JOURNAL OF MATERIALS SCIENCE 24 (1989) 1707–1718

Preceramic polymer pyrolysis

Part 1 *Pyrolytic properties of polysilazanes*

YIGAL D. BLUM, KENNETH B. SCHWARTZ*, RICHARD M. LAINE‡
SRI International, Menlo Park, California 94025, USA

The physicochemical behaviour of characterized polysilazanes has been examined during their pyrolytic transformation into amorphous silicon-based ceramics. Selected polysilazanes bearing different substituents at silicon and nitrogen were synthesized by ruthenium catalysed dehydrocoupling of Si–H bonds with N–H bonds. The relationships between the structure and chemical content of polymers and their pyrolysed ceramic compositions and yields are discussed. Possible reactions occurring during pyrolysis are described in terms of a set of mechanisms based on known behaviour of silazane monomers. The decomposition product patterns at different temperature levels and the compositions of the final ceramics suggest specific kinetically or thermodynamically controlled thermolysis pathways. Additional chemical reactivity has been observed when the amorphous ceramic products at 800° C are heated and crystallized at 1600° C.

1. Introduction

The thermolytic conversion of chemicals to ceramics is one of the steadily growing fields in advanced material science [1–3]. New ceramic applications such as chemical vapour deposited (CVD) coatings, sol-gel-derived high-performance glasses, and polymer-derived ceramic fibres are a result of the chemical reactivity and processability of organometallic or inorganic compounds and polymers. In particular, polysilane and polycarbosilane precursors to silicon carbide (SiC) and polysilazane precursors to silicon nitride (Si_3N_4) are important potential precursors for the fabrication of advanced structural ceramics.

Progress in the use of silazane precursors to Si_3N_4 has mainly concentrated on the development of synthetic methods for preparing polymers with higher ceramic yields and improved selectivity to obtain the desired ceramics [4]. Less attention has been given to the basic relationships between the chemical content and the structure of polymers, or the pyrolysis conditions, and the nature of the ceramic materials derived. Consequently, there are insufficient data concerning the chemical reactions that occur during the thermal transformation of a well-defined polymer to a ceramic network and their kinetics or mechanistic pathways. This information is critical for the design of advanced preceramics and better pyrolytic processes to achieve higher ceramic yields and purities.

This paper presents some correlations between polysilazane chemical compositions and structures and their derived ceramic products. It also shows the feasibility of using transition metal catalysis [5–8] as a synthesis tool for forming new precursors to Si_3N_4 with novel chemical, rheological, viscoelastic, and pyrolytic properties. The precursors described here include a promising polymer prototype based on the monomeric units $-[H_2SiNCH_3]-$ [9, 10]. This family of preceramic polymers has been further investigated for its pyrolytic properties under a variety of thermolytic conditions, as will be described elsewhere.

2. Background

Twenty years ago, Chantrell and Popper [11] envisaged the possibility of converting tractable polymers having an inorganic skeleton to ceramic materials. (Historically, the definition of polysilazane is less restricted from that of organic polymers as M_n values higher than 3000 daltons (a medium size organic oligomer) are rarely known. In this paper we use the definition of polymer for all the preceramic products described by the related literature, and for the nonvolatile products obtained after the dehydrocoupling catalysis. The term oligomer is used to describe either volatile silazanes or the building blocks used in the catalytic polymerization process.) The interest in this approach has increased steadily in the past ten years since the commercialization of polymer-derived silicon carbide fibres [12] and binders [13]. It has been driven by the necessity to improve the performance of ceramic materials for advanced applications. Wynne and Rice [14] have summarized the progress in this growing field and set a series of general empirical rules that should be considered for the design of a proper ceramic precursor. These rules are based on experimental observations and logical assumptions. An optimal polymer should have the following properties: (1) high molecular weight, to reduce volatilization; (2) tractability (meltability, malleability or solubility), to

---

*Present address: Raychem Corporation, Corporate Technology, 300 Constitution Drive, Menlo Park, California 94025-1164, USA.
‡Present address: Department of Material Science and Engineering, University of Washington, Seattle, Washington 98195, USA.

apply the preceramics in the desired shape before the pyrolytic process; (3) polymeric structure that is slightly branched or contains cages or rings, to decrease the polymer skeleton degradation; (4) the presence of latent chemical reactivity, to obtain thermosetting or curing properties; (5) low organic functional group content, to increase ceramic yields and avoid the production of undesired free carbon and carbide ceramics.

Other empirical rules are more specific to a certain type of ceramic material or application. For example, the presence of Si-CH_3 functional groups on polysilazanes consistently results in the production of a significant amount of SiC along with the Si_3N_4 when pyrolyzed under an inert atmosphere [15–25]. Therefore, these groups are detrimental to the goal of producing SiC-free Si_3N_4. Furthermore, by analogy to organic polymers, linear-type preceramic polymers having number average molecular weights (M_n) of 20 000 to 50 000 daltons were thought to be necessary [26] if good ceramic fibres were to be produced. The high molecular weight is needed to increase the tenacity of the preceramic fibres. So far, this goal has not been achieved for any of the nitride precursors, though polymers having satisfactory tenacity have been spun into fibres as a result of other polymer properties [15–25, 27–29].

It is not always possible to combine these desirable polymer qualities in one material. Low organic group content [27–29] or excessive branching may cause the polymer to be intractable, labile, or very sensitive to air and moisture [30–32]. A linear polymer having sufficient molecular weight may be fabricated into an excellent fibre, but it will melt or totally decompose during the pyrolysis if it is not made infusible prior to the thermolytic process [5]. Therefore, the design of an optimal precursor requires a balance between versatile properties and specific demands for the individual application.

The common method for silazane synthesis is the ammonolysis (aminolysis) of halosilanes, which was first discovered more than sixty years ago [33]. In general, the direct ammonolysis products are either low molecular weight cyclomers ($n = 3$ to 5) if R_2SiX_2 (R = alkyl, H; and X is halogen) are used, with the exemption of the H_2SiX_2 aminolysis products that are higher linear oligomers (see below) [31]. When tri- or tetrahalosilanes are introduced as reactants, labile oligomers are initially obtained and readily transformed to intractable polymers by thermal reactivity [30–32]. Recently, higher linear polymeric products having the general unit type $[R_2SiNR']_n$ have been synthesized by direct ammonolysis (aminolysis) methods [34, 35]. However, the intense research efforts in preceramic polysilazanes have been accompanied by the development of alternative synthetic methods. These methods use catalytic [17, 18, 36–41] or high-temperature reactions [15, 16, 19–23, 42–44] to convert (by different pathways) mono- and oligosilazanes to polymers that try to meet the rules set above.

The silazanes used in the following pyrolysis studies are the products of a catalytic approach to the synthesis of a suitable silicon nitride precursors [5–10]. Transition metal catalysts promote ring-opening polymerization by which Si–N bonds are activated and a metathesis (rearrangement) reaction takes place to form new Si-N bonds

$$x\,[\mathrm{R_2SiNH}]_n \xleftrightarrow{\text{catalyst}} [\mathrm{R_2SiNH}]_{xn} \qquad (1)$$

These catalysts can also successfully promote Si–N bond formation derived from dehydrocoupling Si–H with N–H bonds under relatively mild conditions, as in Reaction 2.

$$n\mathrm{R_2SiH_2} + n\mathrm{R'NH_2} \xrightarrow{\text{catalyst}} n/x[\mathrm{R_2SiNR'}]_x + 2n\mathrm{H_2} \qquad (2)$$

Catalytic dehydrocoupling can be used to produce various prototypes of polysilazanes from silane or oligosilazane building blocks. These polysilazane precursors have a wide range of structural and chemical characteristics related to the structure and chemical reactivity of the starting reagents. The synthesis approach can thus be used as a tool to study the effects of variations in polysilazane chemistry on their pyrolytic properties. Some of these silazanes have excellent polymeric properties [45] and pyrolytic characteristics [46] for use as preceramic materials and are under investigation for binder [47], coating [48], and fibre [49] applications.

3. Experimental details

3.1. General methods

All liquid silicon compounds were purchased from Petrarch System Inc., Bristol, PA and were purified by distillation, from CaH_2. Gases were purchased from Matheson Gas Products, Secaucus, NJ, and ruthenium catalyst from Strem Chemicals, Newbury Port, Ma, and these were generally used without further purification. Anhydrous ammonia and monomethylamine used under atmospheric pressure were further dried by passing through a KOH trap. Tetrahydrofuran (THF) and ethyl ether were purchased from Mallinckrodt, Paris, KY, and purified by distillation over sodium-benzoketyl complex under nitrogen. Elemental analyses of polymers and ceramics determined that most of the materials contained oxygen contamination below 1 wt %.

