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Comprehensive Chemistry of Polycarbosilanes, Polysilazanes, and Polycarbosilazanes as Precursors of Ceramics

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I. General Introduction

Among the high-performance non-oxide ceramics, silicon carbide (SiC) and nitride (Si_3N_4) offer unique potentialities as thermomechanical materials due to their stiffness and especially their exceptional structural stability under environmental extremes; SiC and Si_3N_4[1-7] exhibit a very high resistance to oxidation (until ~1400 °C) as well as convenient mechanical properties. Consequently, intense research over the past 20 years has been focused on the elaboration of SiC, Si_3N_4, or Si/C/N-based materials from organosilicon precursors, especially in the field of fibers or matrixes *via* liquid precursors for which the polymer route is quite adequate. The advantages of the pyrolysis of controlled viscosity preceramic polymers include (a) the ability to prepare ceramic forms difficult to obtain by conventional powder processing methods (*e.g.*, fibers, films); (b) processing temperatures lower than those of conventional technologies; and (c) the ability to prepare ceramics with high and controlled purity. To rationalize this approach, Wynne and Rice[8] have set forth a series of general empirical rules that should be considered for the design of a proper ceramic precursor and Seyferth has stated various requirements for this purpose.[9] For instance, in most applications, weight loss and gas evolution should be as low as possible to limit shrinkage. An idealized preceramic polymer should possess a compromise of the following properties, sometimes incompatible: (a) a molecular weight sufficiently high to prevent any volatilization of oligomers; (b) a polymeric structure containing cages or rings to decrease the elimination of volatile fragments resulting from backbone cleavage; (c) viscoelastic properties (fusibility, malleability, or solubility) to apply the polymer in the desired shape before the pyrolytic process; (d) presence of latent reactivity (functional substituents) to obtain thermosetting or curing properties; and (e) low organic group content to increase ceramic yield and avoid the production of undesired free carbon excess. Obviously, different substituents and variations in polymer microstructure will strongly affect the final ceramic compositions. One of the main challenges in the preceramic polymer strategy is to achieve structures in which splitting of the main backbone, due to chain cleavage followed by "backbiting" and evolution of volatile products, are prevented.

It is clear that the various substituents (hydrogen and any other pendent group) play a crucial role on the polymer properties, its thermal behavior, and the pyrolysis mechanisms. Thus, some studies deal with these questions, and general patterns of behavior

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Marc Birot was born in Biarritz, France, in1953 and graduated from ENS Strasbourg in 1976. He received his "3eme cycle" doctoral degree in 1979 on byproducts of dimethyldichlorosilane synthesis from the University of Bordeaux with Prof. Calas. He obtained his Ph.D. degree from the University of Bordeaux in 1985 and then spent a year of postdoctoral study with Prof. Walsh in 1993 at the University of Reading (England) working on disilenes generated by laser flash photolysis. He has been working in J. Dunoguès's group as "chargé de recherche" at the CNRS since 1985. His main research interest is focused on organosilicon chemistry, and he is currently working on polymer precursors of silicon-based ceramics.

Jean-Paul Pillot was born in 1947. He received a M.S. (1969) in chemistry and a Doctorat ès sciences (1979) from the University Bordeaux I under the direction of Dean R. Calas. His thesis was devoted to the use of allyl- and vinylsilanes in organic synthesis. In 1972, he obtained a position at the CNRS. His current research interest includes the search for novel silicon-containing molecules, organosilicon polymers, and precursors for advanced ceramic materials. Parallely, he is also concerned with safety problems in research laboratories and the limitation of chemical waste in the environment.

Jacques Dunoguès was born in 1938. As Engineer from the Ecole Nationale Supérieure de Chimie de Bordeaux, he began to work in the field of organosilicon chemistry in 1959. From 1959 to 1968 he was a research engineer at Rhône-Poulenc Company (Saint-Fons, France) before coming back to the University of Bordeaux I where he obtained his Doctorat d'Etat ès Sciences under the direction of Professor Raymond Calas. Awarded by the French Chemical Society and the French Academy of Sciences, he is actually Directeur de recherche au CNRS (exceptional class) and head of the Laboratoire de Chimie organique et organométallique de l'Université Bordeaux I (Laboratory associated with CNRS:URA 35). He is the author of more than 300 scientific publications, including some reviews, and 30 patents devoted to the development of organosilicon chemistry in the field of monomers and polymers, the use of organosilicon (but also organophosphorus and sulfur) intermediates in organic synthesis, the elaboration of precursors to high-performance ceramics (SiC-, SiCN-, SiBON-, and SiBC-based materials), and the use of electrochemical synthesis in the organosilicon domain. He remains involved in most of these topics.

have been noted. However, detailed mechanisms have not been clearly presented hitherto. One can find an explanation of this lack in the fact that, unlike low-pressure thermochemistry of organosilicon compounds which is well-documented,[10,11] much less is known about the high-temperature behavior of organosilicon compounds in the liquid and solid condensed phases as well as the reaction mechanisms at the gas–liquid (or gas–solid) interface. At this time, a number of reviews present a survey of the literature in this domain;[12–35] many of them are devoted to the synthesis of preceramic polymers and the subsequent precursors obtained upon judicious cross-linking.

Concerning the synthesis of SiC precursors, the common approach consists of the synthesis of polysilanes (PSs) which are further converted, explicitly or implicitly, into polycarbosilanes (PCSs) upon thermolysis. After the pioneering work of Verbeek[36] and of Yajima[37] whose strategy has allowed the production of industrial SiC-based fibers (Nicalon[38] and Tyranno[39]), a number of reports have described the preparation of PSs,[40,41] PCSs,[42] and SiC-based materials upon pyrolysis of the PCSs, after their eventual spinning and curing. PCSs were also prepared by more direct approaches, avoiding PS intermediates.[43]

Concerning Si/C/N- or Si_3N_4-based materials, the potentialities of polysilazanes (PSZs) for making silicon nitride or carbonitride[44–47] were known early, but the first intensive investigations oriented toward the preparation of inorganic materials came from Verbeek.[48] Most routes to such ceramics involve PSZs[49–56] as the basic preceramic polymer precursors. However, some approaches provide polycarbosilazanes (PCSZs, *i.e.*, polymers containing silicon, carbon, and nitrogen inside the main chain as well as Si–N bonds), which also are precursors of silicon carbonitride: this review mainly deals with precursors in this area.

A. Scope and Limitations

In the field of SiC precursors, this review concerns the direct routes to PCSs proposed for the purpose of making SiC materials. Consequently, the common approaches many times reviewed (see above; monomer(s) → PS → PCS) will not be extensively considered, regardless of what the monomers are (usually chloro- or hydrosilanes). In particular, the numerous routes to polysilanes—except polysilacarbosilanes (PSCS) or polysilasilazanes (PSSZ)—are not covered by this review since they have been surveyed on several occasions[57-67] and despite new approaches of these species by electrochemical syntheses.[68-74] Similarly, other routes involving chemically (especially *via* hydrosilylation)[75] or photochemically[76] cross-linked polysilanes will not be detailed since they are similar to the classical way: the conversion of $-(SiSi)-$ into $-(SiC)-$ backbone occurs during the pyrolysis process. On the other hand, the use of PSs for directly making silicon carbide materials (*i.e.*, without the thermolysis step that affords PCSs) has received special attention. Among the numerous reports in this field, one can mention the pioneering works from Baney *et al.*[77] involving methylchlorodisilanes and from West *et al.*[78] dealing with polysilastyrene, as well as copolycondensations with $MeSiHCl_2$ or $MeSiCl_3$.[79,80] Since no further data is given in this review, refer to the papers of these authors to gain more information about the precursors and the resulting ceramics. The work from Schilling[81,82] involving, for instance, vinylchlorosilanes will be briefly mentioned since the participation of the vinyl group allows the formation of polysilacarbosilanes. However, one cannot conclude this brief discussion of the polysilane synthesis without emphasizing the importance of the dehydrocondensation of polyhydrogenosilanes. Harrod[83-86] has reviewed research in this field, but more recently, Corey[87,88] has proposed modifications of the process. At this time, polydehydrocondensation constitutes a common route to PSs. Among the possible entries to SiC-based materials involving this route, the approach of Harrod and Laine, *et al.*[89] from $-(MeSiH)_n-$ prepared by dehydrocondensation of $MeSiH_3$ and that of Corriu[90] from $-[HSi(CH_2CH_2SiMeH_2)]_n-$ should be pointed out because they constitute attractive alternatives. However, to limit the scope of this review, approaches of these types will not be discussed.

To allow comparisons, the Yajima routes will be largely recalled, since they constitute basic references from both fundamental and industrial points of view. Concerning PCSs themselves, a number of reports mention their preparation by methods different from the thermolysis of polysilanes: since the first report by Rochow[91] in 1949 and the further preparation of oligomers,[92] important results concerning the synthesis of high polymers containing the $-(R_2SiCH_2)_n-$ sequence were reported, namely by Weyenberg[93] and Nametkin,[94-96] and studies were developed by Gusel'nikov,[97] Mark,[98-101] and Boileau.[102] Nevertheless, except in particular cases, these very carbon-rich polymers are not considered as convenient precursors of SiC-based materials under the normal pyrolysis conditions. For this reason, they are not taken in account here. At last, the results reviewed by Fritz and Matern[103] dealing with monomeric, cyclic, polycyclic, or linear oligomeric carbosilanes are not considered because the initial purpose of the pioneering work from Fritz was not the synthesis of SiC precursors, despite the potential interest of these studies in this context.

PCSs containing carbon atoms in the main chain, synthesized with the objective of making SiC precursors, are covered with this review, in which a comparison of the typical usual routes to PCSs is given. Studies involving polymers such as, for instance, $-[X_2Si(CH_2)_3]_n-$ or polymers resulting from ring-opening of silacyclopentenes will be reported more briefly since the materials resulting from pyrolysis are much too rich in free carbon. Moreover, PSCSs are especially considered, and their rearrangement into PCSs is compared with the Kumada rearrangement[104] of the poly(dimethylsilane) (PDMS) into PCS according to the Yajima process.

Concerning the field of Si/C/N or Si_3N_4 precursors, the main sources are PSZs and PCSZs. As mentioned above, the latter have been essentially proposed as precursors of Si/C/N-based materials, and their preparation will be examined extensively. In contrast, since the first preparation of silazanes by Stock and Somieski[105] in 1921, a large number of works devoted to the synthesis of PSZs[106] out of the field of ceramic precursors have been covered in the literature. Among the important main approaches to Si−N bond-containing derivatives and PSZ oligomers, one can mention (i) ammonolysis, aminolysis, and hydrazinolysis of halosilanes;[107-118] (ii) ring-opening of cyclosilazanes;[119-128] (iii) synthesis and/or ring-opening of cyclodisilazanes;[129-136] (iv) amino group exchange on silicon;[137-140] (v) Si−Cl/Si−N disproportionation reactions;[141-149] (vi) Si−H/N−H dehydrocondensation;[52,55,150-158] (vii) metalation reactions;[159-161] and (viii) direct synthesis from amines and silicon.[162,163] This review does not deal with all these synthetic methods but is concerned with PSZs and PCSZs elaborated by using some of them with the purpose of making ceramic precursors.

As for SiC precursors, the aim of this section is to provide a comprehensive account. Therefore, emphasis will be placed on work devoted to the relationships between the microstructure of preceramic polymers (*i.e.*, their structural units and substituents), the pyrolysis mechanisms, and the chemical compositions of the resulting ceramics. Only precursors to nearly stoichiometric Si_3N_4 or mainly Si_3N_4/SiC materials with small amounts of free carbon and oxygen, desirable for carbonitride ceramics, will be considered.

As needed for the preparation of fibers, a wide range of methods have been used for curing preceramic polymers. No detailed description of these methods will be given apart from some examples in the course of the current discussion.

At last, sol-gel processes are not covered by this review although various attempts have been carried out in the case of SiC[164,165] or Si/N/O[166,167] precursors.

B. Abbreviations

AIBN	azobis(isobutyronitrile)
Bu	butyl
CMC	composite matrix ceramic
CPMAS	cross-polarization magic angle spinning
CVC	chemical vapor curing
CVD	chemical vapor deposition
DSC	differential scanning calorimetry
ESCA	electron spectroscopy for chemical analysis
Et	ethyl
FTIR	Fourier transformed infrared
GC	gas chromatography
GPC	gel permeation chromatography
HMDZ	hexamethyldisilazane

HMPA	hexamethylphosphortriamide
HPZ	hydridopolysilazane
IR	infrared
Me	methyl
MS	mass spectroscopy
NMR	nuclear magnetic resonance
OCMSZ	oligocyclomethylsilazane
OVSZ	oligovinylsilazane
PBDPSO	polyborodiphenylsiloxane
PCS	polycarbosilane
PCSZ	polycarbosilazane
PDMS	poly(dimethylsilane)
Ph	phenyl
PHPSZ	perhydropolysilazane
PS	polysilane
PSCS	polysilacarbosilane
PSP	polysilapropylene
PSSZ	polysilasilazane
PSZ	polysilazane
PTC	polytitanocarbosilane
PVSZ	poly(vinylsilazane)
rt	room temperature
SEM	scanning electron microscopy
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMS	tetramethylsilane
Vi	vinyl
XRD	X-ray diffraction

II. SiC Precursors

A. The Yajima Strategy

1. Introduction

The extensive work of Yajima is based on the following transformations (Scheme 1):

Scheme 1

$$\text{dichlorosilane} \rightarrow \underset{\text{(PS)}}{\text{polysilane}} \rightarrow \underset{\text{(PCS)}}{\text{polycarbosilane}} \rightarrow \text{SiC material}$$

The second step (thermolysis) is considered to be critical in terms of yield and reaction conditions. Yajima synthesized several PCSs with different structures and compositions that affect the spinnability of the precursors and/or their curing ability and therefore the structure and properties of the final ceramics. However, thermolysis is necessary because the PSs obtained in the first step generally are not convenient ceramic precursors. Here one recalls the two main approaches.

