are attributed to the phenyl–Si vibration. The peaks at 949 cm^{-1} and 698 cm^{-1} are typical for asymmetric stretching of Si–N–Si and Si–C symmetric stretching, respectively.[32,33] Two very strong peaks at 1116 cm^{-1} and 840 cm^{-1} are associated with the cyclic Si_4N_2 skeleton.[28,29] A characteristic sharp peak at 3364 cm^{-1} is assigned to the stretching of the N–H bond. The deformation of N–H is shown as the absorption at 1179 cm^{-1}. A characteristic peak at 2140 cm^{-1}, indicating the presence of Si–H, is seen

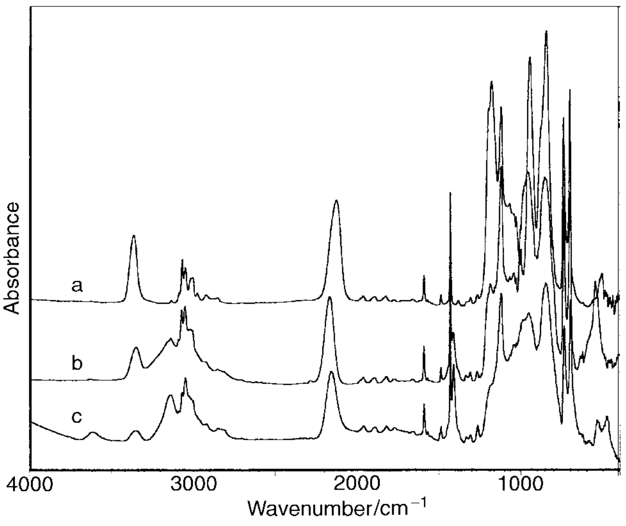
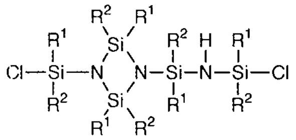


Fig. 2 FT-IR spectra of (a) CPHZ, (b) ClPHZ and (c) PCPHZ.

clearly.[14,15,32,33] The appearance of absorption peaks due to N–H and Si–N–Si bonds indicates the formation of a Si–NH–Si structure in the ammonolysis products.

The cyclosilazanes were then used directly to react with stoichiometric proportions of dichloroalkylsilanes to obtain dichlorocyclodisilazanes **II**, after ammonium chloride was removed as a by-product. As an example, the FT-IR spectrum of *N*,*N*′-bis(hydrophenylsilyl)dihydrodiphenylcyclodisilazane (ClPHZ) is shown in Fig. 2b. It shows a similar spectrum to its corresponding cyclosilazane (Fig. 2a) with an extra absorption peak at 544 cm^{-1} for the stretching of Si–Cl. Since the reaction involves the equilibrium re-distribution of silicon–nitrogen and silicon–chlorine groups, a number of other products can be present in the mixtures including a small proportion of higher boiling components with the structure **II**′ shown below.[28,29]



II′

This was confirmed by the existence of absorption peaks at 3364 cm^{-1} and 1179 cm^{-1} for N–H, although the intensities of these peaks are reduced compared with that of Fig. 2a. However, a peak at 3145 cm^{-1} attributed to the stretching of NH_4^+,[34] indicates that there is a small amount of ammonium chloride left in the compound.

Finally, the polycyclodisilazanes **III** were synthesized by the Wurtz-type polymerization reaction of dichlorocyclodisilazanes with the polymer yields varying between 40 wt% for PCMHZ and 68 wt% for PCMPZ. All the polymers are tractable and can be dissolved in toluene. Some of them are solids, potentially melt processable, compared with most of the polymeric precursors (oligocyclosilazanes) which are largely intractable solids or oligomeric liquids.[6–14] The oligomeric liquids require cross-linking at some stage during pyrolysis. The spectrum (Fig. 2c) of the corresponding polymer (PCPHZ) is similar to that for ClPHZ, but there is a significant decrease in the intensity of the band at 544 cm^{-1} for the stretching of Si–Cl. This indicates that there are some Si–Cl groups remaining at the ends of the polymer chains. The yields of cyclosilazanes **I**, dichlorocyclodisilazanes **II**, polycyclodisilazanes **III** and the state of the polymers are given in Table 2.