3.2. Polymer characterization

Polymer product analyses are described elsewhere [5–8, 45] and will not be discussed in this article. In general, ^1H- and ^{29}Si-nuclear magnetic resonance (NMR), gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), and infrared (IR) techniques were used for chemical characterization. Vapour-phase osmometry (VPO), size exclusion chromatography (SEC), and rheometry were the analytical methods for the polymer property evaluations.

3.3. General catalytic procedure

All reactions were normally run in a magnetically stirred 45 ml Parr stainless steel reactor, equipped with pressure gauge and gas-loading inlet–outlet. Reactants (silanes and oligosilazanes) were added to the loaded catalyst under nitrogen in a dry box. The sealed reactor was heated in an oil bath controlled by thermocouple with an error limit of ± 2° C. Whenever ammonia was used as a reagent, the reactor was pressurized to maximum (usually 80 to 90 p.s.i. (0.55 to 0.62 N mm^{-2})); then the charged gas was allowed to dissolve in the solution. The procedure was repeated until saturation was reached, as determined by the absence of pressure drop. The reaction progress was monitored by the hydrogen pressure buildup at constant reaction temperature. The reactor was periodically cooled and depressurized to release the generated hydrogen and to recharge the autoclave with ammonia.

3.4. Polymer synthesis

3.4.1. *Oligo(Si-diethylsilazane) (ODES)*

To 25 μmol $Ru_3(CO)_{12}$ (16 mg) was added 20.0 mmol diethylsilane (1.76 g). The solution was heated at 60° C under approximately 200 p.s.i. (1.378 N mm^{-2}) ammonia. The reactor was recharged with NH_3 after 1 h and heated again for 2 h until gas evolution ceased. The starting reagent totally disappeared, and a series of linear and cyclooligomers was obtained and analysed by GC and GC–MS.

3.4.2. *Poly(Si-phenylsilazane) (PPS)*

To 25 μmol $Ru_3(CO)_{12}$ (16 mg) was added 10.0 g phenylsilane, and the reactor was heated initially at 60° C, under approximately 200 p.s.i. (1.378 N mm^{-2}) ammonia. The gas phase was replaced periodically with a fresh amount of ammonia and the temperature was maintained for 20 h; the temperature was then raised to 90° C. After 30 h, 5 ml THF was added to decrease the solution viscosity. After 40 h, 8 mg catalyst was added to enhance reactivity. The total reaction time was 50 h. THF was removed by vacuum evaporation at 60° C/200 μm.

3.4.3. *Poly(Si-hexylsilazane) (PHS)*

A reaction between *n*-hexylsilane and ammonia was run using the same quantities and initial conditions as those for PPS synthesis. After 23 h, the temperature was raised to 90° C; after 35 h, an additional 16 mg catalyst was added, followed by a second addition of 8 mg catalyst and 5 ml THF after 44 h. The reaction was terminated after 56 h and solvent was evaporated by vacuum (60° C/200 μm).

3.4.4. *Poly(N-methylsilazanes) (PNMS)*

To 50 g oligo(*N*-methylsilazane) [8] (ONMS; M_n = 1100, M_w = 4000, M_z = 13 000 daltons; viscosity = 5 P) was added 100 mg $Ru_3(CO)_{12}$, and the mixture was heated at 90° C in a magnetically stirred quartz reactor sealed under nitrogen. The reaction was continued for 65 h and the evolved polymer was found to have M_n = 2300, M_w = 23 600, M_z = 128 000 daltons and a viscosity of 98 P.

3.5. Pyrolysis studies

Bulk pyrolysis experiments were conducted under controlled conditions in a quartz tube connected by a manifold to several gas lines and a vacuum pump. The reaction tube was placed inside a Lindberg horizontal tube furnace controlled by a Barber–Coleman 570 programmable controller. This experimental configuration allowed polymer pyrolyses to be carried out under a variety of atmospheres or mixtures of gases. Samples for bulk pyrolysis were loaded into quartz crucibles in a nitrogen dry box and transferred to the furnace. After several evacuation/purge cycles, the samples were heated with a linear ramping schedule under flowing nitrogen. Gas flow rates were typically 60 ml min^{-1} and the standard heating rate was 0.5° C min^{-1}. Samples were heated to 800° C and held at that temperature for 3 h.

Some polysilazane pyrolysis products were subsequently heated to 1600° C in a Centorr Associates high-temperature, controlled-atmosphere furnace. This furnace has a graphite heating element and is capable of generating gas pressures of 2000 kPa. Pyrolysed material was placed in molybdenum crucibles and heated to 1600° C at ~ 10° C min^{-1} in a static nitrogen environment. Gas pressure was ~ 100 kPa at room temperature and increased to ~ 700 kPa at 1600° C. The products of polysilazane pyrolysis and high-temperature treatment were characterized by powder X-ray diffraction techniques for phase identification. Bulk chemical analyses for carbon, hydrogen, silicon, nitrogen and oxygen were performed at Galbraith Laboratories, Knoxville, Tennessee. Periodic duplicate analyses and analysis of commercial Si_3N_4 were also performed to corroborate the results.

To obtain more detailed information on the mechanisms of polymer pyrolysis, thermogravimetric analysis (TGA) experiments were performed. These experiments used a vertical clamshell furnace and a Cahn RG microbalance controlled by an Apple II Plus microcomputer. TGA experiments were performed under conditions identical to the bulk pyrolysis experiments. Sample masses of ~ 30 mg were loaded in quartz baskets and heated under flowing nitrogen. Mass determinations averaged from 300 measurements were collected every 4 min with an error of ± 50 μm at low temperatures and ± 75 μm at temperatures above ~ 600° C.

Several different mass spectrometry experiments were performed to determine the composition of fragments released during the conversion of polysilazane to ceramic material. This was necessary because the evolved fragments during the pyrolysis have a wide range of molecular weights and volatilities with different chemical interactions on chromatographic supports.

Two GC–MS systems were used for analysing volatile decomposition compounds collected from vapours that were carried by the nitrogen flow and passed through a hexane solution trap at − 78° C. One was a Ribermag R 10-10-C equipped with 5 m fused silica capillary column; the carrier gas was helium. This instrument is sensitive to compounds having more than 50 a.m.u. The second instrument used for analysis of gaseous products was an LKB 9000 equipped with a 2 m packed column with 4% carbowax 20 M on Carbopack B, 0.8% KOH.

For identifying heavy pyrolysis fragments, Knudsen cell mass spectrometry was found to be an effective technique [50]. Polysilazane was loaded into a Knudsen cell, a small molybdenum cylindrical container with a very small orifice. The cell was placed in a high-vacuum system with the orifice in line-of-sight with a mass spectrometer ion source and heated to high temperature. The gaseous fragments formed during pyrolysis eventually escaped through the orifice and were detected by the mass spectrometer. Because the cell was at high temperature, the heavy fragments could be detected before they condensed.

Pyrolysis/field ionization mass spectrometry (Py/FIMS) was also used for identifying high molecular weight volatiles [51]. Approximately 50 μg samples were introduced via a heated direct insertion probe, and the samples were heated gradually from room temperature to 500° C under high vacuum.

Lighter, more volatile decomposition products of polysilazane pyrolysis were identified using temperature-programmed-reaction (TPR) mass spectrometry. The polysilazane was heated in a quartz tube under flowing helium. The helium acted as a carrier gas that transported light pyrolysis fragments through a gas line to a mass spectrometer where these fragments could be identified. The gas line was heated to 150° C. The heavy, nonvolatile fragments of polysilazane pyrolysis, which condense rapidly at low temperatures, and were not observed in the TPR studies.

4. Results

Various types of silicon- and nitrogen-substituted oligo- and polysilazanes were synthesized by the transition metal catalytic dehydrocoupling reaction [3, 4]. Their pyrolytic behaviour and the evolution of their ceramic products were examined; the results are discussed below.

4.1. *Si*-dialkylsilazanes

Tetramethyldisilazane was reacted with ammonia in the presence of transition metal catalyst to produce a mixture of cyclic and linear oligomers and polymers [5, 6]

$$\mathrm{H(CH_3)_2SiNHSi(CH_3)_2H + NH_3} \xrightarrow{\mathrm{Ru_3(CO)_{12}/60\ to\ 90^\circ C}} \times \overline{\lfloor[\mathrm{(CH_3)_2SiNH}]_n\rfloor} + \mathrm{H\text{-}[(CH_3)_2SiNH]_n\text{-}Si(CH_3)_2H} + \mathrm{H_2} \qquad (3)$$

The ratio of cyclomers to linear oligomers was dependent on the catalyst type and the reaction conditions. After distillation of the volatile oligomers (150 to 180° C at 40 Pa (300 μm)), the remaining polymeric fraction of ~20 wt % was analysed as linear poly(*Si*-dimethylsilazane) (PDMS) with number average (M_n), weight average (M_w), and Z average (M_z) molecular weight values of 2000, 9600, and 28 100 daltons, respectively.