2. Synthesis of PCS Mark I and Mark II

In an early paper a PCS was obtained from $(Me_2Si)_6$ autoclaved at 400 °C under Ar.[168] This PCS was fractionated, dry spun, and then pyrolyzed under vacuum. The resulting fibers exhibited a tensile strength of 3.5 GPa and a Young's modulus of 200 GPa.[169] IR studies confirmed the PCS nature of the precursor and suggested that Si−H bonds were responsible for cross-linking reactions on heating.[170] The fractionated precursor possessed $\bar{M}_n = 1500$ and a molecular weight distribution between 240 and 25 000, providing a good spinnability.[171] The major drawbacks of this method are the cost of dodecamethylcyclohexasilane and the use of an autoclave. Later, Yajima proposed a simpler and more economical synthesis of a PCS:[172] heating poly(dimethylsilane) (PDMS obtained from Me_2SiCl_2 and Na in xylene) at atmospheric pressure under argon up to 470 °C resulted in a PCS with $\bar{M}_n \approx 950$ in 35% yield. However, SiC fibers could be obtained upon pyrolysis under vacuum after air curing.[173] Finally, the commercially available PCS referred to as Mark I was synthesized by heating PDMS under pressure (50−60% yield).[174] Oxygen in Mark I is less than 1% by weight, and Yajima noted that the properties of the SiC fibers were intimately related to those of the precursor itself: the PCS should contain as many Si−H bonds as possible and its molecular weight should be relatively high. When the Mark I is compared to a PCS synthesized upon pyrolysis of tetramethylsilane (6.8% yield),[175] the precursors were found to possess different structures and compositions, and the ex-TMS fibers did not exhibit comparable mechanical properties.[176] The overall yield from Me_2SiCl_2 to SiC is around 20%; hence constant effort has been made to improve the process. Adding small amounts of $(Ph_2Si)_n$ in PDMS[177] or Ph_2SiCl_2 in Me_2SiCl_2[178,179] resulted in PCS Mark II, obtained similarly to Mark I upon thermolysis. Mark II was said to have a better spinnability than Mark I. Fibers could be prepared with a smaller diameter,[177] a tensile strength of 3 GPa, and a Young's modulus of 200 GPa.[177-180] In 1987 Ishikawa[180] described the synthesis of a PCS under controlled pressure, and low-boiling oligomers could be recycled, improving the overall yield. Later, Burns[181] reported in a patent a chemical modification of Mark I where Si−H bonds were partially substituted by a HCl/CCl_4 mixture, yielding a chlorinated PCS $SiC_{2.13}H_{4.55}O_{0.22}Cl_{0.46}$. Pyrolysis of this precursor under nitrogen resulted in a ceramic material $SiC_{1.47}H_{0.09}O_{0.09}N_{0.01}Cl_{0.03}$. Using *n*-BuLi/*t*-BuOK and $Me_2ViSiCl$, Seyferth[182] obtained a PCS partially substituted at CH_2 positions which could be cross-linked *via* hydrosilylation reactions. More recently, Mackenzie *et al.*[183] have used Me_3SiCl with a $AlCl_3$ catalyst to prepare intermediate chloro-PCSs with different chlorine contents, depending on the reaction time. Subsequent reaction of these intermediates with sodium acetylide gave modified PCSs which could be dry-spun and then cured by UV irradiation in the absence of oxygen. Ceramics fibers were obtained in 85% yield by pyrolysis to 1000 °C. XRD spectra showed broad β-SiC peaks and an average crystallite size of approximately 35 Å. However, as these modifications were concerned with the Mark I polymer, the use of an autoclave remained necessary.

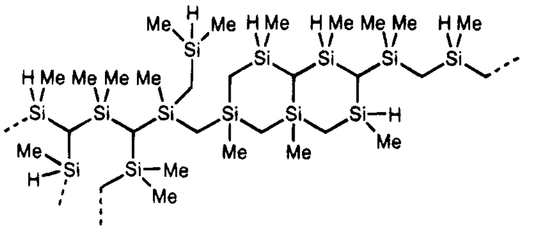
3. Synthesis of PCS Mark III and Related Precursors

To avoid the use of an autoclave, alternative PCS precursors referred to as Mark III[177,184] were obtained from PDMS at ~350 °C under atmospheric pressure, with the use of an initiator or "catalyst" polyborodiphenylsiloxane (PBDPSO).[185] Yields were lower than for the Mark I (48%), but the pyrolysis residues were higher (68%).[186] The initial results showed that the mechanical properties of the obtained fibers were somewhat inferior to those from the Mark I PCSs.[177-179,186] However, the Mark III was further improved,[187] and more recently, PBDPSO has been used to transform PSs containing methyl and phenyl groups into boron-containing PCSs.[188]

4. Structure of Yajima PCSs

From NMR and IR studies,[174] a planar-shaped, ladder-like structure with rings and chains was proposed for Mark I (Scheme 2). It can be noted that carbon and silicon atoms are alternating. In the case of Mark III, besides $-(Ph_2SiO)-$ units due to PBDPSO, $-(Si)_n-$ sequences have also been observed.[186] Assuming a linear chain structure, the Mark I unit has an average of 10 Si atoms with three or four branchings.[189] In contrast, PCS resulting from TMS pyrolysis exhibits a quite different chemical composition with less Si−H bonds.[176] In addition, liquid and solid state ^{29}Si NMR spectra of Mark I showed the presence of two major sites, SiC_4 and SiC_3H. Minor SiC_2H_2 sites were also detected using the CPMAS and INEPT techniques, as well as Si−Si bonds.[189,190] Their physicochemical characterizations, synthetic conditions, and side products strongly suggest that Mark III should be more branched than Mark I[191,192] (cf. Section II.A.7 Mechanisms).

Scheme 2



Monomeric boron derivatives[193] or $AlCl_3$[194] have also been used as an alternative to PBDPSO for preparing PCSs. Polytitanocarbosilane (PTC) was synthesized from Mark III and titanium alkoxide[195] or alternatively from PDMS, PBDPSO, and titanium alkoxide.[196−198] PTC possesses a Mark III-like structure, presumably with Ti−O−Si cross-links.[199] It exhibits a higher average molecular weight and is more easily spun.[200] After curing in air at 170 °C,[196,197] pyrolysis under N_2 at 1700 °C yielded ceramic fibers with higher weight residue. Mechanical properties have maximal values at 1300 °C, and the thermal resistance was claimed to be higher than those of Mark I- or Mark III-derived fibers. Some other polymetallocarbosilanes have been similarly prepared with various metals.[201] On the other hand, the role of Ti with various alkoxides has been investigated.[202] The concentration of Ti in the precursor and the ceramic, as well as the pyrolysis residue, are linearly related, but an insoluble fraction appears in the PTC at high values. Surprisingly, O and C remain almost constant in the ceramic. Song[203] had obtained similar results starting from PTC synthesized in different ways. Upon pyrolyzing under vacuum, oxygen, or ammonia, Si/Ti/C/O, Si/Ti/O, and Si/Ti/O/N materials could be obtained. When heated at higher temperatures, TiC, anatase, and TiN crystallized, respectively.[204]

5. Pyrolysis of PCSs

Three to six steps have been involved in the pyrolysis processes of air-cured and noncured PCSs.[176,205,206] Below 550 °C, essentially distillation of monomers or low boiling silane oligomers is observed. In the case of Mark III, homolytic Si−Si bond splitting occurs[205] since no Si−Si bonds were detected at 600 °C. This cleavage is progressive from 350 to 600 °C, and Mark III synthesized above 380 °C (instead of 330−350 °C usually) is more resistant to oxidation.[207] Cured PCSs undergo a relatively low weight loss during this stage.[176,206] From 550 to 800 °C, pyrolysis of noncured PCSs affords hydrogen and methane as well as significant amounts of methylsilanes.[208] Above 800 °C, the density increases and the final materials are obtained with significant proportions of free carbon[179,209] and oxygen,[210,211] especially in Mark III-derived fibers.[199] As foreseeable, oxygen, largely introduced during the curing step carried out under air[176,212] or ozone,[178] remains in the ceramic.[213] Although hydrogenosilanes are known to be easier to oxidize than simple disilanes, the situation is apparently different in the case of polysilanes, since in Mark III PCS Si−Si bonds are oxidized first, which reflects that the oxidation temperature of Mark III[186] is lower than in Mark I.[174,214]

The properties of the SiC fibers are closely related to the oxidation degree of the PCS: fibers with higher oxygen content exhibit lower mechanical properties.[212,215] Comparative studies between air and γ-ray curing ended up with similar conclusions and suggested an attack on the Si−H bonds.[216] However, Okamura has proposed a method of strengthening O-cured SiC fibers by fast neutron irradiation.[200]

6. Recent Results

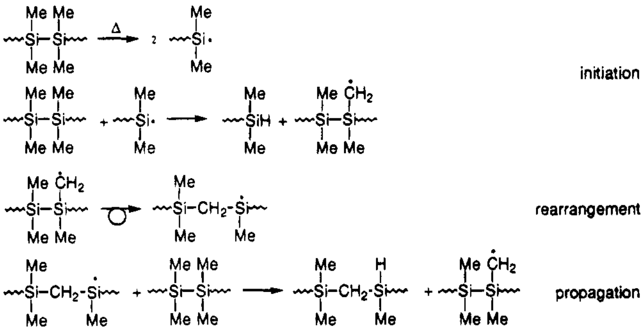
Most of the recent work is devoted to the lowering of oxygen and free carbon content in the fiber and, more generally, to an improvement of the mechanical properties at higher temperature. Thus, Lipowitz[217] has obtained a nearly pure, nanocrystalline SiC fiber with less than 0.1% oxygen by melt-spinning of various precursors, cross-linking, and then heating at 1600 °C, while a dense structure and high tensile strength were preserved by using a nonspecified additive. Polycrystalline silicon carbide-based fibers have also been prepared by treatment of the precursors with B_2H_6,[218] BCl_3,[219] or boron vapor.[220] Especially in the last case, polycrystalline SiC fibers with improved thermal stability were obtained. In addition, curing Yajima PCSs by γ-ray or electron irradiation followed by heat treatment at 1200−2000 °C resulted in a "High Nicalon" SiC fiber with 0.4% oxygen[200,216,221,222] and improved thermal properties.[223] Takeda[224] has recently reported C/Si ratios ranging from 0.84 to 1.68. In particular he could obtain a ceramic composition $SiC_{1.05}O_{0.02}$ under thoroughly controlled conditions. To our knowledge, no information has been given on the thermal treatment of PCSs for obtaining Si/C $\approx$ 1. The nature of the pyrolysis atmosphere probably plays a capital role in the loss of carbon. In a more recent paper,[225] this author has described a "High Nicalon type S" fiber containing 0.2% by weight of oxygen, while the C/Si ratio was only 1.05. This fiber was found to possess a higher Young's modulus and a better oxidation resistance at 1400 °C. The control of the C/Si ratio using a copolymer route ($0.8 \leq C/Si \leq 2.1$) was previously proposed,[192,226] but these results concerned only bulk materials. Several reports[227-231] were devoted to the synthesis of SiC fibers with low oxygen content and high tensile strength; in particular upon chemical vapor curing (CVC) with halogenated hydrocarbons, alkenes, or alkynes, Hasegawa[229,230] has obtained fibers containing 1.5–1.7% oxygen which possess improved thermal stability, while Toreki[228] has prepared fibers with excellent tensile strength (up to 4.4 GPa) using the dry-spinning technique. However, the prepared fibers are free carbon-rich and their oxidation resistance is unfortunately reduced.

In conclusion, the current trends of efforts to improve the Yajima strategy concern mainly the following: (i) the preparation of oxygen-free fibers; (ii) the lowering and the control of the free carbon ratio; (iii) the introduction of boron in the ceramic fibers.

7. Mechanisms

As mentioned previously, polysilanes are beyond the scope of this review, so the creation of the silicon–silicon bond is not discussed here. The thermal conversion of PSs into PCSs, often called the Kumada rearrangement,[104] was first suggested to involve a radical mechanism,[174] referring to the pyrolysis of hexamethyldisilane[232,233] (Scheme 3).

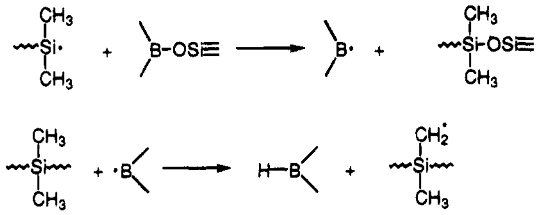
Scheme 3



More recently, the gas phase pyrolysis of permethylated tri- and tetrasilanes has been found to involve silylene and silene species,[234,235] and the radical mechanism is contested for explaining the Kumada rearrangement. The formation of silylenes and silenes will be discussed below.

Concerning the Mark III synthesis, PBDPSO was first believed to act as a trapping agent for the low molecular weight components resulting from the thermal decomposition of PDMS and to enhance the hydrogen abstraction from methyl groups by boron radicals (Scheme 4), the boron being released in gaseous products.[186]

Scheme 4



More recently, in studies carried out on PCSs oligomers, Ishikawa[236] has suggested that PBDPSO did not participate in the Kumada rearrangement but accelerated the dehydrocoupling of Si–H bonds to form Si–Si bonds. In our own work, we did not observe any significant difference in the gaseous composition when polysilapropylene was pyrolyzed in the presence of PBDPSO (*vide infra*).[191] In contrast, heat treatment of PDMS or dodecamethylcyclohexasilane without PBDPSO exhibited quite different behaviors.[237] Gas analyses given in Table 1 suggest that dimethylsilylene would be a major intermediate in the pyrolysis of $(Me_2Si)_6$, and PBDPSO should be regarded as a Lewis acid favoring the silicon–carbon bond cleavage by forming a complex, therefore weakening the Si–Me bond. Ishikawa *et al.*,[238] reinvestigating the reaction, have concluded that the acceleration of the propagation reaction by coupling Si–H bonds is related to the Lewis acid character of the boron derivative.