The molecular weights of the polycyclodisilaznes showed typical polymodal distributions as expected for products of the alkali dechlorination reaction.[35,36] The calculated values of $\bar{M}_n$, $\bar{M}_w$ and the polydispersity $\bar{M}_w/\bar{M}_n$, which is a measure of the width of the molecular weight distribution for all the samples, are given in Table 3. It can be seen clearly that the molecular weights of the polymers ($\bar{M}_w$) are $\geqslant$1600 and are much higher than those of the corresponding cyclosilazanes **I**.

3.2 Pyrolytic yield

The pyrolytic yields (Table 4) are very much dependent on the molecular weights of the precursors and their structures. Except for cyclohydrophenylsilazane (CPHZ), all the other cyclosilazanes show low pyrolytic yields due to the low molecular weights of the compounds as they volatize easily during heating. The pyrolytic yields of the dichlorocyclodisilazanes are higher compared with those of the corresponding cyclosilazanes, particularly for the compounds with the hydrogen–silicon group. This is probably because of cross-linking during the reaction at ≈175 °C.[37] The polycyclodisilazanes give the highest pyrolytic yields. This indicates that in the case of polymeric precursors suitable for the synthesis of engineering ceramics, a high molecular weight favours a high pyrolytic yield.

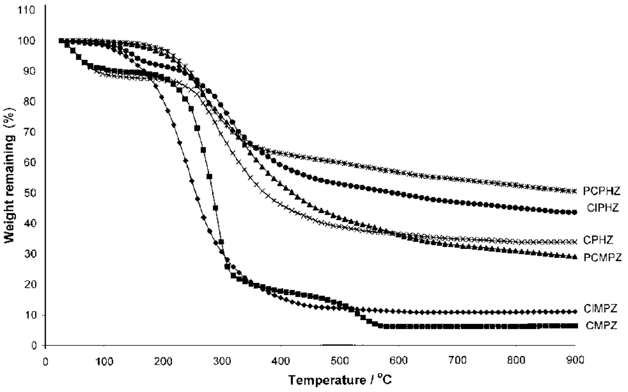


Fig. 3 Thermogravimetric traces of the PCMPZ and PCPHZ polycyclodisilazane series.

The effect of the phenyl substituent, compared with methyl group, on the pyrolytic yields of the polycyclodisilazanes precursors is also noticeable. The polycyclodisilazane with methyl groups (*e.g.* PCDMZ and PCDMMHZ) lead to lower pyrolytic yields than the polycyclodisilazanes with phenyl groups (*e.g.* PCMPZ and PCDMPHZ). As in polysilanes this could be attributed to the retardation of depolymerization by the bulky phenyl group and the easy removal of phenyl radicals following a radical coupling reaction to form a cross-linked structure.[33,38]

The influence of reactive groups such as Si–H and N–H in the precursors on the pyrolytic yield is striking (Table 4). Polymers without reactive groups (PCDMZ and PCMPZ) show very low pyrolytic yields. The pyrolytic yields are improved when some reactive groups are in the polymeric structures (PCDMMHZ and PCDMPHZ). The highest pyrolytic yields are observed in the polymers with even more reactive groups, *i.e.* PCMHZ and PCPHZ. This is because of the cross-linked structures generated during pyrolysis of the polymers containing reactive groups. Typical thermograms of the precursors **I**, **II** and **III** without reactive groups (PCMPZ series) and with reactive groups (PCPHZ series) are shown in Fig. 3. Curves CMPZ and CPHZ for cyclosilazanes exhibit a similar shape at the beginning (<250 °C). Here three regions are apparent in the thermogravimetric curves: (i) as low molecular weight compounds evaporate rapidly between 40 and 250 °C, there is an initial 12–15% weight loss; (ii) 250–370 °C, where an additional weight loss of 65% for CMPZ and 30% for CPHZ occurs, the thermogram shows an increased

Table 2 The yields (wt%) of tri/tetracyclosilazanes **I**, dichlorocyclodisilazanes **II**, and polycyclodisilazanes **III**; see Scheme 1. The state of **III** is also given