Pyrolysis of this polymer yields negligible amounts of ceramic products. The TGA results (Fig. 1) indicate that weight loss is fairly continuous between 150 and 500° C, at which point the rate of decomposition is slightly enhanced. Because the polymeric fraction is the nonvolatile residue (180° C/40 Pa) of Reaction 3, polymer volatility cannot account for the low ceramic yield. Such behaviour is explained only by a cleavage of Si–N backbone, enhanced by parallel Si–C bond cleavage that starts above 450° C.

The catalytic dehydrocoupling of diethylsilane with ammonia shown in Reaction 4 produces a similar mixture of oligomers [5, 6].

$$\mathrm{Et_2SiH_2 + NH_3} \xrightarrow{\mathrm{Ru\ or\ Pt/60^\circ C}} \mathrm{H\text{-}[Et_2SiNH]_n\text{-}Et_2SiH} + \overline{\lfloor[\mathrm{Et_2SiNH}]_n\rfloor} + \mathrm{H_2N\text{-}[Et_2SiNH]_n\text{-}H} + \mathrm{H\text{-}[Et_2SiNH]_n\text{-}H + H_2} \qquad (4)$$

The oligo(*Si*-diethylsilazane) (ODES) products contain only low molecular weight cyclic and linear oligomers (M_n = 300 to 400 daltons). Pyrolysis of this material gives a negligible ceramic yield. This is not unexpected, given that vacuum distillation provides almost no nonvolatile materials.

4.2. Si-monosubstituted polysilazanes

The use of monosubstituted silanes in the catalytic dehydrocoupling reactions with ammonia provides an additional reactive site on each silicon atom. This third Si–H bond permits the formation of two- and three-dimensional polymers. The potential increase in latent reactivity of the resultant polymer (Si–H and Si–NH_2 functional groups) allows for a controlled degree of cross-linking. The higher dimensional structure of cross-linked polymers should suppress the decomposition pathways that lead to volatile silazanes and result in higher ceramic yields. The choice of the organic substituent will affect the polymerization kinetics and the regio- or chemioselectivity of polymerization when multifunctional step-reaction polymerization is available. These groups also have a major impact on the polymer properties as well as on the derived ceramic yields and compositions.

Phenyl (C_6H_5), hexyl (C_6H_{13}) and ethyl (C_2H_5) monosubstituted silanes ($RSiH_3$) were reacted catalytically with ammonia, Reaction 5, to form bridged,

$$\mathrm{RSiH_3 + NH_3} \xrightarrow{\mathrm{Ru_3(CO)_{12}/60\ to\ 90^\circ C}} \underset{\text{(linear intermediate)}}{\mathrm{\text{-}[RSiHNH]_n\text{-}}} \rightarrow \mathrm{[RSiHNH]_x[RSi(NH_2)NH]_y[RSi(NH)_{1.5}]_z} \qquad (5)$$

branched, or ring-type polymeric products after initial formation of linear oligomeric intermediates.

The physical and the pyrolytic properties of polymers synthesized by Reaction 5 are strongly dependent on the chemical properties and behaviour of the substituted organic groups. Linear polymerization and the subsequent bridging or cross-linking processes are strongly influenced by steric effects. The ethylsilane reaction produces a cross-linked, infusible soft rubber after only 6 h at 60° C [8]. Meanwhile, poly(*Si*-phenylsilazane) (PPS) is still a liquid after 30 h at 60° C (M_n ~ 850 daltons), but transforms to a meltable solid (M_n ~ 1200 daltons) when the temperature is raised to 90° C. The poly(*Si*-hexylsilazane) (PHS), also a liquid after 30 h at 60° C, does not solidify after an additional 26 h at 90° C despite having M_n ~ 2200 daltons, nearly twice that of the phenyl analogue. Clearly, the steric bulk of the phenyl and hexyl groups inhibit extensive cross-linking even after longer reaction periods and at higher final reaction temperature.

TABLE I Polymer and pyrolytic properties of PPS and PHS aliquots

	R group	Reaction time (h)*	Pyrolysis temp. (°C)†	Mn‡ (daltons)	Pyrolysis yield (wt %)	Elemental analysis (wt %)				
						C	H	N	Si	O
1	Phenyl	20 (BP)§	-	850	-	60.6	5.8	9.6¶	22.9	0.5
2	Phenyl	20	800	-	50	50.8	1.1	14.3	27.2	5.4
3	Phenyl	50 (BP)§	-	1220	-	55.7	5.8	15.7	20.8	1.2
4	Phenyl	50	800	-	69	41.5	1.1	21.4	29.9	6.3
5	Phenyl	50	1600	-	-	33.6	0.2	23.9	39.3	0.7
6	Hexyl	30 (BP)§	-	850	-	56.1	11.5	9.1¶	21.2	0.5
7	Hexyl	30	800	-	24	21.2	0.5	26.6	49.4	1.2
8	Hexyl	56 (BP)§	-	2210	-	53.3	9.8	14.8	20.4	2.2
9	Hexyl	56	800	-	36	16.0	0.9	32.2	49.9	0.9
10	Hexyl	56	1600	-	-	9.0	0.1	34.4	54.9	0.5

*The polymerization degree in Reaction 4 is extended with time due to changes of reaction conditions.

†The 1600° C pyrolysis is the continuation of the 800° C in a Centorr furnace.

‡ M_n was measured by VPO technique.

§BP = polymer analysis before pyrolysis.

¶The oligomer species are substantially linear, but the N : Si mole ratio is lower than 1.00 due to the presence of free silane and silyl terminal groups.

4.2.1. Pyrolysis studies

The effects of the organic substituents on polymer molecular weight, ceramic yields and pyrolysis products are shown in Table I. The high ceramic yields obtained with the poly(*Si*-phenylsilazane) precursors result from extensive carbon incorporation. Calculation of the partial weight loss of elements during pyrolysis of the 50 h Si-phenylsilazane reveals that the gaseous products are mainly organic. Small quantities of nitrogen-containing compounds are also released but loss of silicon is not observed. The 20 h *Si*-phenylsilazane, which has an excess of silicon relative to Si_3N_4 stoichiometry, apparently does lose silicon during pyrolysis because of the presence of volatile silicon species coinciding with direct skeleton fragmentation. This difference demonstrates the necessity of cross-linking or branching to achieve good ceramic yields.

The *Si*-hexylsilazane pyrolysis products have lower carbon contents than those of the phenyl analogue, which can partially explain their relatively low ceramic yields. The low ceramic yields given by the 56 h *Si*-hexylsilazane are also attributed to the loss of compounds containing ~ 6 wt % Si and ~ 10 wt % N. The release of silicon and nitrogen containing compounds is even more pronounced for the 30 h oligomeric mixture that contains remains of the volatile hexylsilane, low molecular weight oligomers, and linear species that can be thermally degraded.

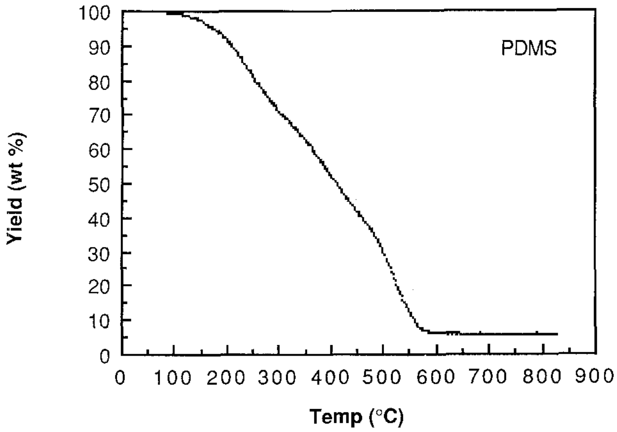


Figure 1 The TGA profile of 1,1-polydimethylsilazane (PDMS).