By using liquid and solid state NMR spectroscopies, Taulelle *et al.* have studied the very early stage of the transformation of PDMS into Mark I- and Mark III-type PCSs.[190] Besides the previously assigned sites in the ^{29}Si NMR spectra, a SiC_2SiH ($\delta \approx -42$ ppm) environment has been characterized in both processes. SiC_3Si ($-8 < \delta < -12$ ppm) units have been detected in the Mark I polymer but are not significantly formed in Mark III. However a signal at −66 ppm in Mark III could be assigned to $SiCSi_2H$ environments, supporting the Lewis acid role of PBDPSO.

Table 2 indicates that disproportionation reactions of gaseous silanes in the presence of PBDPSO occurred to some extent, but they do not account for the global composition of the gaseous fraction in the Mark III synthesis shown in Table 1.

These considerations as a whole explain the structural differences between Mark I and Mark III. The former is described as a completely decomposed PDMS with alternating silicon and carbon atoms (Scheme 2). The latter still contains Si–Si bonds but should be more cross-linked. The proposed Mark III structure would be constituted with polysilane chains connected through highly branched carbosilane nodes[191] (Scheme 5). Their structural differences

Table 1. GC Analysis of Gases from the PS → PCS Transformation (% mol)[191]

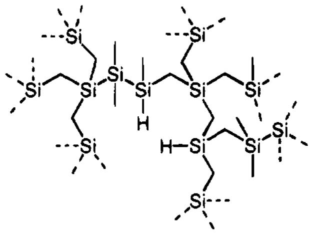
	H_2	CH_4	$MeSiH_3$	Me_2SiH_2	Me_3SiH	Me_4Si
$(Me_2Si)_6$, autoclave, 450 °C, 50 h	14.4	9.0	0.8	72.7	3.0	–
PDMS (Mark I prec.) autoclave, 470 °C, 14 h	41.6	19.8	1.8	35.0	1.7	–
PDMS, 5% $(Ph_2Si)_n$ (Mark II prec.) autoclave, 470 °C, 3.5 h	40.6	14.4	2.5	38.4	4.1	–
PDMS, 550 °C, 9.5 h	32.6	10.3	2.8	49.2	5.0	–
PDMS, 3% PBDPSO (Mark III prec.), 380 °C, 9.5 h	25.9	8.7	0.2	21.0	44.1	–
PDMS, 3% $AlCl_3$, 400 °C, 3 h	23.7	8.6	0.2	11.9	26.9	27.9[a]

[a] Plus 0.7% ethane.

Table 2. Effect of PBDPSO on Gases from the PDMS → PCS Transformation (% mol)[191]

	H_2	CH_4	C_2H_6	$MeSiH_3$	Me_2SiH_2	Me_3SiH	Me_4Si
blank	41.1	14.2	0	1.2	40.2	3.3	0
0.1 g of PBDPSO, 17 h, autoclave, 370 °C	29.5	37.7	1.9	10.2	15.3	5.2	0.1

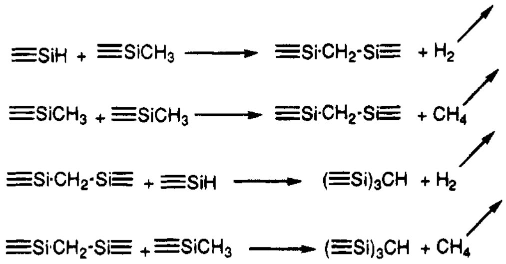
Scheme 5



affect their rheological properties as well as their reactivity in the curing and pyrolysis steps and finally the composition and the properties of the resulting ceramics.

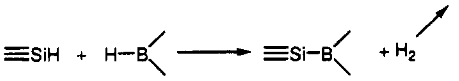
The thermolysis of PDMS giving PCS has also been studied from a theoretical point of view.[239] The Kumada rearrangement as well as condensations involving Si–H, C–H, and Si–C bonds to form hydrogen and methane have been simulated by calculations using $Me_3SiSiMe_2SiMe_3$ and Me_3SiCH_2-$SiHMeCH_2SiMe_2H$ as representative models. Reactions such as depicted in Scheme 6 have been presented as concerted processes, initiated by homolytic cleavages, governed by considerations of electronegativity. This concerted scheme was applied to a variety of local situations in the polymer and accounts well for the observed results, although the reaction temperature (up to 450–500 °C) and, therefore, the energy given to the system authorize a number of hypotheses.

Scheme 6



Concerning Tyranno fiber precursors, the role of $Ti(OR)_4$ has not been intensively investigated but, as previously indicated, the modification of PCS is believed to occur *via* the formation of Si–O–Ti bridges.[195] However, recent IR and NMR studies could not find direct evidence of Si–O–Ti groups, but the authors concluded that it could not be rejected.[240,241] Similarly, improvement of SiC materials by introduction of boron[218–220] has not given rise to mechanistic studies. However, from investigations concerning the cross-linking of various PCSs with $H_3B{:}NR_3$ complexes, it has been inferred that a dehydrocondensation reaction (Scheme 7)[242] would account well for the branching. Nevertheless, this conclusion needs confirmation.

Scheme 7

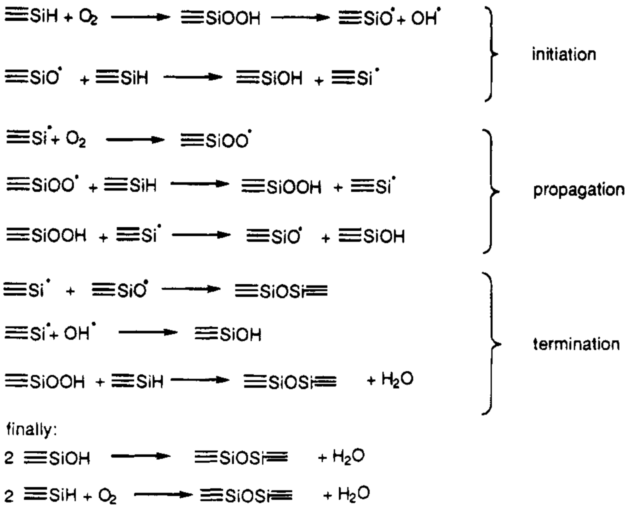


Regarding the pyrolysis processes, it can be assumed that reactions involved in the thermolysis step progressively end as the pyrolysis proceeds. Above 550–600 °C the gases are essentially composed of methane and hydrogen. As the Si–H bond is more reactive than the C–H bond, the SiC network is built firstly around silicon atoms (formation of SiC_4 tetrahedra) whereas the tetrasubstitution of carbon atoms (formation of CSi_4 units) occurs at higher temperature (600–800 °C).[190,192] It has been proposed that the concerted interpretation of the Kumada rearrangement[239] could be applied to the condensations occurring in the mineralization step; thus, a rationalized interpretation takes into account all the thermal modifications from the preceramic polymer to the precursor and, finally, to the inorganic material. Above 1200 °C, the tensile strength of the fiber decreases, while an increase of the electrical conductivity is observed, due to the organization of carbon.[243]

Once again the pyrolysis atmosphere should play a crucial role. Thus, the homolytic cleavage of Si–Me bonds affording methyl radicals, the formation of methane by capture of H• is favored in a hydrogen-rich atmosphere and decreases the carbon content of the ceramic. Recently, Naslain *et al.*[244] have shown that the pyrolysis of PCSs under an hydrogen atmosphere allows the carbon content of SiC ceramics to decrease, resulting in C/Si ratios close to the stoichiometry, very likely *via* the elimination of pendent methyl groups as methane.

As far as oxidation is involved in the curing step, the Si–H bond plays a central role. Although oxidation of C–H bonds would occur to some extent,[206] the process shown in Scheme 8 has been proposed for explaining common oxygen curing.[245]

Scheme 8



In conclusion, intensive efforts have been put forth to improve the Yajima strategy. The Mark I PCS has proven to be a very useful precursor for SiC fiber preparation on an industrial scale. However, the almost exclusively used starting product, PDMS, introduces severe drawbacks such as the use of sodium in massive amounts, a low overall yield, the need of an autoclave, and a high reaction temperature. Besides, a lack of knowledge about the structure and the reactivity of the PCSs makes optimizing the synthesis and the properties of the precursors difficult.

B. Other PCSs

1. Introduction

As a consequence of the Yajima work, a large number of attempts to synthesize effective silicon carbide ceramic precursors have been made, especially for fibrous materials, from sources other than PDMS. Among the wide variety of alternative organosilicon polymers, this review is concerned with polycarbosilanes, *i.e.*, polymers with Si−C bonds in their backbone. Several routes have been used to obtain such polymers, including the following:

(1) ring-opening polymerization reactions
(2) polycondensation of chloromethylchlorosilanes
(3) copolymers with 1,3-disilapentanes
(4) polycondensation of chlorosilanes with methylene halides
(5) polycondensation of chlorosilanes with acetylides
(6) hydrosilylation reactions
(7) polycondensation of chlorosilanes with unsaturated hydrocarbons
(8) dehydropolycondensation of hydrogenosilanes.

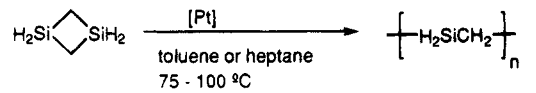
This does not concern the creation of silicon−silicon bonds, for reasons given in the Scope and Limitations, Section I.A, but the condensation, ≡C−H + H−Si≡, to form carbon−silicon bonds.

2. PCSs from Ring-Opening Polymerization Reactions

a. Poly(silmethylene)s. As previously mentioned in the General Introduction, poly(silmethylenes) for uses other than precursors are not considered in this review.

In 1986, Smith[246] claimed the preparation of poly(silmethylene) by ring-opening polymerization of small amounts of 1,3-disilacyclobutane in heptane, using Pt-group metal derivatives as catalysts (Scheme 9). The polymer was reported to yield 85% SiC when pyrolyzed 1 h at 900 °C under argon. TGA showed a 10.1% weight loss at 900 °C, and its IR spectra indicated that cross-linking involving dehydrocondensation of Si−H and C−H bonds began at 500 °C. The Si−H loss was practically complete at 700 °C, and crystallization of the residue started at 900 °C. The polymer was said to be fusible, but no further details were given, especially about the synthesis of the monomer, and the linear structure of the polymer was not proven.[247] Further, Wu and Interrante synthesized linear poly(dichlorosilmethylene) *via* ring-opening polymerization of 1,1,3,3-tetrachloro-1,3-disilacyclobutane with platinum catalyst. Direct reduction of this polymer in benzene led to poly(silmethylene) with $\bar{M}_n = 12\ 300$. Narrow IR absorption bands, NMR spectra, and elemental analysis were consistent with the expected linear formula. TGA data indicated a weight loss between 100 and 600 °C, and the ceramic yield was 87%. The XRD pattern of a sample heated at 1000 °C showed the formation of β-SiC with an average crystallite size of 2.5 nm. Interrante noted the unusually low crystallization temperature and pointed out the essential role of Si−H bonds in the formation of the network, suggesting a mechanism *via* silylene intermediates,[248] as recently proposed by Corriu *et al.*[249] for the thermal cross-linking of poly(silethylene). However, considering the tedious synthesis of the monomer (pyrolysis of 1,1-dichlorosilacyclobutane at 840 °C),[250] this method is only suitable for the preparation of very small amounts of PCS.

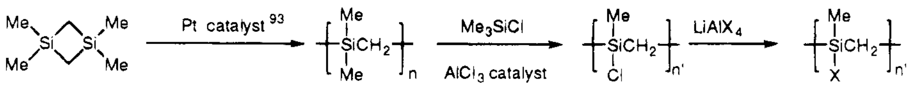
Scheme 9



b. Poly(methylsilmethylene)s. The first synthesis of a linear poly(methylsilmethylene) or polysilapropylene (PSP) was reported by us, starting from 1,1,3,3-tetramethyl-1,3-disilacyclobutane[251] **1** according to Scheme 10.[252]

The ring-opening polymerization of **1** was previously described as an ionic reaction,[253] and the ring strain, estimated 17.2 kcal·mol^{-1}, was thought to be the driving force of the reaction, as nonstrained cycles are unreactive.[254] Poly(dimethylsilmethylene) **2** obtained by bulk polymerization at 80 °C has $\bar{M}_n$ value of 200 000−250 000 relative to polystyrene standards. It is a gummy polymer, thermally stable up to 600 °C under inert atmosphere, which readily decomposes at 200 °C in the presence of oxygen. Its TGA residue is only 3.5% at 1000 °C. Substitution of methyl groups by chlorine atoms was achieved by Me_3SiCl with an $AlCl_3$ catalyst while TMS distilled off.[255] Chain cleavage occurred as $\bar{M}_n$ of the chloro derivative decreased to 2000−2300. Poly(methylchlorosilmethylene) **3** possessing $-SiMe_2Cl$ terminals is soluble in polar solvents, and its linear structure was confirmed by comparison with the NMR and IR spectra of short-chain model oligomers.[256] Studies of the stereochemical effects induced by the asymmetric silicon atoms concluded that the polymer was atactic.