Polymer	I	II	III	State of III
PCDMZ	74	60	54	Viscous liquid
PCMPZ	85	65	68	Viscous liquid
PCMHZ	70	60	40	Solid
PCPHZ	70	68	58	Solid
PCDMMHZ	74	60	43	Viscous liquid
PCDMPHZ	74	62	48	Viscous liquid

Table 3 The molecular weights and polydispersity of the polycyclodisilazanes

Polymer	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
PCDMZ	3260	1230	2.7
PCMPZ	1740	860	2.0
PCMHZ	1600	930	1.7
PCPHZ	3050	1340	2.3
PCDMMHZ	1920	730	2.6
PCDMPHZ	3200	1320	2.4

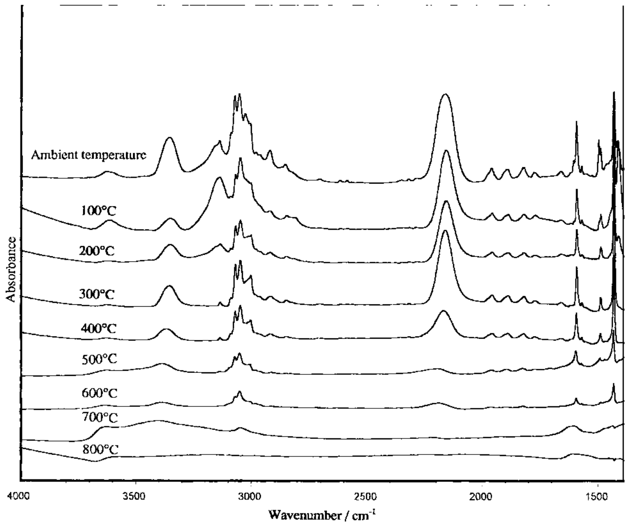


Fig. 4 FT-IR spectra of PCPHZ at ambient temperature and after pyrolysis to various temperatures.

gradient; (iii) 370–900 °C shows a further weight loss of 16%. The pyrolytic yield of CPHZ is 28 wt% higher than that of CMPZ.

In the case of the polycyclodisilazanes (PCMPZ and PCPHZ) the thermogravimetric curves are different in shape, especially at the beginning, compared with those of the cyclosilazanes (CMPZ and CPHZ), but these also show three regions: (i) a slower rate of weight loss of *ca.* 10% occurs between 40 and 250 °C and this is characteristic for a high molecular weight polymer; (ii) an additional weight loss of 50% for PCMPZ and 25% for PCPHZ occurs over a much broader temperature range (250–530 °C); (iii) subsequently, a further weight loss of *ca.* 10% occurs as the sample is heated to 900 °C. The pyrolytic yield of PCPHZ with reactive groups is 20 wt% higher than that of PCMPZ without reactive groups. ClCMPZ and ClCPHZ also show three regions of weight loss and a low weight loss at the beginning (similar to the polycyclodisilazanes). The distinct increase in pyrolytic yields in polycyclodisilazane precursors with reactive groups can be attributed directly to the thermal cross-linking capability of hydrosilane (Si–H) and amine (N–H) groups.

In order to study the pyrolysis process further, poly[*N*,*N*′-bis(hydrophenylsilyl)dihydrodiphenylcyclodisilazane] (PCPHZ) was chosen and heated to different temperature up to 800 °C in nitrogen and then characterized by FT-IR spectroscopy. Analysis of the FT-IR results (Fig. 4) in conjunction with the thermogravimetric results (Fig. 3) allows a more detailed study of the cross-linking process. It can be seen that, as heating progressed to 300 °C, there are no significant changes in the FT-IR spectrum except for the disappearance of the peak at 3145 cm^{-1} which corresponds to the decomposition of ammonium chloride between 200 and 300 °C. After 300 °C, there is a significant decrease in the intensity of the N–H stretch (3408 cm^{-1}) and the Si–H band (2140 cm^{-1}) and finally an elimination of these two bands at 800 °C. These phenomena are associated with the cross-linking occurring during the pyrolysis as illustrated by the possible reactions shown in Scheme 2.[6,13–16,22,39,40]