Examination of the chemical composition of the pyrolysis products as shown in Table II demonstrates that polymeric precursors of the same type with higher nitrogen contents have correspondingly higher N : Si mole ratios in the final material. For both hexyl- and phenylsilazanes, the more highly polymerized material is transformed to a ceramic product with N : Si ratios close to stoichiometric Si_3N_4. It is clear that all materials produced from polymer pyrolysis to 800° C have hydrogen present in significant concentrations. The high mole ratios of hydrogen cannot be accounted for in terms of C–H bonds alone, based on the residual carbon, and point to the presence of Si–H and/or N–H bonded species in the pyrolysis product [29].

The inorganic materials derived from the pyrolysis of the hexyl and the phenyl substituted polysilazanes were heated further to 1600° C. This resulted in the crystallization of α- and β-Si_3N_4 from the previously amorphous pyrolysis products. Changes in chemical composition during the high-temperature treatment include a significant decrease in the carbon and hydrogen content. Stoichiometric calculations indicate that only small amounts of SiC (~ 5 wt %) can possibly be produced at 1600° C. This observation is supported by the absence of SiC in the XRD pattern.

TGA studies of the cross-linked 50 h *Si*-phenylsilazane and 56 h *Si*-hexylsilazane (Fig. 2) reveal that

TABLE II Chemical compositions of PPS and PHS aliquots and their derived ceramic products

R group	Reaction time (h)	Pyrolysis temp. (°C)	Elemental analysis (mole ratio)				
			C	H	N	Si	O
1 Phenyl	20 (BP)	-	6.17	7.09	0.84	1.00	0.04
2 Phenyl	20	800	4.36	1.16	1.05	1.00	0.35
3 Phenyl	50 (BP)	-	6.25	7.80	1.51	1.00	0.10
4 Phenyl	50	800	3.24	1.03	1.43	1.00	0.37
5 Phenyl	50	1600	2.00	0.14	1.22	1.00	0.03
6 Hexyl	30 (BP)	-	6.18	15.2	0.86	1.00	0.04
7 Hexyl	30	800	1.00	0.28	1.08	1.00	0.04
8 Hexyl	56 (BP)	-	6.10	13.5	1.45	1.00	0.19
9 Hexyl	56	800	0.75	0.51	1.29	1.00	0.03
10 Hexyl	56	1600	0.38	0.05	1.25	1.00	0.01

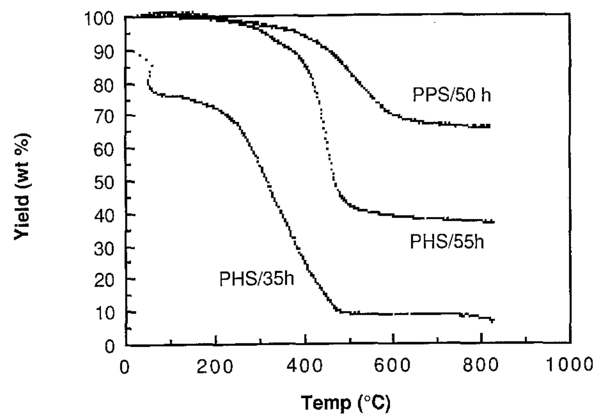


Figure 2 The TGA profiles of (a) PPS (50 h), (b) PHS (30 h) and (c) PHS (56 h).

both are stable to 250° C. Only small mass fractions are lost below 400° C, the range in which retroversion and redistribution reactions of the silicon–nitrogen skeleton are usually detected (see Section 5). The significant differences in thermal reactivity between the phenyl and the hexyl polysilazanes are found in the temperature region between 400 and 550° C. Si–C bond cleavage for the hexyl group is rapid above 400° C and indicates lower kinetic or thermodynamic barriers. The phenyl group is cleaved slowly, suggesting different chemical reactivity, and probably involves carbon–carbon interactions that generate the high carbon content.

The third TGA profile in Fig. 2 tracks the pyrolytic behaviour of the linear, low molecular weight 30 h hexylsilazane. The initial weight loss results from volatilization of unreacted hexylsilane (boiling point of 114° C) that is present in a concentration of ~12 mol % as determined by NMR and SEC. In contrast to the 56 h sample, there is only one degradation step at the region over 300° C.

4.3. Poly(*N*-methylsilazane) (PNMS)

Polymer growth by coupling of linear oligosilazanes through chain extension, branching or cross-linking is another potential advantage provided by the catalytic dehydrocoupling process. According to the general empirical rules described above, an optimal Si_3N_4 precursor should be a tractable, nonvolatile silazane without $Si\text{-}CH_3$ or larger organic substituents but containing functional groups with latent reactivity. It has already been demonstrated that Si–H bonds may provide the desired latent reactivity, allowing the precursor to thermoset during pyrolysis. Oligo(*N*-methylsilazane), $HNCH_3\text{-}[H_2SiNCH_3]_n\text{-}H$ (ONMS), seems to be an ideal candidate that combines many of the optimal precursor properties together with the potential for chain extension by catalytic dehydrocoupling. ONMS, first reported by Aylett and Burnett [31, 32], was studied again as a potential ceramic precursor by Seyferth and Wiseman [18]. They produced ONMS by reacting dichlorosilane with methylamine

$$H_2SiCl_2 + 3CH_3NH_2 \xrightarrow{\text{ether/0° C}}$$

$$\underset{x=10;\ 64\%}{HNCH_3\text{-}[H_2SiNCH_3]_x\text{-}H}$$

$$+ \underset{36\%}{\boxed{[H_2SiNCH_3]_4}} + 2CH_3NH_3Cl \qquad (6)$$

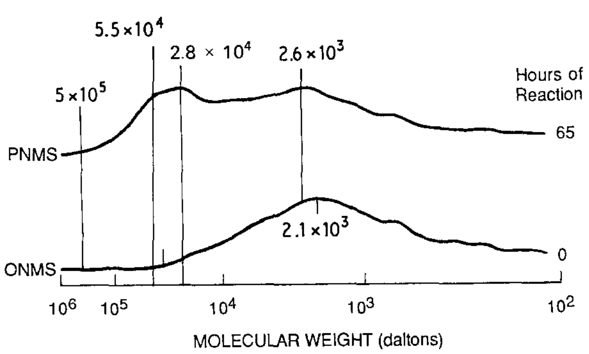


Figure 3 The SEC chromatograms of ONMS and PNMS (65 h).

A considerable fraction of cyclotetramer was obtained that did not contribute to the ceramic yield because of its volatility. The linear oligomer was isolated by distillation and gave a pyrolysis yield of 39%.

The Si–H and Si–NRH functional groups on ONMS are available for dehydrocoupling in the presence of catalyst under mild conditions or supply thermosetting reactivity at elevated temperatures. Higher oligomer (x = 17 to 21) was produced by changing the aminolysis reaction conditions, and the volatile fraction was reduced to 10 to 15 wt % [8]. This latter oligomer was catalytically polymerized using $Ru_3(CO)_{12}$ under a variety of conditions, and the pyrolysis properties of the resulting polymers were examined. Variations in temperature, the amount and type of catalyst, and the use of solvents were found to affect the polymerization process [45, 49]. During the reaction period, the degree of polymerization increased, reflected by values of M_n = 2000 to 2800 daltons, M_w = 20 000 to 50 000 daltons, and M_z = 80 000 to 500 000 daltons for the liquid polymer before transformation to a gel. Fig. 3 shows typical size exclusion chromatography (SEC) results for a catalytic polymerization product, PNMS, in comparison with the initial oligomeric reactant, ONMS. During the process, viscosity increased dramatically from 1 to 5 P up to 4000 to 6000 P. The polymers at the higher viscosities exhibited non-Newtonian behaviour, yet maintained their tractability.

4.3.1. *Pyrolytic characteristics*

To evaluate PNMS as a ceramic precursor and study the thermolytic steps of pyrolysis, we performed a series of bulk pyrolysis, TGA, and powder XRD experiments on catalytically produced polymers and compared the results with those of similar experiments on the initial oligomer, ONMS. The ceramic yields are shown in Table III along with the results of elemental analysis. These data disclose a series of significant findings. First and foremost, the ceramic yields of the catalytically treated polymer are substantially higher than the untreated ones, but the ceramic compositions are almost the same for each of the environmental conditions. Therefore, although catalytic chain extension or cross-linking increases the ceramic yields, the monomer molecular structure controls the ceramic compositions. As determined from Table IV, the high hydrogen content found in the pyrolysis products is

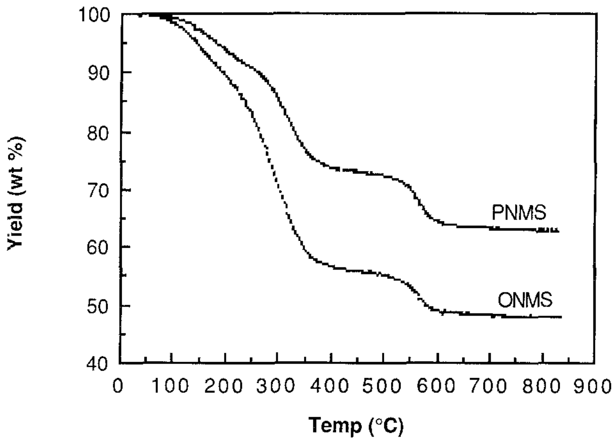


Figure 4 The TGA profiles of ONMS compared to PNMS under the same inert pyrolytic conditions.

partially associated with the inorganic Si–H and N–H remaining and not with the carbon residue alone.