Scheme 10

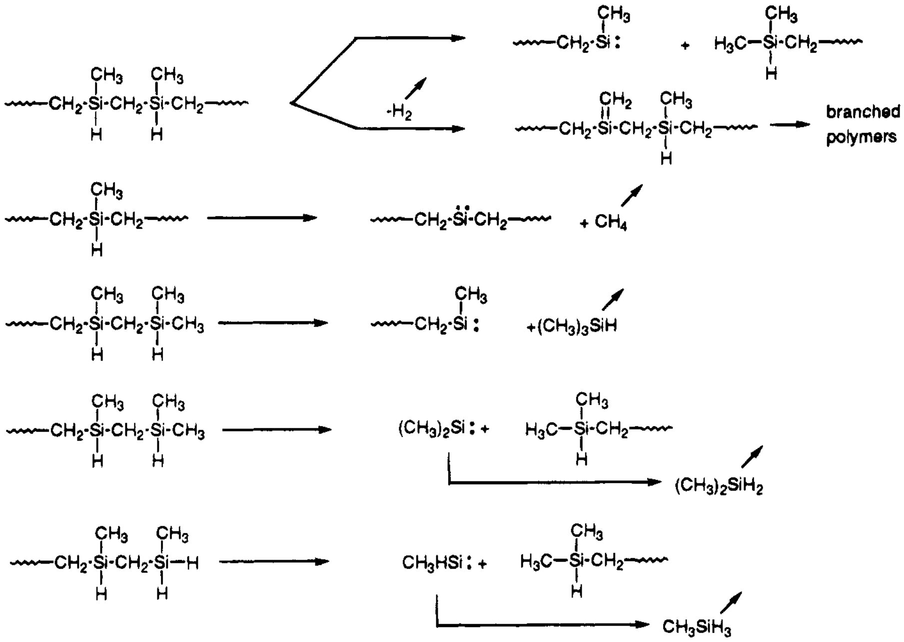


1 2 3 4, X=H
4-*d*, X=D

Table 3. Composition of the Pyrolysis Gases of Polysilapropylene (% mol)[191]

	H_2	CH_4	C_2H_6	$MeSiH_3$	Me_2SiH_2	Me_3SiH	Me_4Si
P atm, 400 °C, 16 h	62	5.8	0.2	9.9	14.1	7.3	0.7
autoclave 400 °C, 16 h, 3% PBDPSO	64.6	9.9	0.2	3.1	16.5	6.4	1.3

Scheme 11



Otherwise, only one methyl group per silicon site was replaced by a chlorine atom whose deactivating effect avoided further substitution. Subsequent reduction of **3** by lithium aluminum hydride or deuteride afforded the corresponding hydrogeno- or deuteriopoly(methylsilmethylene) **4** and **4**-*d*, respectively.[252] The linear structure of PSP was clearly proven by NMR studies of short-chain models which also showed the presence of syndiotactic and isotactic sequencies. PSP is a liquid oligomer with $\bar{M}_n = 2000-2300$ which contrasts with the high softening temperature of Yajima's PCS (≥300 °C), although the reported $\bar{M}_n$ values are comparable. This reflects the branched structure of the Yajima precursor. The TGA of PSP showed only a 5% weight residue (compared to 60% for the commercially available PCS), but the sample contained traces of chlorine and probably metallic salts. Hydrolysis of the reaction mixture to eliminate salts have raised the pyrolysis residue to 19% at 1000 °C, and the thermal stability of poly(dimethylsilmethylene) has also been improved.[242] Similar results have been reported by Wu and Interrante.[248]

When treated in an autoclave at 450 °C, PSP became progressively insoluble, and pyrolysis of this solid gave a ceramic yield up to 85% as expected. However, heat treatment at 400–500 °C under argon provided 65% of a soluble, solid precursor with $\bar{M}_n = 8600$ and a ceramic yield of 44.5%.[242] Elemental analysis of the latter polymer indicated loss of C and H relative to PSP, reflecting the thermal cross-linking. The appearance of an IR absorption band at 950 cm^{-1} in the low-boiling fraction[191] was assigned to the formation of cyclic moieties.[251] SiC_4[191] and SiC_2H_2[242] sites were characterized by ^{29}Si NMR, but no Si–Si or $Si-CH_2CH_2-Si$ could be detected using both techniques.[191] GC analysis of the gaseous mixture showed that hydrogen was the predominant gaseous product, accompanied by some methane and methylsilanes (Table 3) and traces of other monosilanes, ethane, and propane.[252]

Flash pyrolysis experiments with PSP showed the formation of linear, tetrasilylated and cyclic, tetra- or pentasilylated carbosilanes at 500 °C, plus di- or trisilylated linear, cyclic, and bicyclic carbosilanes at 900 °C.[191] These results can be compared to the mass spectra of short-chain models or polymers **3**, **4**, and **4**-*d* which exhibit characteristic fragmentations such as splitting of Si–H(D) or $Si-CH_2$ bonds and formation of six-membered rings.[257] For the thermal cross-linking of PSP, a mechanism involving silene and silylene intermediates explains the formation of cyclic compounds and the different gases, as well as the branching and SiC_4 or SiC_2H_2 sites[242] (Scheme 11), in good agreement with a previous proposal from Interrante.[247,248] These concepts are supported by the earlier work of Auner[258] about the gas phase pyrolysis of 1,3-disilacyclobutanes.

Of course, homolytic cleavages are presumed to become more and more important as the temperature increases.

Interrante *et al.*[259] have also reported a modified route to PSP from 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane (Scheme 12), and their results are consistent with our work. Ring-opening polymerization was performed with chloroplatinic acid catalyst at 80 °C, and the average molecular weight of the polymer decreased when increasing the amount of catalyst. Higher PSP polymers were prepared with $\bar{M}_n$ = 6000 and 35 000 with corresponding ceramic yields of 10 and 20%, respectively. Similarly, a preliminary heat treatment at 400 °C provided a cross-linked precursor with a 66% ceramic yield.

Scheme 12

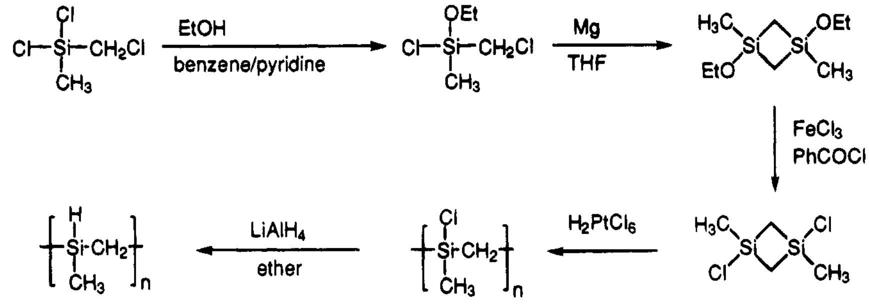


Table 4. Poly(silmethylene) Derivatives

starting polymer	reagent	product	yield (%)[a]	$10^{-3}\bar{M}_n$	ceramic yield (%)
3	Na	**5**	39.4_s	4.25	11.4
3	K	**6**	48.8_s	4.93	43.5
3	Me_2NH	**7**	94.4_s	2.48	33.5
3	$MeNH_2$	**8**	90.6_s	3.58	24.7
3	NH_3	**9**	77.5_s	4.12	37.5
4	H_2O	**10**	99.1_s	2.96	54.3
4	1,3-butadiene	**11**	96.8_i	–	14.0
4	1,4-divinylbenzene	**12**	96.2_i	–	24.7

[a] s and i for soluble and insoluble fractions.

Broad β-SiC XRD peaks were reported for a sample heated to 1600 °C for 4 h.

PSP has proven to be a useful model to have a better understanding of structural effects on thermolysis as well as curing reactions of PCSs because of its defined linear structure. Unfortunately, the multistep synthesis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane remains tedious and expensive; consequently, it does not allow operation on large scale. Some attempts have been made to prepare it by using electrochemical techniques.[260,261] The electrochemical synthesis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane was performed in 18% yield, and the preparation of its precursor, $ClMe_2SiCH_2SiMe_2CH_2Cl$, was carried out in a 43% yield. Some other PCS have also been prepared using an electrochemical route.[262]

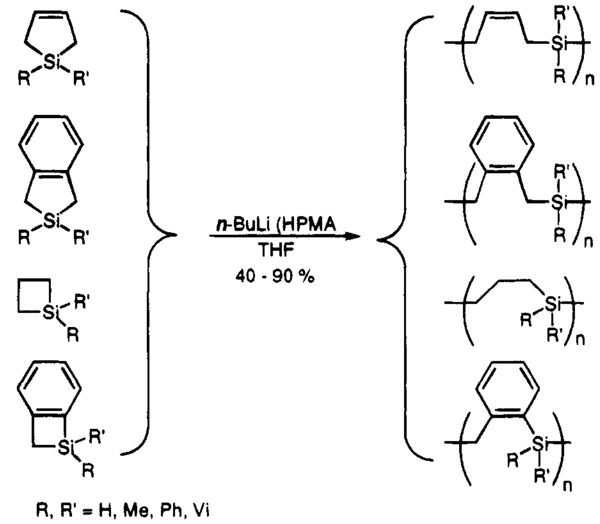
c. Derivatives of Poly(silmethylene)s. As noted above, the ceramic yield of PSP is quite low in the absence of thermal treatment, due to its linear structure. The presence of reactive Si–Cl or Si–H bonds in **3** and **4** prompted us to study the cross-linking of these polymers with various bridges.[263] The results are summarized in Table 4.

The TGA residues of these polymers are rather low, even for the insoluble compounds **11** and **12**. This likely results from intramolecular condensation reactions resulting in the formation of volatile cyclic species. All the samples pyrolyzed at 1200 °C contained a significant amount of oxygen (14–24%), and hydrogen was still present. Pyrolytic residues were analyzed using ESCA, XRD, and Raman techniques, while the organometallic–inorganic transition was investigated by analysis of the evolved gases. Nitrogen-based polymers did not release nitrogen-containing gases (except the linear compound **7**), and the ceramics were still amorphous at 1400 °C, corroborating that nitrogen inhibits crystallization.[264]

Seyferth[265] has proposed a modification of poly(dimethylsilmethylene) by deprotonation of the methylene groups at low temperature with strong bases such as *n*-BuLi or *t*-BuOK. Functionalization was achieved by addition of dimethylchlorosilane and/or vinyldimethylchlorosilane. However, the pyrolysis of these modified polymers still gave very low ceramic yields (2%), probably because steric factors prevented their cross-linking *via* thermal hydrosilylation. Reactions of the vinyldimethylsilyl-substituted PCSs with $[(MeSiH)_{0.8}MeSi)_{0.2}]_x$ and AIBN as an initiator gave a hybrid polymer. Pyrolysis of this material to 1500 °C under argon provided a ceramic residue in 68% yield containing about 91% of SiC.[265] Very recently, Interrante[266] has reported the preparation and TGA studies of substituted poly(silmethylene)s. He concluded that electronegative substituents disfavor the formation of a "cationic" silicon center; therefore, the corresponding compounds are less reactive toward ring-opening polymerization reactions. Moreover, aromatic groups increased the TGA residue from 20 to 50%, whereas the linear PCS with ethoxy groups provided very low ceramic yields.

d. Poly(silapentene)s and Poly(silabutane)s. Weber *et al.* have described the anionic ring-opening polymerization of various 1-silacyclopent-3-enes,[267] 3,4-benzosilacyclopentenes,[268] silacyclobutane,[269] or 2,3-benzosilacyclobutenes[270] with *n*-BuLi/HMPA as the catalyst (Scheme 13). These polymers exhibit M_n values in the range 680–1800, except those derived from methylphenyl- (171 000) and dimethylsilacyclopentene (744 000).[271] TGA analyses showed a major weight loss at 450 °C, and char yields were generally low (0–20%). They became higher (20–57%) when

Scheme 13

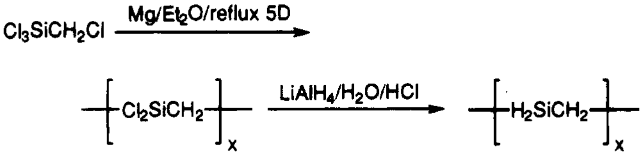


vinyl or SiH_2 groups were present,[269,272] which might reflect the branched nature of the polymers as well as cross-linking *via* hydrosilylation reaction. The mechanism is apparently different for poly(1,1-divinyl-1-silacyclobutane) which exhibited a 45% ceramic yield.[269] The large weight loss was probably due to the nature of the polymers: linear structure, low molecular weight, and presence of C_4 or C_5 blocks, whereas poly(1,1-divinyl-1-silacyclobutane) contained only C_3 units. Due to their low char yields and their high carbon content, these polymers exhibit interesting properties but cannot be considered as efficient SiC precursors, and in fact no extensive study of the materials resulting from their pyrolysis has been reported to our knowledge.