3.3 Crystallization

Crystalline phases were observed when the pyrolytic residues were heated to >1500 °C in nitrogen. Depending on the structure and chemical composition, different amounts of silicon nitride and silicon carbide were formed. The XRD patterns (Fig. 5) of the Si_3N_4 powder and the ceramic residues derived from PCMHZ which gave the highest ceramic yields showed that the residues were amorphous up to 1200 °C in nitrogen, and then gradually crystallized as the temperature was increased. The prominent peaks representing the presence of α-Si_3N_4 with small peaks at $2\theta = 36°$, 61°, and 72° corresponding to β-SiC were observed at 1600 °C and more β-SiC was formed as the temperature was increased to 1700 °C.[32,41] The chemical analysis (Table 5) of this crystallized ceramic residue after heat treatment at 1600 °C leads to a composition containing 70.0 wt% Si_3N_4, 25.4 wt% SiC,

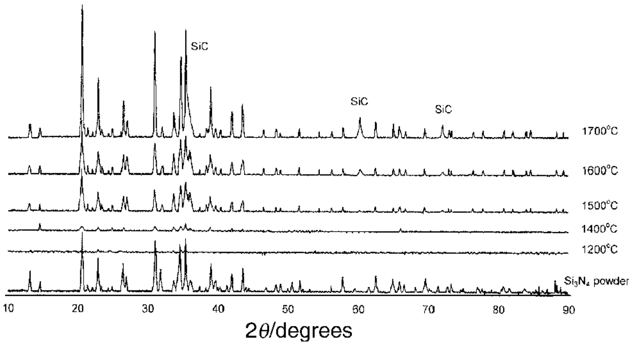
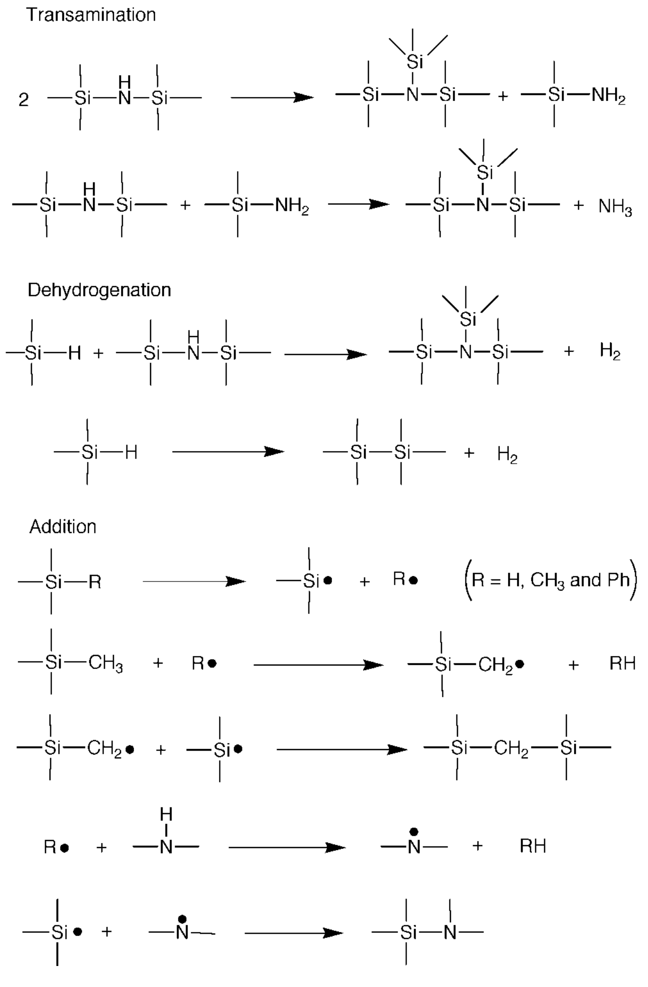


Fig. 5 XRD patterns of PCMHZ after heating to different temperatures up to 1700 °C for 3 hours in nitrogen.