Fig. 4 exhibits TGA plots of ONMS and PNMS pyrolysed under nitrogen. Both plots demonstrate similar thermolytic behaviour: (a) a moderate decrease between 100 and 230° C; (b) a faster decomposition between 230 and 350° C; (c) a plateau in the range 350 to 500° C; and (d) further decomposition between 500 and 600° C. After the last stage no further decomposition is observed up to 900° C. These pyrolysis steps indicate different chemical processes that are further characterized by the mass spectrometry (MS) experiments described below. The major difference in weight loss behaviour between ONMS and PNMS occurs in the temperature range between 100 and 350° C. The final weight loss segment shows exactly the same proportional losses for both.

To obtain the full effect of the catalytic process, the polymerization reaction must proceed over a significant period of time. This is demonstrated in Table III by run 4, where the oligomer is pyrolysed in the presence of catalyst without a preliminary catalytic treatment. Neither the ceramic yield nor the composition of the pyrolysis product were affected relative to the oligomer pyrolysed without the catalyst present.

TABLE III Pyrolytic results of ONMS and PNMS under various conditions

Polymer Run No.	Temp. (°C)	Ceramic yield (wt %)	Elemental analysis (wt %)				
			C	H	N	Si	O
ONMS*							
1[§]	–	–	23.1	8.8	26.0	41.9	0.5
2	800	50	20.3	1.1	34.5	43.2	0.6
3	1600	41	13.1	0.1	34.1	53.2	0.5
4[†]	800	48	18.6	0.9	34.4	43.5	2.9
PNMS[‡]							
5[§]	–	–	21.6	8.0	25.3	44.9	0.5
6	800	61	18.6	1.4	34.5	45.7	0.3
7	1600	49	7.2	0.1	36.4	56.4	0.2

*N-methylsilazane before catalytic treatment; M_n = 1200 daltons; viscosity = 5 P.

[†] $Ru_3(CO)_{12}$ was mixed with a noncatalysed oligomer in weight ratio of 1 : 500 and the mixture was warmed gently only until the solution became homogeneous.

[‡] N-methylsilazane after catalytic treatment; M_n = 2500 daltons; viscosity = 140 P.

[§] Polymer before pyrolysis.

Analysis of the material treated at 1600° C shows that the N : Si ratio (Table IV) now reaches the stoichiometry of crystalline silicon nitride. This coincides with the appearance of α- and β-Si_3N_4 in the XRD pattern. No evidence for SiC is seen from XRD. The H : Si mol ratio decreases to 0.05 and the residual hydrogen may be associated with ceramic carbon or moisture impurities. Comparison between the 800 and 1600° C results of both ONMS and PNMS pyrolysed under nitrogen relates the additional weight loss ($\sim$ 19 wt %) above 800° C to the removal of some of the excess carbon, hydrogen, and nitrogen originally present in the amorphous products.

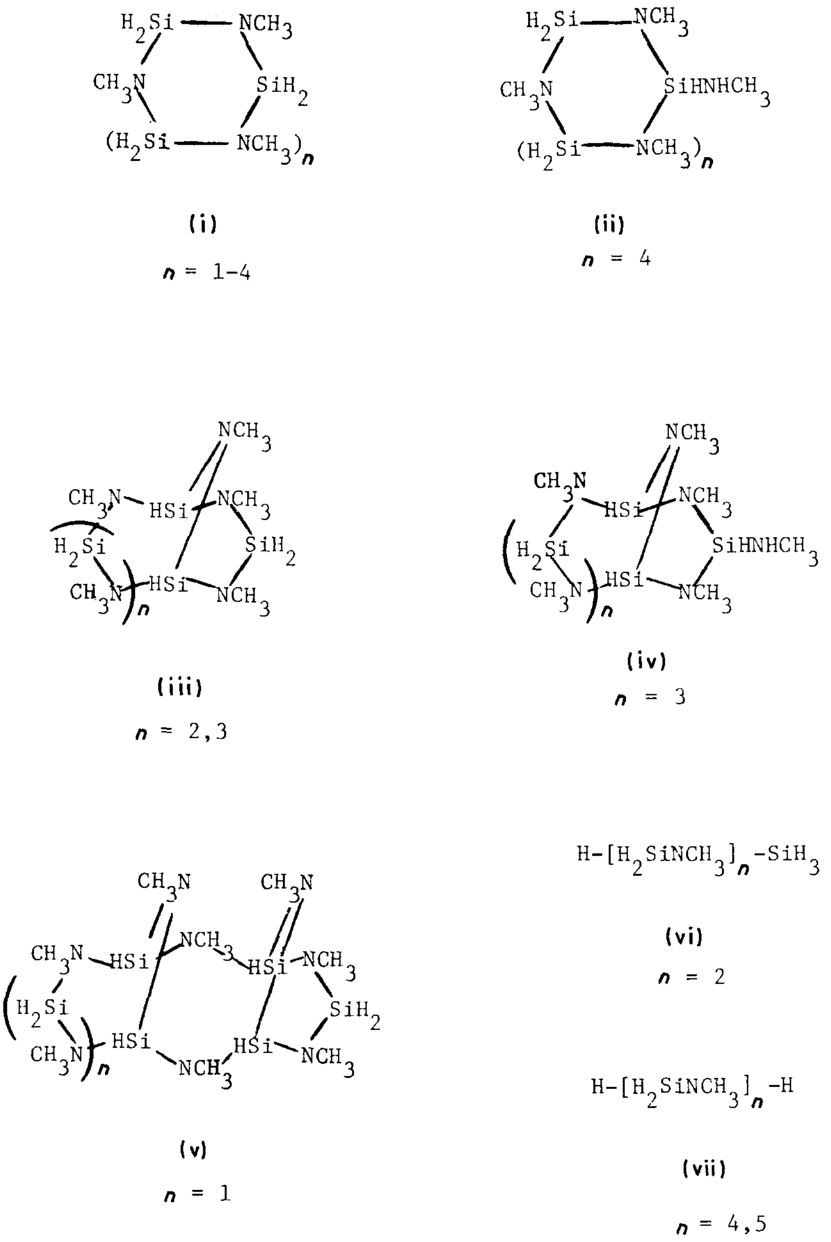
4.3.2. Mass spectrometry studies

A detailed evaluation of the events that occur in the TGA studies is critical to understanding the chemical transformations that occur during the heating process. Correlation of the mass spectrometric (MS) results with the TGA profiles provides some explanation of the weight loss mechanisms. However, because of the wide range of molecular weights and chemical species evolved during pyrolysis, not all volatile products can be followed simultaneously. Furthermore, GC-MS methods requires different columns to cover a range of products having different volatility, polarity or sensitivity toward different column packing. Therefore, a variety of MS instruments were used so as to overlap the whole spectrum. The techniques included high-vacuum instrumentation for nonvolatile fragments, helium atmosphere equipment for the very low molecular weight compounds, and two GC–MS sets for low and high molecular weights. The combined results are qualitatively summarized in Table V and can be correlated to the different areas of reactivity observed by the TGA plots.

The proposed volatile silazane structures include cyclic, linear and bridged oligomers, as illustrated in Scheme I. The three different decomposition stages shown by TGA are corroborated by the MS results. The first stage includes the generation of oligosilazanes, which continues into the second. The second stage is characterized by the evolution of SiH_4 and CH_3NH_2. Decomposition above 500° C involves loss of carbon together with the incorporation of the organic residue providing carbonized material in the amorphous mixture.

TABLE IV Chemical compositions of ONMS and PNMS and their derived ceramic products

Polymer run no.	Temp. (°C)	Elemental analysis (mole ratio)				
		C	H	N	Si	O
ONMS						
1	–	1.29	5.88	1.24	1.00	0.02
2	800	1.10	0.71	1.60	1.00	0.02
3	1600	0.57	0.05	1.28	1.00	0.02
4	800	1.00	0.58	1.58	1.00	0.12
PNMS						
5	–	1.12	5.00	1.13	1.00	0.02
6	800	0.95	0.86	1.51	1.00	0.01
7	1600	0.30	0.05	1.29	1.00	0.01



Scheme I Proposed structures of volatile silazanes released from PNMS during pyrolysis.