3. PCSs from Chloromethylchlorosilanes

The synthesis of PSs involving chloromethylchlorosilanes as comonomers[81,82,273-275] is not considered here (cf. Section I.A. Scope and Limitations). Interrante's work cited in Section II.B.2 employed chloromethylsilanes, but it has been covered under ring-opening polymerization. This section deals with polycarbosilanes synthesized directly from chloromethylchlorosilanes. As (chloromethyl)dimethylchlorosilane possesses the desired $Si-CH_2$ unit, it has been naturally used in SiC precursor chemistry, but usually as a minor comonomer to avoid the introduction of large amounts of carbon and because the $-Me_2SiCH_2-$ fragment is not a cross-linking site. Whitmarsh and Interrante[276] have prepared a highly branched PCS by Grignard coupling of $ClCH_2SiCl_3$ with Mg in diethyl ether, followed by reduction with $LiAlH_4$ (Scheme 14). Addition of a CuCN catalyst was found to increase the molecular weight during the Grignard reaction,[277] while reduction *in situ* followed by filtration of the salts was said to improve the overall yield.[278] Alternatively, cyclic aliphatic ethers have also been employed.[279]

Scheme 14



IR and NMR data suggested almost exclusive head-to-tail coupling as no evidence of Si−Si or $Si-CH_2-CH_2-Si$ units was found. The chlorinated intermediate possessed an average of 15.4 units and its composition $[CH_2SiCl_{1.7}(OEt)_{0.15}(Et)_{0.15}]_n$, showed the participation of ether in the reaction. Reduction led to an oligomer/polymer mixture $[CH_2SiH_{1.85}(Et)_{0.15}]_n$ with $\bar{M}_n = 745$ and a broad distribution. NMR spectroscopy denoted the presence of residual CH_2Cl, SiH, SiH_2, and SiH_3 groups while elemental analysis indicated 1.63% chlorine and less than 0.02% oxygen.[276,277] When pyrolyzed to 1000 °C under N_2, overall ceramic yields of 58−80% were obtained. Holding at 80−200 °C to perform cross-linking resulted in >80% final char yield, close to the theoretical value (83%), assuming the complete conversion of the polymer into SiC.[280] Ceramic yields as high as 89% were even observed when the hydridopolycarbosilane $[CH_2SiH_{1.85}(Et)_{0.15}]_n$ was treated with titanium catalyst to effect cross-linking *via* dehydrogenative coupling reaction prior to pyrolysis.[278] XRD and solid state ^{13}C NMR studies confirmed that the ceramic was essentially composed of silicon carbide and the presence of free carbon was not indicated.[34] $[CH_2SiCl_{1.7}(OEt)_{0.15}(Et)_{0.15}]_n$ could also be transformed by ethanol into $[CH_2Si(OEt)_{1.85}(Et)_{0.15}]$ and then converted to a siloxypolycarbosilane $[CH_2SiO]_n$ by a sol-gel process.[281] Pyrolysis of this gel between 600 and 1000 °C gave a silicon oxycarbide glass which contains 40% oxygen.[282]

(Chloromethyl)trichlorosilane leads to an attractive precursor which is surprisingly claimed not to be very oxygen-sensitive. Its low cross-linking temperature and molecular weight might raise problems in fiber preparation; however, it could be suitable for matrix applications.

4. PCSs from 1,3-Dichloro-1,3-disilylmethanes

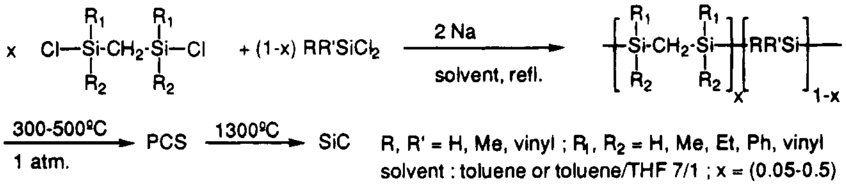
As PDMS is a highly microcrystalline solid soluble only at high temperature in uncommon solvents,[283] several authors have attempted to prepare copolysilanes $(Me_2Si)_n(RR'Si)_{n'}$. The lack of crystallinity increases the solubility, and moreover, varying R and R′ allows one to change the C/Si ratio in the polymers. Relating to the subject of this review, *i.e.*, PCS precursors, an approach to polysilacarbosilanes (PSCSs) that could be easily transformed into PCS upon being heated at atmospheric pressure and then pyrolyzed to SiC ceramic was proposed by the authors of this review (Scheme 15).[284]

This approach was attractive, especially when $R_1 = Me$ and $R_2 = H$, since it consists of introducing into the main chain the desired carbosilane sequence, theoretically formed upon thermolysis. This is equivalent to the synthesis of a partially thermolyzed PDMS. This molecular building-block strategy leads to soluble polymers. Unlike PDMS, these copolymers are easily separated from the formed salts by filtration without hydrolysis. Consequently, they exhibit a low oxygen content.

Various starting 1,3-dichloro-1,3-disilylmethanes were prepared by silylation of methylene chloride[285] (Scheme 16) instead of methylene bromide as previously reported.[286]

Typical yields are in the range 30−70% when THF is added to the mixture of the reactants. Although

Scheme 15



Scheme 16

$$CH_2Cl_2 + R_1R_2SiClX + 2\,Mg \xrightarrow[Zn]{THF} (R_1R_2XSi)_2CH_2 \quad X = Cl, H$$

zinc is needed to allow the reaction to proceed, its role is not clearly understood. Indeed, it is entirely recovered. Zinc is suggested to mechanically clean and perhaps activate the magnesium surface, but intervention of a redox Mg/Zn couple has not been rejected. Other metals such as Al, Cu, Cd, or Hg are less efficient or ineffective. Under these conditions Me_2SiCl_2 and methylchlorodisilanes do not lead to the expected products, but the THF ring is opened. With less reactive chlorosilanes, $-SiCH_2Cl$ groups can be detected, suggesting a three-step reaction: first the chlorosilane would form a chloromethylsilane, then convert into an organometallic Grignard reagent, which would be further trapped by a chlorosilane (Scheme 17).

Scheme 17

$$\equiv SiCl \xrightarrow[slow]{[ClCH_2MgCl]} \equiv SiCH_2Cl \xrightarrow[fast]{Mg}$$

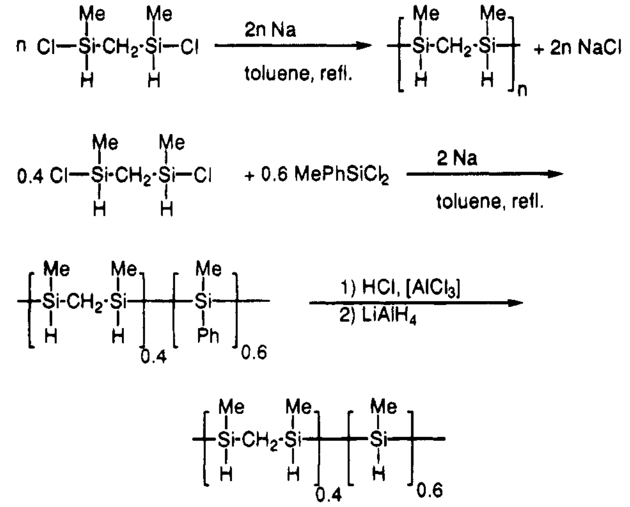
$$\equiv SiCH_2MgCl \xrightarrow{\equiv SiCl} \equiv SiCH_2Si$$

PSCSs obtained according to Scheme 15 are soluble greases. Higher yields were obtained when high values of x, as well as toluene/THF mixtures,[287] or $MeSiCl_3$-free Me_2SiCl_2[283] were used. Elemental analyses and IR spectra revealed residual chlorine less than 2% by weight. The PS motifs were characterized by UV spectroscopy, but no appreciable Si−O linkages could be detected by ^{29}Si NMR. A typical PSCS was prepared in 60−70% yield from 0.15 $(HMeClSi)_2CH_2$ and 0.85 Me_2SiCl_2 (Table 5). The proportion of CH_2 groups in the liquid PSCSs is statistically well-related to the value of x, but the structure of the PSCS has not been completely determined.

Soluble PSCSs exhibit low TGA residues (<10%) because they are not significantly cross-linked. A thermal treatment at 450−500 °C under an inert gas at atmospheric pressure afforded PCSs in 20−50% yield with $\bar{M}_n = 1000-3000$ which had up to 80% ceramic yield (Table 6). The transformation proceeded with gas evolution and residual Si−Si linkages were detected by UV spectroscopy. The increase of the C−H/Si−H ratio in the resulting PCS showed that cross-linking *via* Si−H bonds occurred.

This strategy allowed us to prepare organosilicon polymers which could be transformed into spinnable ceramic precursors at lower temperature and without using an autoclave. According to this approach, adjustable C/Si ratios (from 0.8 to 2.1) were obtained in the ceramic by varying the substituents: obviously, hydrogen decreased this ratio, whereas the presence of phenyl groups strongly increased it.[192] Recently, ceramics with low oxygen and free carbon content have been obtained (Scheme 18), and fibers are under current investigation.[288]

Scheme 18



5. PCSs Directly from Dihalomethanes

The previous section concerning PSCSs involved methylene chloride only for the preparation of monomers. Recently Sartori *et al.*[289] have prepared a series of PCSs by direct condensation of dichlorosilanes and methylene bromide with Na in xylene (Scheme 19) and studied their transformation into ceramics. Phenylmethyldichlorosilane led to a PCS with $\bar{M}_n \approx 8500$ in 81% yield. NMR and elemental analysis were consistent with an average molecular formula $[PhMeSi(CH_2)_{1.5}]_n$. Pyrolysis of this polymer at 1100 °C led to a 18.3% ceramic yield (theoretical 28%, assuming SiC as the product). Similarly, Ph_2SiCl_2 and CH_2Br_2 gave a PCS with $\bar{M}_n \approx 3600$ in 98%

Table 5. Selected PSCSs from Dichlorosilanes and Disilylmethanes

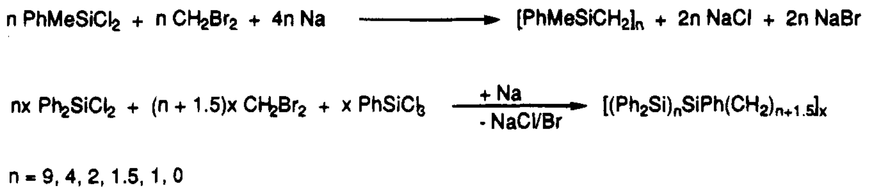
dichlorosilane	disilylmethane	x	reaction time (h)	overall yield (%)	PSCS yield (%)	PSCS
Me_2SiCl_2	$(ClHMeSi)_2CH_2$	0.15	30	96	71	**13**
Me_2SiCl_2	$(ClMe_2Si)_2CH_2$	0.25	24	75	26	**14**
$MeHSiCl_2$	$(ClMe_2Si)_2CH_2$	0.25	24	85	76	**15**
$MeViSiCl_2/Me_2SiCl_2$ (1/9)	$(ClHMeSi)_2CH_2$	0.05	30	91	47	**16**
$MeViSiCl_2/Me_2SiCl_2$ (2/8)	$(ClHMeSi)_2CH_2$	0.05	30	91	45	**17**

Table 6. Conversion of PSCS into PCS

entry	temperature (°C)	reaction time (h)	PCS[a] yield (%)	softening temp (°C)	ceramic yield (%)
13	470	3.5	46	140	62
14	500	36.0	29	<20	–
15	400	1.2	60$_i$	>250	88
16	480	2.0	50$_i$	>250	72
17	320	1.0	90$_i$	>250	18

[a] i = insoluble.

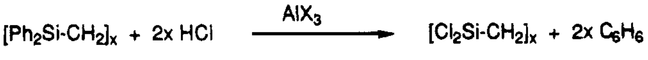
Scheme 19



yield which had a 23% ceramic yield when pyrolyzed at 1100 °C. The average molecular formula was found to be $[Ph_2Si(CH_2)_{1.06}]_n$. No oxygen was detected, and the Si–Si bond content was less than 1%.[290]

Sartori *et al.* have also investigated the halogenation of poly(diphenylsilmethylene)[291] or poly(methylphenylsilmethylene)[292] with hydrogen halides and catalytic amounts of aluminum halides (Scheme 20).

Scheme 20



Reduction of a poly(chlorocarbosilane) by lithium aluminum hydride afforded a poly(hydridocarbosilane) $[(H_2Si)_{1.5}SiH(CH_2)_3]_x$ whose ceramic yield reached 30.9%.[293,294] This rather low yield, despite the likely beneficial effect of the Si–H bond in promoting cross-linking, is understandable in light of the relatively poor thermal stability of the carbon–carbon linkages. Heteroelement-containing PCSs can be prepared by adding small amounts of a chloro derivative of B, Ti, or Zr to the reactants.[295] Copolymers from sodium condensation of diphenyl- and dimethyldichlorosilanes with dibromomethane have been used as binding agents in the production of sintered SiC materials.[296] Some attempts have also been carried out starting from dichlorosilanes and phenyldichloromethane[297,298] or phenyldibromomethane.[299]

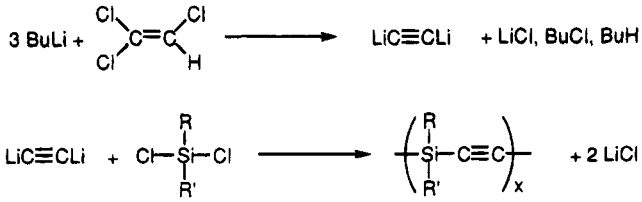
Despite some attractive properties (*e.g.*, thermal stability), the products cannot be considered as good SiC precursors because of the low char yields and (or) high content of free carbon. Nevertheless, some observations must be pointed out: using vinylated dichlorosilanes, phenyldibromomethane, and magnesium, not only ≡Si–H bonds but also $\equiv Si-CH=CH_2$ groups could be preserved,[299] whereas in the Schilling's conditions,[300] the vinyl groups are consumed in important proportion.

Generally, PCS prepared from dihalomethanes are obtained in good yields but with moderate molecular weight. In particular, the use of the inexpensive methylene chloride seems to be an alternative to the Yajima PCS if fibers can be easily obtained from polymers with Si–H bonds. Very recently, Sartori[301] has reported the preparation of a copolymer from phenylchlorosilanes and methylene bromide for the production of oxygen-free SiC fibers.