Table 4 The pyrolytic yields (wt%) of tri/tetracyclosilazanes **I**, dichlorocyclodisilazanes **II** and polycyclodisilazanes **III**, see Scheme 1

Polymer	I	II	III
PCDMZ	0	7.4	10.5
PCMPZ	6.0	10.5	28.4
PCMHZ	10.4	42.5	68.8
PCPHZ	33.3	43.1	49.8
PCDMMHZ	0	5.0	14.5
PCDMPHZ	0	20.0	32.2



Scheme 2

3.4 wt% SiO_2 and 1.2 wt% free carbon calculated by assuming all nitrogen atoms are bonded to Si as Si_3N_4 and by assigning the residual Si atoms to SiC and SiO_2, in that order. The SiC formed over 1600 °C in nitrogen can be explained by either an excessive Si–C bond content in the original polymer which directly causes the carbide formation,[12] or by the reaction between Si_3N_4 and free carbon generated during pyrolysis of the precursor at temperatures above 1450 °C, as shown below:[42]

$$Si_3N_4 + 3C \xrightarrow{1450\,^{\circ}C} 3SiC + 2N_2$$

The presence of phenyl groups in the precursors (*e.g.* PCMPZ, PCPHZ) leads to more C formed in the pyrolyzed residues.[43–45]

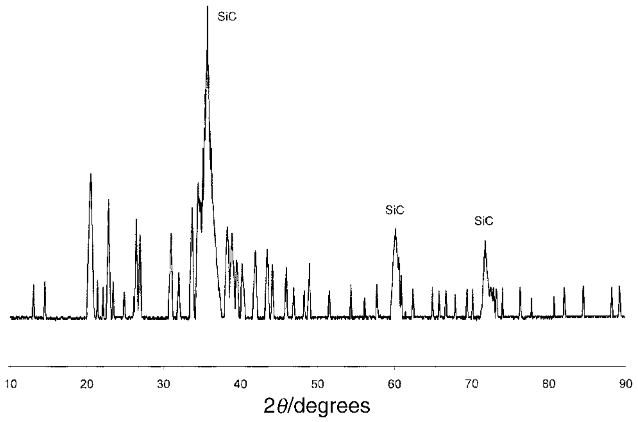


Fig. 6 XRD pattern of PCPHZ after heating to 1600 °C for 3 hours in nitrogen.

Table 5 Carbon, nitrogen and oxygen contents in the pyrolytic residue of PCMHZ after heating to 1600 °C for 3 hours in nitrogen

C (wt%)	N (wt%)	O (wt%)
8.82	28.0	1.80

Thus, the XRD patterns of their crystallized ceramic products showed more prominent peaks representing β-SiC (Fig. 6). The relationship between the structure and composition of the polymeric precursor and the final composition of the ceramic can be utilized advantageously to tailor the final compositions of SiC–Si_3N_4 powder blends and the microstructures of the ceramic components produced.

It is well known that conventional Si_3N_4–SiC composites derived from powder mixtures show several disadvantages. The SiC inclusions retard the sintering of the Si_3N_4 matrix and therefore require large amounts of sintering aid and a sintering temperature in excess of 1800 °C. The distribution of phases in the microstructure is inhomogeneous and the high temperature strength is low because of increased amounts of grain boundary phase caused by the addition of high amounts of sintering aid. The use of precursors as developed in this work will help overcome these disadvantages by uncovering alternative routes for the production of Si_3N_4–SiC powder blends.

The production of such powder blends will help discontinuously reinforced ceramic matrix composites (CMC) forming technology. These consist of a matrix phase (typically silicon nitride) to which a reinforcing phase (such as silicon carbide particles) is added. Si_3N_4–SiC composites offer high strength, toughness and oxidation resistance at high temperatures and their mechanical properties can be further enhanced if the sinterability and microstructural homogeneity can be improved together with a reduction in the processing temperatures and overall production costs. The potential demand for discontinuous CMC far outweighs that for continuous CMC. The industrial base for discontinuous CMC is healthy and growing rapidly especially in the areas of cutting tools and extrusion dies.

4 Conclusions

Several polycyclodisilazanes which are novel precursors for silicon nitride-based ceramics have been synthesized and characterized. The pyrolytic yield of each precursor was very dependent on its molecular structure and composition. Polymers with functional groups (Si–H and N–H) that provide latent reactivity displayed higher pyrolytic yields because of the cross-linked structures formed during pyrolysis. Polymers with higher molecular weights give higher pyrolytic yields. The pyrolytic residues crystallized at >1500 °C in nitrogen form mixtures of α-Si_3N_4 and β-SiC. The amount of SiC in the ceramic residue depended on the composition of the polymeric precursor and this could be utilized to produce the required SiC–Si_3N_4 powder blend.

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