5. Discussion

The pyrolysis results primarily demonstrate the strong relationship between the nature of the preceramic silazane and the pyrolysis-derived products. The functional groups that are bound to the Si–N based skeleton and polymer's configuration dominate the ceramic yields and chemical compositions of the pyrolysed products. In rationalizing the results of this investigation, hypothetical mechanisms are suggested with respect to current knowledge about thermolysis chemistry in general and polysilazane pyrolysis in particular. The postulated mechanisms have not been shown to be directly applicable to the conversion of polysilazanes to ceramic products.

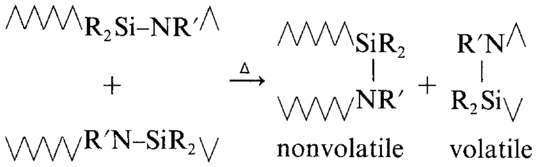
TABLE V Mass-spectrometry analysis of volatiles generated during the pyrolysis process of PNMS

Temp. range (%)	Pyrolytic products
70–250	Silazanes with mol. wt of 150, 167, 236, 265, 295, 322 a.m.u.
250–450	Silazanes with mol. wt of 177, 238, 265, 297, 322, 351, 354, 381, 408 a.m.u. CH_3NH_2, SiH_4
450–600	CH_4(major), C_2H_4, C_2H_6, C_3H_6, C_3H_6, C_3H_8, CH_3CN, $CH_3CH{=}NH$(?)

5.1. Dependency on polymer structure

From our own studies and those of others [15–25, 27–29, 34, 35, 42–44], it is apparent that polymer structure is a major factor in determining the ceramic yields. The pyrolysis of poly(Si-dimethylsilazane) (PDMS) confirms the observation that linear polymers without latent reactivity are unfavourable preceramics. This is further corroborated by the results on the pyrolysis of the linear, low-molecular weight PHS, PPS, and ONMS aliquots. In comparison, the relatively branched, cross-linked, or ring-type (necklace) polymers, which were developed after further catalytic treatment of each oligomer type, exhibited higher ceramic yields. These results actually confirm the general observation for the best preceramics available today; namely that all consist of necklace, sheet, or branched-type structures. The presence of a cross-linked structure or the capability of a polymer to cross-link further at low temperatures retards the thermolytic retroversion reaction that causes the splitting out of volatile cyclomers and linear oligomers from the polymer skeleton. This phenomenon is regarded as a universal observation [14] and has been repeatedly reported to occur during pyrolysis of both organic, siloxane and preceramic polymers. Conversely, the retroversion reaction is promoted by polymer flexibility in the temperature range 200 to 450° C [17–25, 27–29, 34, 35]. The retroversion reaction competes kinetically with the cross-linking process. Therefore, any factors that constrain the flexibility (e.g. cross-linking, branching, rings, cages and bulk organic groups) or increase the latent reactivity of the polymer will result in higher ceramic yields [14].

The retroversion reaction is generally a metathetical rearrangement, as illustrated in Reaction 7. Interaction between the nitrogen lone pair of electrons and the empty d-orbitals of the silicon is suggested to form a penta-coordinated silicon followed by redistribution of the nitrogen–silicon bonds. The interacting groups may belong to the same or different polymer chains. If the same chain loops back on itself, then oligocyclomers split out from the linear polymer and cause the degradation.



(7)

The MS patterns observed during the pyrolysis of PNMS in the temperature ranges 100 to 230 and 230 to 350° C further support the retroversion assumption. This is implied by (a) the appearance of evolved silazanes with masses of 265 and 322 a.m.u. (structures (ii) and (iii) in Scheme I) within the two different TGA ranges, (b) the detection of the more volatile cyclo trisilazane (177 a.m.u.) at the higher temperature range, and (c) the formation of cyclic and bicyclic (bridged) volatile silazanes.

The release of methylamine and silane at temperatures above 250° C suggests other rearrangement pathways that lead to a cross-linking process. The formation of amines (or ammonia) and the rearrangement of hydrides around the silicon atoms are regularly observed among the volatiles generated during pyrolysis of polysilazanes [15–25, 27–32, 42–44]. Amine release may result via condensation of two pendant amine groups ($-R_2Si-NHR$; R = H, organic group, silyl group), as exemplified by Reaction 8. This reaction is actually the driving force for the condensation–polymerization type reaction developed by Verbeek and Winter in which multiaminosilane monomers are successfully condensed to preceramic silazane resins [15, 16, 42–44]. The thermal replacement of one silylamine group with another is also known as transamination [31, 32, 52] and may occur even at relatively low temperature in the presence of a catalyst.

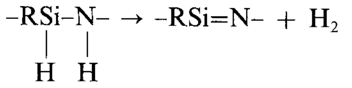
$$2R_3Si-NHR' \xrightarrow{\Delta} R_3Si-NR'-SiR_3 + R'NH_2 \quad (8)$$

Reaction 9 describes a possible process for polysilazane degradation

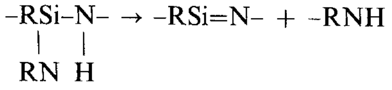
$$2\ R'NH-R_2Si-H \xrightarrow{\Delta} R'NH-R_2Si-NHR' + R_2SiH_2 \quad (9)$$

to silanes at elevated temperatures [31, 32, 53], similar to the amine rearrangement. Both Reactions 8 and 9 are responsible for increasing the cross-linking level.

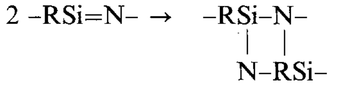
Another hypothetical pathway for a cross-linking process via silylimine intermediates can be postulated if silicon–nitrogen double bonds can be formed as shown in Reactions 10 and 11. Silylimines will spontaneously couple with a second silylimine species or insert into a silicon–nitrogen bond [54, 55]



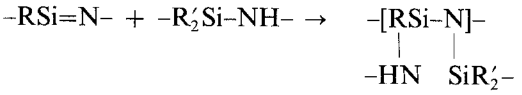
$$-\underset{\displaystyle H}{\underset{|}{RSi}}-\underset{\displaystyle H}{\underset{|}{N}}- \rightarrow -RSi{=}N- + H_2 \quad (10)$$



$$-\underset{\displaystyle RN}{\underset{|}{RSi}}-\underset{\displaystyle H}{\underset{|}{N}}- \rightarrow -RSi{=}N- + -RNH \quad (11)$$



$$2\ -RSi{=}N- \rightarrow \begin{array}{c}-RSi-N-\\ |\quad\ |\\ N-RSi-\end{array} \quad (12)$$



$$-RSi{=}N- + -R_2'Si-NH- \rightarrow \begin{array}{c}-[RSi-N]-\\ |\qquad |\\ -HN\quad SiR_2'-\end{array} \quad (13)$$

5.2. Influence of organic functional groups

5.2.1. Ceramic compositions

The chemical structure of the monomeric unit appears to control the final ceramic compositions. Elemental analyses of ceramic products derived from *N*-methylsilazanes having different molecular weights and limited structural changes reveal almost identical chemical content regardless of the degree of polymerization. In contrast, different aliquots taken during the formation of both PPS and PHS show a direct relationship between nitrogen-enriched polymers and higher nitrogen-to-silicon mole ratio in the ceramic products. Consequently, species containing Si–C bonds can be essentially eliminated from the ceramic compositions in spite of the high carbon content.

As expected, different organic substituents on the polymer result in the formation of various carbon and carbide species as a consequence of their individual chemical reactivity. In related studies, organo-substituted polysilazanes were pyrolysed to nitrogen-deficient and carbon-rich products that were suggested to include SiC [15–25, 27–29, 34, 35, 42–44]. This postulate was rationalized by the fact that further heating above 1500° C indeed led to the transformation of the amorphous products to mixtures of Si_3N_4 and SiC crystallites. Explanations for SiC formation involved either (1) excessive Si–C bond content on the original polymer, which directly causes the carbide formation, or (2) the high-temperature heterogeneous reaction between carbon and silicon nitride. Reaction 14 is

$$Si_3N_4 + C \xrightarrow{>1450^\circ C} SiC + N_2 \quad (14)$$

thermodynamically favoured above 1450° C and provides silicon carbide [56].