6. Poly(silylacetylene)s

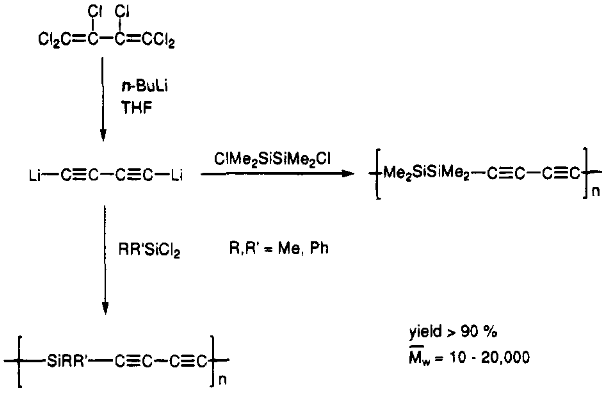
Barton's and Corriu's groups have almost simultaneously investigated the use of poly(silylacetylene)s as precursors to SiC fibers. These soluble polymers are easily prepared by co-condensation of dichlorosilanes with dilithioacetylenes. Barton[302] has obtained polymers with average molecular weights in the range 20–30 000 and TGA residues varying from 20 to 80% at 1100 °C (Scheme 21). Melt-spun fibers were thermally or photochemically cured and pyrolyzed to SiC-based ceramics with various contents of free carbon.

Scheme 21



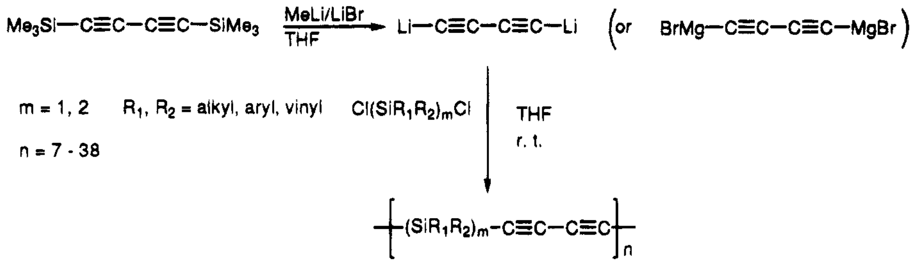
With hexachlorobutadiene as starting material, Barton *et al.* have synthesized poly(silyldiacetylene)s or poly(disilyldiacetylene)s[302b] in good yields (Scheme 22). The TGA data indicated a 20% weight loss at 1000 °C, partly due to a thermally induced cross-linking, while DSC revealed a strong exotherm between 100 and 150 °C. As ^{13}C NMR spectroscopy showed no evidence of an sp carbon, the authors concluded that poly(silyldiacetylene)s cross-link *via* a 1,2-addition mechanism, as previously reported by Rutherford and Stille[303] for poly(butadiyne)s.

Scheme 22

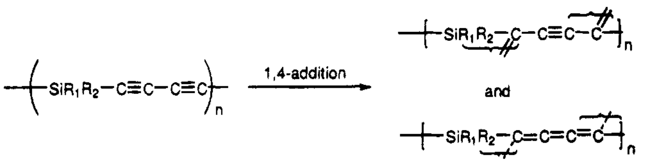


Similarly, poly(silyldiacetylene)s prepared by Corriu[304] from dichlorosilanes and diacetylene dilithium or di-Grignard reagents (Scheme 23) were pyrolyzed under argon at 1400 °C to give SiC-based ceramics in 63–87% yields, with large amounts of free carbon depending upon the nature of the substituents at silicon atoms. Interestingly, although 1,2-addition was not rejected, ^{13}C NMR and IR spectroscopy suggested that the preceramic polymers underwent a low-temperature cross-linking essentially *via* 1,4-addition to the triple bonds (Scheme 24), depending on steric factors.[304d] Poly(silyldiacetylene)–metal oxide composites were also pyrolyzed to various silicon carbide–metal carbide mixed ceramics in 50–60% yields.[305] When heated to 1250–1400 °C under

Scheme 23



Scheme 24



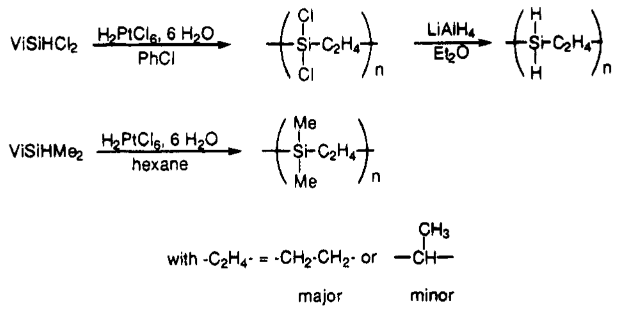
N_2, both carboreduction and nitridation took place, and mixed SiC−metal nitride ceramics could be obtained in 64−84% yields.[306] Besides, $FeCl_3$-doped poly(silyldiacetylene)s exhibited interesting conductive properties.[307] Recently, sodium acetylide was reacted with dichlorosilanes activated by pyridine, giving yields and molecular weights higher than with acetylenic di-Grignard or dilithium salts,[308] but no pyrolysis study of the resulting polymers has been reported to our knowledge.

In conclusion, although ceramic fibers have been obtained,[302a] poly(silylacetylene)s generally give SiC materials with much free carbon, but they can be used in carboreduction reactions. For instance, pyrolysis of a polymer−silica composite would result in stoichiometric silicon carbide material.

7. PCSs from Hydrosilylation Reactions

Corriu *et al.*[309,310] have applied the hydrosilylation of vinylhydrogenosilanes, first described by Curry,[311] to prepare linear poly(silethylene)s, using Pt or Rh derivatives as catalysts (Scheme 25).

Scheme 25

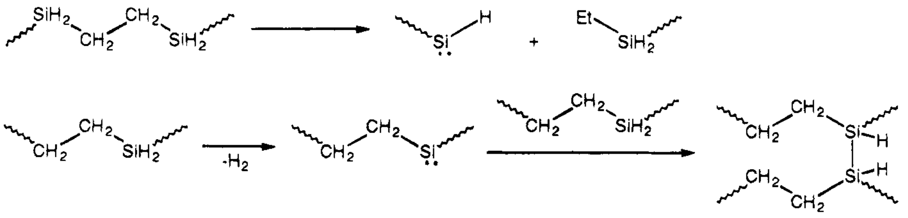


The number-average molecular mass of these polymers varied from 960 in hexane to 5500 in chlorobenzene, and the yields were in the range 64−78%. NMR spectroscopy revealed that linear $-SiCH_2CH_2-$ units arising from a β-hydrosilylation mode were predominantly formed (70−85%) rather than branched −SiCHMe− units. Ceramic yields at 1400 °C under nitrogen varied from 12 to 62%, depending on the presence of terminal vinyl groups that allowed the polymer to be cured *via* a hydrosilylation reaction at low temperature, as shown by the observation of an exotherm at 200 °C in the DSC curves and the decrease of Si−H and vinyl IR absorption bands.[312,313] The thermal degradation of poly(silethylene) and poly(dimethylsilethylene) was investigated by TG/MS analysis and solid state NMR. Both fragmentation and cross-linking mechanisms appear to be strongly dependent on the substituents on the silicon atoms. Random homolytic chain cleavage accounts for the formation of the volatile and gaseous products detected during the degradation of poly(dimethylsilethylene)s, whereas silylene intermediates have been suggested to explain the facile elimination of hydrogen at 380 °C, as well as the formation of $-SiEtH_2$ terminals and the fragmentation of poly(silethylene) by 1,1-cleavage of Si−H and Si−C bonds.[249] Moreover silylenes would explain the cross-linking *via* the formation of Si−Si bonds (which could also come from dehydrocondensation) (Scheme 26), followed by the Kumada rearrangement.

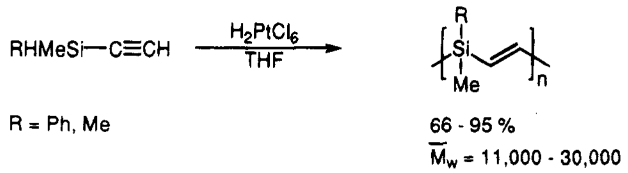
An alternative strategy starting from dihydrogeno- and divinylsilanes has been also proposed by the same authors to access to similar products.[314]

Catalytic hydrosilylation of ethynylsilanes $R_2HSiC{\equiv}CH$ (R = Me, Et, Ph) with $H_2PtCl_6{\cdot}6H_2O$ affords soluble poly(silvinylene)s with average molecular weights in the range 11 400−110 700, depending on the substituents.[315] Their NMR data are consistent with a regular α,β structure (Scheme 27). TGA residues at 1000 °C vary from 18% (R = Et) to 40% (R = Me), with maximum weight loss at 450−500 °C. Fibers were surface cross-linked by UV irradiation and then pyrolyzed under helium flow to 1100 °C. The resulting SiC materials were characterized by SEM. Similarly, allyldichlorosilane or allyldiphenylsilane have been polymerized in various solvents.[316] The Si−aryl bonds were cleaved using

Scheme 26



Scheme 27



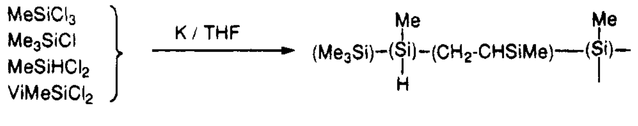
$HCl/AlCl_3$, and the chlorinated polymers were reduced in situ by $LiAlH_4$, giving quantitatively poly(silpropylene)s with average chain lengths ≈ 7–35. The linear structure of the polymer with $-SiH_3$ and $-SiH_2$allyl chain ends was demonstrated by NMR studies. Pyrolysis of polymers with average chain lengths ≈ 20–35 gave ceramic materials in 45–50% yield (55% theoretically)[316] which can be compared to "polysilacyclobutane" obtained upon ring-opening polymerization.[269] Oligomeric materials exhibited lower ceramic yields. TGA/MS studies showed three steps in the polymerization process: hydrogen elimination at 250 °C, then a partial depolymerization reaction which explains the lower yields, and finally a ceramization step.

The polymers prepared from alkenylmonohydrosilanes *via* hydrosilylation reaction are generally linear without built-in functionality for latent reactivity, so they exhibit low ceramic residues. Moreover, their pyrolysis often results in SiC materials containing a very large amount of free carbon. However the polymers prepared by Corriu *et al.*, especially $-(H_2SiC_2H_4)_n-$, offer, after cross-linking, attractive potentialities for the fabrication of matrixes. More generally, hydrosilylation might be useful as a chemical curing method for making matrixes since no gas evolves during the cross-linking step.

8. Other Polysilahydrocarbons

The preparation of PCSs by reacting chlorosilanes with unsaturated compounds in the presence of a metallic reducing agent has been demonstrated, leading to polymers with high contents of carbon. Schilling first synthesized mixed polymers by dechlorinating silanes (for instance Me_2SiCl_2, $MeViSiCl_2$, $MeSiHCl_2$, and Me_3SiCl) with potassium (Scheme 28). Pyrolysis to 1200 °C under unconfined inert atmosphere gave SiC materials in 50–60% yields.[287,317] The presence of branched silyl units in the polymer backbone was critical to provide significant ceramic yields. Schilling[275,300] has introduced the important concept of branching which defines the ability of a precursor to afford a high ceramic yield. The participation of vinyl groups produces a partial branching, but cross-linking is achieved upon thermal hydrosilylation. Further development and improvement of the process have been proposed by Noireaux and Reyx *et al.*[318–321]

Scheme 28



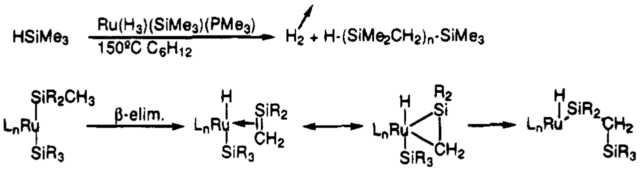
Sartori *et al.*[322,323] have recently prepared copolymers from diphenyl- or dimethyldichlorosilane and styrene with weight-average molecular mass in the range 1300–2100 in good yields. No pyrolysis study was reported except the low-temperature transformation of the PS blocks into PCS units.[324] This route proves to be a relatively easy way to prepare PCSs, but the structure and composition of the obtained precursors are difficult to control. In any case, the C/Si ratio in the polymer is high. However, low-oxygen-containing SiC fibers have been recently reported from the catalytic disproportionation of methylchlorodisilanes with t-Bu_4PCl[77] in the presence of styrene.[325] The crude fibers were cured with ammonia and then pyrolyzed to 1200 °C. Ceramic fibers (25 μm diameter), probably made of Si/C/N, with tensile strength ~1 GPa and containing only 0.9% weight oxygen were obtained in 25% yield. No weight loss was observed up to 1500 °C.

9. PCSs from Dehydropolycondensation Reaction

Dehydrocondensation involving ≡Si–H and ≡C–H bonds occur at high temperatures, especially during the pyrolysis of the precursors. Here we only discuss such a condensation prior to pyrolysis, *i.e.*, for the purpose of making the PCS precursors.

Dehydrogenative coupling of hydrogenosilanes with transition metal complexes as the catalysts, developed first by Harrod *et al.*,[326] affords PS, but in these syntheses the C–H bonds are not involved. Recently, Berry *et al.*[327] have reported the synthesis of oligomeric carbosilanes from trimethylsilane under mild conditions, using a ruthenium complex $Ru(H)_3(SiMe_3)(PMe_3)$ as the catalyst. PCSs of the general formula $H(SiMe_2CH_2)_nH$ with n ~ 8 were presumed to be formed although only carbosilane oligomers containing four silicon atoms were actually identified. The authors have proposed a mechanism involving the formation of an intermediate η^2-silene ligand (Scheme 29). A hydrogen acceptor such as *tert*-butylethylene readily catalyzed the reaction at 80 °C, suggesting that elimination of H_2 from the metal is the rate-determining step.[328]

Scheme 29



These results can be related to the thermal formation of PCSs from tetramethylsilane,[103] where cleavage of C–H bonds is also involved. They are more directly connected to the treatment of polymethylsilane with Ti or Zr catalysts. Seyferth observed that such cross-linking resulted in a higher retention of carbon,[329] while more recently, Laine and Harrod have concluded that dimethylzirconocene had an influence in promoting Si–C bond formation during the pyrolysis of polymethylsilane.[330] Although vinylsilane was found to yield a PCS when polymerized with a titanium catalyst,[331] investigations suggested a complex mechanism involving several processes, including perhaps ≡Si–H/≡C–H dehydrocondensations, but more likely during the pyrolysis step. The polymers are precursors of high char yield carbon-rich materials; however, stoichiometric SiC may be produced by copolymerization of vinylsilane with methylsilane.

C. Conclusions

Intensive investigation to development of precursors to SiC and related compounds started more than 20 years ago. Despite this long period, only Nicalon (SiC_xO_y) and Tyranno ($SiC_aO_bTi_c$) fibers are industrially available, while the Yajima-type Mark I PCS (Shin-Etsu) is the only commercially available preceramic polymer. The improvement of the mechanical properties of this type of fiber has given rise, and still justifies, extensive studies; the proportion of oxygen can be considerably lowered (fibers practically free from oxygen are now obtained), the free carbon content can be controlled and strongly reduced. Otherwise, from new approaches or specific studies, relationships between the nature and the structure of the precursor and the microstructure and the properties of the final inorganic material have been characterized. Among the main features one can specify the following:

(i) Well-defined linear precursors possessing a PS or PCS structure afford very low char yields unless an appropriate treatment or the pyrolysis itself produces a subsequent cross-linking; indeed, without branching, back-biting reactions generate cyclic or linear low-boiling oligomers which distill. The branching concept introduced by Schilling accounts for such a situation. A reasonable ceramic yield is only obtained after sufficient cross-linking increases the softening temperature and decreases the solubility.

(ii) PS thermolysis into PCS precursors provides not-well-defined complex structures. In the industrial Mark I PCS, the nonlinear backbone contains alternating silicon and carbon atoms, while in Mark III the chains are more branched but PS sequences remain in important proportion. Consequently the Mark III PCS does not prefigure accurately the final material. This explains why the Mark III approach was not preferred to the Mark I one for making fibers, despite the milder conditions of its preparation, being performed at atmospheric pressure instead of using an autoclave.

(iii) The synthesis of a well-defined, liquid polysilapropylene has confirmed that the industrial Yajima's PCS, an amorphous solid with a softening temperature higher than 300 °C, cannot be assigned to $-(HMeSiCH_2)_n-$, although they possess comparable molecular weights. Indeed, under the Yajima conditions (470 °C in an autoclave), the decomposition of PSP is faster than the conversion of PDMS into PCS. Considering that the high temperature treatment allows several types of mechanisms, homolytic cleavage has not been rejected for explaining the Kumada rearrangement, but it is thought that formation of silylenes and silenes seems more likely. All of these interpretations explain the evolution of monosilanes and other silylated species as well as methane before the cross-linking. The formation of hydrogen is closely connected with the presence of Si−H bonds responsible for the branching, either *via* thermal or catalyzed hydrosilylation or dehydrocondensation reactions. This explains why PDMS, which does not contain Si−H bonds, is not a good precursor, affording very low char yields upon pyrolysis.

(iv) The industrial method for curing "SiC" fibers consists of using air at temperature around 200 °C to oxidize Si−H bonds (and eventually Si−Si bonds if the conversion of PSs into PCSs is not complete). Mechanisms of cross-linking using electron-beam or X-ray irradiation namely involves carbon radicals. As expected, oxygen allows the formation of silicon oxycarbide SiC_xO_y in which silicon is involved in SiC_4, SiC_3O, and likely, SiC_2O_2 tetrahedra. Above 1100 °C, oxygen can produce SiO, and above 1300 °C, CO upon reaction with free carbon (Scheme 30).

Scheme 30

$$SiC_mO_n + (4-m+n)C \longrightarrow SiC_4 + nCO\nearrow$$

Consequently, although oxygen delays the crystallization of SiC, it appears to be not desirable, at least in important proportion in fibers, since their mechanical properties are altered above 1100 °C.[332,333] At present, this problem has been resolved by using cross-linking methods involving irradiation. Whatever the method, it can be assumed that Si−H bonds play a major role in cross-linking reactions, although C−H and Si−C bonds are not totally unreactive, participating in some extent in the process.

(v) Moreover, the presence of pendent methyl groups in the polymer generally leads to a major loss of carbon as methane. This confirms the influence of the structure of the preceramic polymers on the composition of the resulting inorganic materials. Thus, from models having the same chemical composition and different structures such as $-(MeHSiCH_2)_n-$ or $-(H_2SiCH_2CH_2)_n-$, pyrolysis leads to a material richer in free carbon in the latter case because of the absence of methyl groups which are partially converted into methane in the former case. Similarly, the pyrolysis of $-(MeHSi)_n-$ affords silicon carbide containing elemental silicon. To avoid the elimination of these methyl groups, it is necessary to catalyze dehydrocondensation reactions involving the cleavage of C−H bonds. The resulting inorganic material can then be constituted with almost stoichiometric silicon carbide. However, when the pendent substituents are vinyl or phenyl groups, the pyrolysis affords free carbon-rich materials due to the preliminary polymerization of vinyl moieties in the former case and subsequent formation of carbon during the mineralization step. These considerations illustrate the influence of the structure of the precursor on the composition of the resulting inorganic material.

Concerning the role of free carbon, its presence in significant amounts in the material weakens the resistance to oxidation. Of course, its distribution plays a prominent role, not only in problems related to oxidation, but also to delay the growth and coalescence of SiC crystallites. For materials having an atomic C/Si ratio close to the stoichiometry, crystallization of SiC from the amorphous ceramic occurs at a relatively low temperature. Once more, the importance of a backbone with alternating silicon and carbon atoms, first emphasized by Yajima, must be pointed out, since it allows the formation of smaller SiC crystallites after mineralization,[334] when compared to ceramics resulting from the pyrolysis of precursors in which this alternation does not occur.

(vi) From the perspective of making fibers, it also appears that the best precursors present alternating silicon and carbon atoms in the main chain. The formation of branching nodes prefiguring the SiC structure should also be beneficial. Stoichiometric SiC fibers have been recently made, but their thermomechanical potentialities have not been completely defined at present.

III. Si_3N_4 and Si/C/N Precursors

A. Introduction

Silicon nitride has been known as a valuable refractory material for over a century.[335,336] Thus, crystalline Si_3N_4 ceramics produced by direct reaction of nitrogen or ammonia with silicon metal in sintering or hot-pressing forming techniques are noted for their chemical inertness, good strength resistance, and extreme hardness.[6,337–340] Another way to make Si_3N_4 that can produce forms with various shapes is chemical vapor deposition (CVD) process using mixtures of gases, typically SiH_4/NH_3 and $SiCl_4/NH_3$, in carriers. The composition of the obtained ceramics depends on the compositional, thermal, and surface variations in the deposition environment. In the last few years, it has become very desirable to directly produce Si_3N_4 ceramics as strong, high modulus, small diameter continuous fibers that could be used in ceramic matrix composites materials (CMC) offering high oxidation resistance and strength.

A promising approach has emerged by using organosilicon polymers: polysilazanes (PSZs), polycarbosilazanes (PCSZs), and various nonvolatile resinous materials obtained from silsesquiazanes. It has been known for many years that the reaction of ammonia with silicon tetrachloride yields a heterogeneous material containing Si, N, and H, leading to pure silicon nitride after pyrolysis.[44,341] In 1961, Aylett *et al.*[45] reported the pyrolysis at 520 °C *in vacuo* of an oligomeric liquid PSZ, $[(MeNHSiH)NMe]_x$, yielding a lustrous, copper-colored solid of approximate composition Si_2NC. They anticipated that a whole range of compatible materials may be made by this way, giving silicon nitride and possibly carbonitrides. Also, they emphasized that chemists so far had not shown great interest in these degradative procedures but that there was a great need for preparative and structural studies on such substances in order to establish a general pattern of behavior. In 1963, Andrianov *et al.*[126] obtained resins *via* the pyrolysis at 400–550 °C of PSZs, and almost at the same time, Chantrell and Popper[47] suggested the use of inorganic and organometallic polymers as precursors of Si/C/N-containing ceramics. A few years later, the pioneering works of Verbeek[36,48] and Yajima[37] concerning the preparation of ceramic fibers has sparked intensive efforts to synthesize polymeric ceramic precursors for use in the fabrication of fibers, coatings, and binders. Thereafter, it was shown that a large variety of organosilicon polymers and, in particular, polymetalloxoorganosiloxanes afforded ceramics upon pyrolysis.[342–344]

Although PSZs have been known for many years,[159,345–347] they received little attention from the perspective of applications until Verbeek renewed interest in their utilization as precursors to Si/C/N ceramics. From a general synthetic point of view, they have been the subject of many reports and the chemistry of Si–N bond-containing derivatives is well-documented.[107–163] Basically, the Si–N bond is most commonly created by the ammonolysis and aminolysis of halogenosilanes. Owing to the fact that this bond is cleaved under various conditions and that it undergoes disproportionation reactions, a wide range of preparative routes to oligomers and polymers have been reported. One can find in the General Introduction main references concerning the basic chemistry of PSZs. Moreover, as a beneficial consequence of the preceramic polymer development, novel routes to PSZs have recently been reported. Among these methods one can mention the transition metal dehydrocoupling,[52] the "direct synthesis",[162] and the ionic ring-opening of cyclodisilazanes, yielding for the first time high average molecular weight linear PSZs.[348,349]

B. PSZ Precursors of Si_3N_4

1. Ammonolysis of Tetrachlorosilane

Inorganic compounds prepared by the ammonolysis of chlorosilanes were reported many years ago.[335,350,351] Thus, silicon tetrachloride and ammonia are known to react under various conditions to give a silicon diimide, "$Si(NH)_2$" (Scheme 31), leading to Si_3N_4 after heating up to 1250 °C.[352]

Scheme 31

$$SiCl_4 + 6\,NH_3 \longrightarrow \text{"}Si(NH)_2\text{"} + 4\,NH_4Cl$$

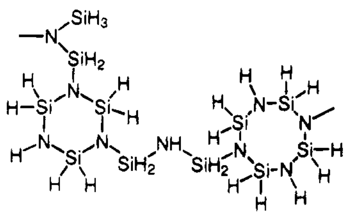
The structure of the intermediate products as well as the mechanism and utility of this reaction have been discussed by Mukherjee *et al.*[340] On the other hand, the formation of $-(SiCl_2NH)_x-$ polymeric materials has also been observed.[353] Ammonolysis of tetrachlorosilane is more particularly useful in the CVD process,[354] although this reaction has also been used for preparing fibrous Si_3N_4.[355] Anyway, this route does not appear usable for obtaining fusible or soluble preceramic polymers.

2. Perhydropolysilazanes (PHPSZ)s

Aylett[46] emphasized that PSZs without carbon substituent had poor storage stability. Since these compounds contain SiH–NH linkages, they lose hydrogen so readily that in practice they also undergo cross-linking. Nevertheless, the ammonolysis product of dichlorosilane in benzene as the solvent, initially reported by Stock and Somieski,[105] has recently been the subject of renewed interest. Thus, Seyferth *et al.*[356,357] have reinvestigated this reaction in polar solvents. The oil initially obtained as a nonvolatile residue was not very viscous. At room temperature, its viscosity increased gradually; after 3–5 days a glassy solid was formed without significant weight loss. So, it was apparent that this product did not possess the ideal structure with $-(H_2SiNH)-$ units. It was postulated that the high functionality of the reactants allowing $\equiv$Si$-$H/$=$N$-$H dehydrocondensation might be responsible for the formation of a three-dimensional network. After pyrolysis at 1150 °C, the brown crystalline solid (69% yield) was identified as a mixture of α- and β-Si_3N_4. The maximum char yield was 69% (94% theoretical if the pyrolysis produced only hydrogen). As foreseeable, from its stoichiometry (Si/N = 1), undesired elemental silicon was also found in the resulting ceramic. Moreover, the authors found that below 400 °C, the major evolved gas was ammonia (probably besides hydrogen), apparently formed *via* disproportionation of the PSZ.[357] At higher temperature, $H_3SiNHSiH_3$ was also formed. To decrease the free silicon content, the ammonolysis product was pyrolyzed in a N_2 stream. Thus, the XRD pattern of the obtained brown solid showed the presence of α-Si_3N_4 containing only a trace of silicon, thanks to the nitridation of silicon at high temperature.

H_2SiCl_2 is a gaseous compound which is very sensitive to moisture and oxygen, exhibiting some hazardness due to the possible disproportionation, $\equiv$Si$-$H/$\equiv$SiCl, yielding silane. However, the stable complexes obtained from polychlorosilanes and tertiary amines[358,359] brought out beneficial effects in various polycondensation reactions.[360] Taking advantage of this property, Isoda *et al.*[361] succeeded in the preparation of a spinnable precursor by using the complex, $H_2SiCl_2{\cdot}2py$. The tentatively proposed oligomeric structure is formed of rings linked by linear segments (Scheme 32).

Scheme 32



The SiH_3 groups probably arise from a disproportionation process taking place at relatively low temperature. This is consistent with the fact that Seyferth *et al.*[357] observed low molecular weight rearrangement products containing SiH_3 groups in the volatile fragments during the pyrolysis of their precursors. Nevertheless, introduction of pyridine offers several advantages: stabilization of the dichlorosilane, increase in molecular weights, catalytic role in the thermal cross-linking (pyridine was found to catalyze $\equiv$Si$-$H/$=$N$-$H dehydrocondensation as well as disproportionation of $-$NHSi$\equiv$ groups), and beneficial introduction of a very small percentage of carbon in the ceramic.[362-367] Isoda *et al.* succeeded in the preparation of small diameter (10$-$30 μm) ceramic fibers upon pyrolysis. The stoichiometry of the starting oligomers (Si/N $\approx$1) as well as the formation of nitrogen-rich volatile compounds, *i.e.*, $SiH_x(NH_2)_{4-x}$ related compounds resulting from disproportionation reactions at NH sites and backbone cleavages,[367] account for the excess of silicon in the obtained Si_3N_4-based materials.