The polysilazanes pyrolysed in this research demonstrate that neither the polymer Si–C bonds nor the development of ceramic carbon in the product mixture ultimately leads to the formation of silicon carbide. The hexyl and phenyl groups used in the present investigation are much larger than the methyl substituents, and especially the phenyl ones can be easily condensed to graphitic-type products [57, 58]. The PPS (50 h) derived product (800° C) contains excess nitrogen relative to stoichiometric silicon nitride regardless of the large excess of ceramic carbon, whereas the PHS product has nitrogen–silicon mole ratio close to that of crystalline silicon nitride. The small silicon excess in the latter case is probably a result of minor amounts of Si–C, Si–H or Si–Si bonds. Further heating of both materials from 800 to 1600° C leads to further carbon release. The nitrogen-to-silicon mole ratio is very close to that of silicon nitride, coincident with possible presence of 4 to 6 wt % silicon carbide as estimated by mass calculation. There is no evidence for crystalline carbides in the XRD spectra, which contain only a mixture of α- and β-Si_3N_4.

Similar characteristics are found for PNMS-derived ceramics, where a carbon fraction of 17 to 20 wt % is consistently produced. Again, the excess nitrogen prevents the formation of Si–C bonded species and high-temperature treatment (1600° C) results in further reduction of the carbon content and adjustment of the nitrogen-to-silicon stoichiometry closer to that of Si_3N_4, confirmed by the appearance of mainly α-phase crystallite pattern in XRD.

The chemical reactivity of the N-methyl groups (N–C and C–H bond cleavage compared to C–C bond formation) is observed in the temperature region of 500 to 600° C, somewhat lower than found regularly for Si-methyl substituents [27–29]. The difference is rationalized by the respectively lower bond dissociation energy of N–CH_3 bonds compared with Si–CH_3 [59]. Hydrocarbon incorporation as ceramic carbon should occur at the same temperature, probably by interactions inside the solid lattice and not in the gas phase. The latter demands higher temperatures than described here [57, 58]. Therefore, the reactivity of the organic groups toward the above processes should be enhanced by their bonding to nitrogen or silicon atoms inside the solid lattice. Radical species generated by C–H and N–C homolytic bond dissociation are proposed as likely initiators for carbonization and carburization processes. Such mechanisms were assumed for the Si-methyl group activity in the thermal conversion of poly(*Si*-dimethylsilane) to polycarbosilane followed by the formation of SiC at elevated temperatures [60, 61].

Alkyl groups greater than methyl should react differently during the thermolysis process. The residual carbon content of the PHS-derived materials is relatively lower than might be expected for large hydrocarbon groups and even lower than the carbon content found in the *N*-methylsilazane derived ceramics. This discrepancy can be understood by the lower energy of activation required for the Si–C bond cleavage of this longer alkyl group relative to methyl. Metal–alkyl bonds are subject to a β-elimination mechanism [62], if the alkyl group contains more than one carbon, as illustrated in Reaction 15. Indeed, the TGA for PHS suggest release at 450° C – approximately 100 to 150° C lower than needed for Si–CH_3 bond activation.

$$M\text{-}CH_2CH_2R \xrightarrow{\Delta} M\text{-}H + CH_2{=}CHR \qquad (15)$$

The TGA plots of the analogous phenyl-substituted polymers reveal Si–C bond activation at temperatures as low as 400° C. The β-elimination mechanism is not possible for aromatic rings, but stable radical formation may ease the Si–C bond cleavage. Simultaneously, the phenyl groups can react with each other inside the solid lattice to form fused graphite-like ceramic materials [57, 58].

The contradiction between the present results and those found in the current literature about the formation of SiC species is probably a result of using different polymer substituents. The related studies consist of pyrolysing Si–CH_3 substituted polymers [15–25, 27–29, 34, 35, 42–44]. The presence of methyl groups may lead to the thermal formation of Si–CH_2–Si intermediate links during pyrolytic conversion similar to those obtained during polysilane-to-polycarbosilane conversion [60, 61]. These intermediates are generally proposed to lead to SiC following thermolysis.

5.2.2. Ceramic yields

The ceramic yields are clearly affected by the pyrolysis behaviour of the hydrocarbon substituents. Ceramic yields increase as a direct consequence of carbon incorporation, unless facile Si–C cleavage pathways and subsequent volatilization is possible. Additional specific reactivity of substituents may also affect the ceramic yields. For example, silicon-dimethyl substituted silazanes totally decompose even if the polymer has a necklace structure [63] or is a cross-linked polymer [35] rather than the linear structure described in this paper.

Replacement of at least one silicon-organic substituent by hydrogen leads to moderate ceramic yields even for low molecular weight and linear oligomers (e.g. PHS (30 h), PPS (20 h) and ONMS). The Si–H groups supply latent reactivity to thermoset the polymer by a cross-linking process. Indeed, other linear polyhydridosilazanes developed recently such as $[CH_3SiHNH]_{n/2}[CH_3SiHNCH_3]_{n/2}$ [35] and $[CH_3SiHNH]_n$ [34] demonstrate similar pyrolytic behaviour (ceramic yields of ~ 40 wt %). According to the literature, latent reactivity can be provided by an excess of amido sites (Si–NH_2) [64] or (–NH–) groups on the main chain of a silazane having no pendant organic groups ($[SiH_2NH]_n$) [27–29]. Both result in higher cross-linking by transamination–condensation reactions even at room temperature.

The inhibition of retroversion reactions is another secondary effect caused by the polymer substituents. Bulky organic groups impose certain polymer conformations that may suppress its capability to loop back and form reactive interactions with itself [14].

For example, pyrolysis of the 50 h PPS occurs without loss of silicon, and the hexyl analogue reveals only minor skeletal decomposition.

5.3. Amorphous ceramic structures and reactivities

The structural arrangement and chemical reactivity of polymer-derived amorphous ceramics is one of the most intriguing questions in this field of research. Currently, the hydrogen content has usually been neglected when elemental analyses were used for calculating Si_3N_4, SiC, and C mole ratios in the product compositions. Yet, evidence shows that amorphous materials at 900 to 1100° C still contain Si–H, N–H and C–Si–N bonds [29–32]. The consistent lack of XRD pattern at this temperature range points out that the structures are random and disordered. Therefore, the above calculation procedure can be justified only for a preliminary estimation of the nitrogen excess or deficit, which allows us to predict the potential build-up of silicon or silicon carbide moieties if further heating takes place. The description of the polymer-derived, amorphous ceramics as a mixture of crystalline ceramics (e.g. Si_3N_4, SiC, etc.) is probably incorrect. The reduction in hydrogen content coincides with the nitrogen-to-silicon ratio adjustment at 1600° C and the appearance of a crystalline pattern in the XRD spectra, which reinforces the above statement.

6. Conclusions

The results discussed above clearly demonstrate the critical relationship between the polymer chemical content and structure and the evolution of the pyrolysis products. Organic substituents have a variety of decomposition pathways that result in materials with a wide range of carbon contents. Functional groups that provide latent reactivity can compete against the retroversion reaction in polymers having high conformational flexibility in order to maintain high ceramic yields. These factors are important for better design and tailoring of superior ceramic precursors. Future development in understanding the various thermal mechanisms that occur during the pyrolysis process will also result in improved chemical and pyrolytic processes with increased ceramic yields and decreased impurities.

Acknowledgements

We gratefully acknowledge the support for this research from the Strategic Defense Sciences Office through the Office of Naval Research Contracts N00014-84-C-0392 and N00014-85-C-0668.

References

1. C. J. BRINKER, E. D. CLARK and D. R. ULRICH (eds), "Better Ceramics Through Chemistry I", Materials Research Society Symposium Proceedings, Vol. 32 (North-Holland, New York, 1984).
2. *Idem,* "Better Ceramics Through Chemistry II", Materials Research Society Symposium Proceedings, Vol. 73 (Material Research Society, Pittsburgh, 1986).
3. L. L. HENCH and D. R. ULRICH (eds), "Ultrastructure Processing of Ceramics, Glasses and Composites" (Wiley, New York, 1984).
4. R. M. LAINE, Y. D. BLUM, D. TSE and R. GLASER, in "International Symposium on Inorganic and Organometallic Polymers", edited by M. Zeldin, K. J. Wynne and H. R. Allcock, ACS Symposium Series 360 (American Chemical Society, Washington, 1987) p. 125.
5. Y. D. BLUM and R. M. LAINE, *Organomet.* **5** (1986) 2081.
6. R. M. LAINE and Y. D. BLUM, US Pat. 4612383 (September 1986).
7. R. M. LAINE, Y. D. BLUM, R. D. HAMLIN and A. CHOW, in "Ultrastructure Processing of Advanced Ceramics", edited by D. D. Mackenzie and D. R. Ulrich (Wiley, New York, 1987) p. 761.
8. Y. D. BLUM, R. M. LAINE, K. B. SCHWARTZ, R. M. PLATZ, D. J. ROWCLIFFE, A. L. DODGE, J. M. McLEOD and D. L. ROBERTS, International Patent Application PCT/US86/02266 (October 1986).
9. Y. D. BLUM, R. M. LAINE, K. B. SCHWARTZ, D. J. ROWCLIFFE, R. C. BENING and D. C. COTTS, in "Better Ceramics Through Chemistry II", Materials Research Society Symposium Proceedings, edited by C. J. Brinker, D. E. Clark and D. R. Ulrich (Materials Research Society, Pittsburgh, 1986) p. 389.
10. K. B. SCHWARTZ, D. J. ROWCLIFFE, Y. D. BLUM and R. M. LAINE, *ibid.*, p. 407.
11. P. G. CHANTRELL and E. P. POPPER, in "Special Ceramics – 4", edited by E. P. Popper (Academic, New York, 1964) p. 87.
12. S. YAJIMA, T. SHISHIDO and H. KAYANO, *Nature* **264** (1976) 237.
13. K. NIIHARA, T. YAMAMOTO, K. SUGANUMA, T. TAKEMOTO, T. NISHIKAWA and M. OKUMURA, in "Ultrastructure Processing of Ceramics", edited by D. D. Mackenzie and D. R. Ulrich (Wiley, New York, 1987) p. 891.
14. K. J. WYNNE and R. W. RICE, *Ann. Rev. Mater. Sci.* **14** (1984) 297.
15. W. VERBEEK, US Pat. 3853567 (December 1974).
16. G. WINTER, W. BERBEEK and M. MANSMANN, US Pat. 3892583 (July 1975).
17. D. SEYFERTH and G. H. WISEMAN, US Pat. 4482669 (November 1984).
18. *Idem,* in "Ultrastructure Processing of Ceramics, Glasses and Composites", edited by L. L. Hench and D. R. Ulrich (Wiley, New York, 1984) p. 265.
19. J. H. GAUL Jr, US Pat. 4340619 (July 1982).
20. R. H. BANEY and J. H. GAUL Jr, US Pat. 4310651 (January 1982).
21. J. H. GAUL Jr, US Pat. 4395460 (July 1983).
22. *Idem,* US Pat. 4312970 (January 1982).
23. G. E. LEGROW, T. F. LIM, J. LIPOWITZ and R. S. REAOCH, in "Better Ceramics Through Chemistry II", Materials Research Society Symposium Proceedings, edited by C. J. Brinker, D. E. Clark and D. R. Ulrich, Vol. 73 (Materials Research Society, Pittsburgh, 1986) p. 533.
24. J. P. CANNADY, US Pat. 4535007 (August 1985).
25. *Idem,* US Pat. 4543344 (September 1985).
26. P. FLORY, "Principles of Polymer Chemistry" (Cornell University Press, New York, 1962).
27. D. SEYFERTH, G. H. WISEMAN and C. PRUD'-HOMME, *J. Amer. Ceram. Soc.* **66** (1983) C-13.
28. D. SEYFERTH and G. H. WISEMAN, *Amer. Chem. Soc. Polym. Div. Polym. Preprint* **25** (1984) 10.
29. M. ARAI, S. SAKURADA, T. ISODA and T. TOMIZAWA, *ibid.* **27** (1987) 407.
30. R. R. WILLIS, R. A. MARK and S. A. MUKHERJEE, *Am. Ceram. Soc. Bull.* **62** (1983) 904.
31. B. J. AYLETT, *Organomet. Chem. Rev.* **3** (1968) 151.
32. B. J. AYLETT, G. M. BURNETT, L. K. PETERSON and N. ROSS, *Soc. Chem. Ind. (London) Monograph* **13** (1961) 5.
33. A. STOCK and K. SOMIESKI, *Ber. Dtsch. Chem. Ges.* **54** (1921) 740.
34. M. ARAI and T. ISODA, *Jpn Kokai Tokkyo Koho* JP61 89230 (1986).

35. B. ARKLES, *J. Electrochem. Soc.* **133** (1986) 233.
36. A. A. ZHDANOV, G. V. KOTRELEV, V. V. KAZAKOVA and YE. P. REDKOZUBOVA, *Polym. Sci. USSR* **27** (1985) 1593.
37. K. A. ANDRIANOV, B. A. ISMAILOV, A.M. KONOV and G. V. KOTRELEV, *J. Organomet. Chem.* **3** (1965) 129.
38. K. A. ANDRIANOV, G. V. KOTRELEV, B. A. KAMARITSKI, I. H. UNITSKI and N. I. SIDOROVA, *ibid.* **16** (1969) 51.
39. E. G. ROCHOW, *Mon. Chem.* **95** (1964) 750.
40. C. R. KRUGER and E. G. ROCHOW, *J. Polym. Sci. A* **2** (1964) 3179.
41. G. REDL and E. G. ROCHOW, *Angew. Chem.* **B76** (1964) 650.
42. B. G. PENN, J. G. DANIELS, F. E. LEDBETTER III and J. M. CLEMONS, *Polym. Engng Sci.* **26** (1986) 1191.
43. B. G. PENN, F. E. LEDBETTER III, J. M. CLEMONS and J. G. DANIELS, *J. Appl. Polym. Sci.* **27** (1982) 3751.
44. B. G. PENN, F. E. LEDBETTER III and J. M. CLEMONS, *Ind. Engng Chem. Process. Des. Dev.* **23** (1984) 217.
45. A. W. CHOW, R. D. HAMLIN, Y. D. BLUM and R. M. LAINE, *J. Polym. Sci.*, Part C: *Polym. Lett.* **26** (1988) 103.
46. K. B. SCHWARTZ and Y. D. BLUM, in preparation.
47. K. B. SCHWARTZ, D. J. ROWCLIFFE and Y. D. BLUM, *Adv. Ceram. Mater.* **3** (1988) 320.
48. S. J. LENHART, Y. D. BLUM and R. M. LAINE, *Corrosion*, in press.
49. Y. D. BLUM, R. D. HAMLIN, A. W. CHOW and R. M. LAINE, unpublished results.
50. B. J. WOOD, R. D. BRITTAIN and K. H. LAU, *Carbon* **23** (1985) 73.
51. H. D. BECKEY, "Field Ionization Mass Spectrometry" (Pergamon, Elmsford, New York, 1971).
52. V. BAZANT, V. CHVALOVSKY and J. RATHOUSKY, "Organosilicon Compounds" (Academic, New York and London, 1965) p. 82.
53. B. J. AYLETT and M. J. HAKIM, *J. Chem. Soc. A* (1969) 1788.
54. A. U. KLINGEBIEL, D. BENTMANN and A. MELLER, *J. Organomet. Chem.* **144** (1978) 381.
55. D. R. PARKER and L. H. SOMMER, *ibid.* **110** (1976) C1.
56. M. MORI, H. INOUE and T. OCHIAI, in "Progress in Nitrogen Ceramics", Vol. 65, edited by F. L. Riley (Nato ASI Series, 1983) p. 149.
57. D. L. TRIMM, in "Pyrolysis Theory and Industrial Practice", edited by L. F. Albright, B. L. Crynes and W. H. Corcoran (Academic, New York, 1983) p. 203.
58. P. S. VIRK, A. KOROSI and H. N. WOEBCKE, in "Thermal Hydrocarbon Chemistry", Advances in Chemistry Series 183, edited by A. G. Oblad, H. G. Davis and R. T. Eddinger (American Chemical Society, Washington D.C., 1979) p. 67.
59. R. WALSH, *Acc. Chem. Res.* **14** (1981) 246.
60. Y. HASEGAWA and K. OKAMURA, *J. Mater. Sci.* **18** (1983) 3633.
61. S. YAJIMA, Y. HASEGAWA, J. HAYASHI and M. IIMURA, *ibid.* **13** (1978) 2569.
62. J. K. KOCHI, "Organometallic Mechanisms and Catalysis" (Academic, New York, 1978) pp. 246–58.
63. D. SEYFERTH and Y. F. YU, European Pat. Application 86 305 444.1 (July 1986).
64. Y. NAKAIDO, Y. OTANI, N. KOZAKAI and S. OTANI, *Chem. Lett.* (1987) 705.

Received 15 October 1987
and accepted 4 August 1988