Interestingly, to prevent the formation of free silicon, the pyrolysis of PHPSZ was performed under ammonia or hydrazine,[367,368] readily yielding imidated preceramic polymers, *i.e.*, polymers containing additional N$-$H and NH_2 groups resulting from the condensation of Si$-$H bonds with these gases. In addition, nitridation under a nitrogen atmosphere at high temperature (1350 °C) was observed, corroborating that the pyrolysis atmosphere plays a crucial role in the yield and the chemical composition of the final ceramic.

The "direct synthesis" of tris(dimethylamino)silane from silicon and dimethylamine (Scheme 33) followed by reaction with amines or ammonia constitutes an alternative to the PHPSZ route to silicon nitride which does not require the use of a chlorosilane.[162,369]

Scheme 33

$$Me_2NH + Si \xrightarrow{250\ ^{\circ}C,\ Cu\ cat.} (Me_2N)_3SiH \quad (Rdt > 90\%)$$

In the presence of ammonia and with *p*-toluenesulfonic acid as the catalyst, this monomer readily undergoes transamination reactions, leading to a soluble precursor. Pyrolysis of this precursor at 1550 °C affords high yields of high-purity α-Si_3N_4.

3. Pyrolysis/Nitridation of Organosilicon Polymers under Ammonia

Pyrolysis of cross-linked PCSs, PSs, and PSZs under ammonia or hydrazine constitutes a general route to highly pure Si_3N_4,[370-374] which has been used for the conversion of both bulk precursors and oxygen-cured PCS fibers.[375] Partial replacement of carbon is possible when using a gas carrier containing ammonia thus enabling the preparation of ceramics with controlled composition.[376,377]

It has been shown in our laboratory[378] that sulfur is useful in the cross-linking of PCS fibers at temperatures of 200$-$250 °C. This pretreatment resulted in an increase of 10$-$20% in weight due to the fixation of sulfur. When these fibers were pyrolyzed under ammonia, displacement of sulfur by nitrogen occurred above 450$-$500 °C. PSZs have also been shown to react with sulfur in a solvent before pyrolysis under ammonia.[379]

In the case of oligomeric PHPSZ precursors, the catalytic action of pyridine on the reaction of the Si$-$H bonds of the precursor with the N$-$H bonds of ammonia has been demonstrated[367] (as well as in the presence of a transition metal catalyst).[55]

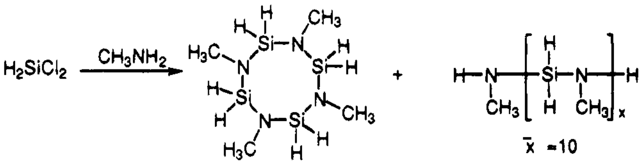
C. PSZ and PCSZ Precursors of Si/C/N Ceramics

The fact that pure Si_3N_4 is expected to readily crystallize above 1200$-$1300 °C is detrimental to the thermal stability and performance of ceramic fibers. Thus, Isoda *et al.*[380] have reported that stoichiometric Si_3N_4 fibers exhibited a catastrophic drop in their mechanical properties above 1300 °C. In addition, the crystallization temperature of Si_3N_4 is known to be lowered by the presence of free silicon.[381] In order to delay Si_3N_4 crystallization, the presence of a suitable second refractory phase in the material seemed desirable. Accordingly, considerable effort has been put forth during the last few years to prepare ternary Si/C/N systems and a wide range of PSZ oligomers bearing various adjacent hydrocarbon groups on silicon and nitrogen have been investigated as ceramic precursors. In the same way, polymers containing hydrocarbon groups in the main backbone have led to useful precursors.

1. Poly(N-methylsilazane)s and Poly(methylcyclosilazane)s

a. Aminolysis of dichlorosilane. Seyferth and Wiseman[357] turned to the aminolysis of dichlorosilane with methylamine in the hope of obtaining non-cross-linked precursors with better processability than those obtained from the ammonolysis of dichlorosilane (Scheme 34).

Scheme 34



Removal of the cyclotetramer by distillation resulted in the preparation of oligo-*N*-methylsilazanes with $\bar{M}_n \approx 600$ ($x \approx 10$). The ceramic obtained upon pyrolysis of this precursor consisted of silicon nitride while no elemental carbon was found (from IR spectroscopy characterization). Unlike PHPSZ, a low char yield (38%) was obtained. Thus, it is clear that the presence of N−Me bonds prevents thermal cross-linking, in spite of their relatively low bond dissociation energy.[10] This means that Si−H bonds alone are not able to induce the formation of a sufficiently branched backbone under pyrolysis and corroborates the fact that N−H bonds are also involved in the degradation mechanisms.

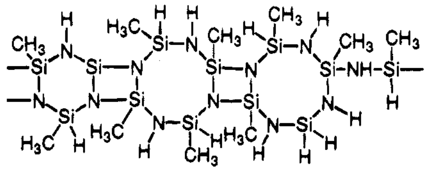
b. KH Dehydrocoupling of PSZs Containing Si−H and N−H Bonds. In addition to their investigations concerning the use of $-(H_2SiNH)-$ and $-(H_2SiNMe)-$ oligomers, Seyferth and Wiseman[357,371,382–385] have developed a method consisting of the ammonolysis of methyldichlorosilane. As usually observed in these reactions, they obtained an oil mainly containing a mixture of six- and eight-membered silazane rings (OCMSZs). TGA of this oil gave a poor ceramic yield (20%). Interestingly, based on the work of Fink,[386,387] these authors have found that the use of strong bases (*i.e.*, KH instead of NaH) led to a polymeric silylamide of type $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]$. Next, this material was quenched with MeI and pyrolyzed to provide ceramics in high yields (Scheme 35).

Scheme 35

$$CH_3SiHCl_2 \xrightarrow[Et_2O,\ 0^\circ C]{NH_3} \underset{\text{oligomers}}{(CH_3SiHNH)_x} \xrightarrow[THF,\ RT]{KH} \xrightarrow[THF,\ RT]{CH_3I} \text{Polymer}$$

Since silazanes containing Si−H and N−H bonds had previously been reported to give a variety of linear and branched chain compounds, as well as undergoing ring contractions *via* the formation of four-membered rings under KH treatment, Seyferth *et al.*[385] have postulated that the white solid polymer was of the form depicted in Scheme 36, which constitutes only a picture for understanding the polycondensation process, but not an accurate structure, because of the very broad signals obtained in liquid and solid state ^{29}Si NMR investigations.

Scheme 36



This strategy has been extended to PSZs possessing Si−H and N−H bonds and various saturated or unsaturated hydrocarbon groups. Dehydrocoupling ≡Si−H/H−N< has also been used to balance the silicon excess which results from the pyrolysis of various precursors containing Si−H bonds such as the sodium dechlorination product of methyldichlorosilane, $[(CH_3SiH)_x(CH_3Si)_y]_n$. Two ways have been investigated:[383]

(1) the "graft" polymer method consisting of the copyrolysis of both PS and polysilylamide after quenching with MeI

(2) the "combined" polymer method consisting of KH treatment of PS and PSZ resulting from the ammonolysis of $MeSiHCl_2$, followed by MeI quenching, before pyrolysis.

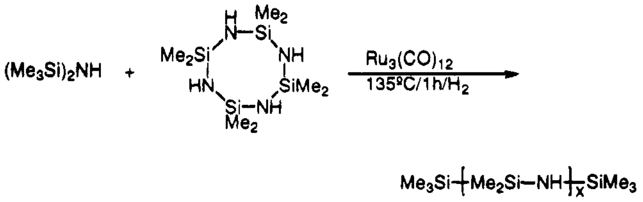
c. The Transition Metal-Catalyzed Dehydrocoupling. Laine and Blum *et al.*[52,151,153,365,388,389] have found an alternative route to the alkali metal dehydrocondensation process reported by Seyferth, providing routes to different types of oligo- and polysilazanes. Thus, they have intensively investigated the transition metal catalyzed dehydrocoupling ≡Si−H/ >N−H to prepare PSZ oligomers (*e.g.*, the dehydrocondensation of various hydrogenosilanes such as Ph_2SiH_2, $PhSiH_3$, Et_3SiH, $n\text{-}C_6H_{13}SiH_3$, etc. with amines and ammonia, Scheme 37).

Scheme 37

$$R_2SiH_2 + R'NH_2 \xrightarrow{\text{catalyst}} H_2\nearrow + \left[SiR_2\text{-}NR'\right]_x$$

They have pointed out that, in theory, the dehydrocoupling reaction could be used to make any type of PSZ, including the use of $MeSiH_3$ as the starting material.[154] In practice, because of the dangers of handling silanes such as $MeSiH_3$ or SiH_4, it is easier to prepare an oligomer via ammonolysis and modify it catalytically to obtain an attractive ceramic precursor. Ring-opening polymerization can also be promoted by transition metals as shown in Scheme 38.

Scheme 38



Interestingly, they have found that the transition metal-catalyzed route is applicable to oligomers possessing N−Me substituents.[52,55] Thus, oligo-*N*-methylsilazanes possessing ≡SiNHMe groups at their extremities were catalytically dehydrocoupled in the presence of the ruthenium catalyst to form poly(*N*-methylsilazane)s containing less than 10% cyclomers ($x \approx 18-20$ instead of 10) as shown in Scheme 39.[154]

Scheme 39

$$\mathrm{MeNH\text{-}[H_2SiNMe]_x\text{-}H} \xrightarrow{\mathrm{Ru_3(CO)_{12}/90^\circ C/THF}} \text{Polymer} + \mathrm{H_2}\nearrow$$

Depending on the conditions, they prepared tractable, processable precursors with suitable viscoelastic properties for making coatings, fibers and three dimensional objects. Pyrolysis studies concerning oligomers with $\bar{M}_n$ values ranging from 600−700 to 1620 showed that the char yields increased from 40 to 65−70%. From a mechanistic point of view, these authors found that the rate-determining step was an Si−H oxidative addition to the active catalyst. When using ruthenium, one of the active species was identified.[390] As is usually the case in polycondensations involving PSZs, linear polymerization and subsequent bridging or cross-linking processes were strongly influenced by steric effects. Also, $Ru_3(CO)_{12}$ is a suitable catalyst for the preparation of poly(methylcyclosilazane)s from OCMSZs under similar conditions, yielding more practical precursors. At last, Blum *et al.*[55] have shown that the elimination of organic groups under ammonia occurred at a much lower temperature when the catalyst was incorporated in the polymer (200 °C instead of 400 °C).

To overcome the volatility of OCMSZs, other routes to Si/C/N preceramic polymers have been proposed using the ammonolysis product of methyldichlorosilane. Thus, Matsumoto *et al.*[391] polymerized OCMSZs by heating in a closed reactor at 250 °C and formed high molecular weight, viscous liquid polymers (ceramic yield: 38%). Meanwhile, Isoda and Funayama *et al.*[392] have reported methods using tertiary amine-methyldichlorosilane complexes.

2. PSZ Resins

In his pioneering work, Verbeek[48] reported an original precursor obtained from the thermal condensation/deamination of tris(*N*-methylamino)methylsilane (Scheme 40).

Scheme 40

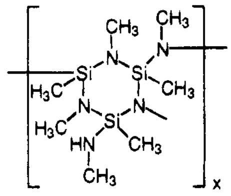
$$\mathrm{RSi(NHMe)_3} \xrightarrow{520\,^\circ\mathrm{C/3h}} \mathrm{MeNH_2} + \text{precursor}$$

$\mathrm{R = CH_3, Ph}$

In view of preparing ceramic fibers, this author suggested various routes to perform pretreatment/cross-linking of the fibers made from this precursor, later used by others. Then, Penn *et al.*[49,393,394] developed these preliminary results and tentatively proposed the structure shown in Scheme 41 for the obtained preceramic polymer.

They have shown that SiC/Si_3N_4 fibers exhibiting high tensile strength can be prepared after curing under humidity and pyrolysis at 1200 °C. In the same way, Mazaev[395] and co-workers have reported the pyrolysis above 1000 °C of a methylsilazane polymer initially described by Andrianov,[126] yielding a ceramic consisting of a mixture of α- and β-Si_3N_4 and β-SiC. Similarly, the thermal conversion of various methylsilazane oligomers into thermoplastic PSZs has been investigated, and this transformation was considered to involve three stages: (a) increase in viscosity, (b) formation of gel-like compounds with various softening temperatures, and (c) formation of insoluble and infusible solids.[396] Finally, Si/C/N fibers which were amorphous up to 1400 °C have been reported from PSZs comprising binary components, *e.g.*, Me_2SiNH and MeSiNH structural units.[397]

Scheme 41



3. "Silazanolysis" Reactions

As pointed out above, ammonolysis of chlorosilanes results in copious amounts of ammonium chloride which is difficult to remove. This byproduct is undesirable since it contributes to the introduction of chlorine in the precursors while it acts as a catalyst in the splitting of Si−N bonds. To overcome this problem, the previously known Si−Cl/Si−N disproportionation involving hexamethyldisilazane (HMDZ), leading mainly to trimethylchlorosilane instead of hydrogen chloride as byproduct, was extended to the synthesis of a wide range of precursors.

a. Hydridopolysilazane (HPZ). When trichlorosilane and HMDZ are mixed, an exothermic reaction occurs due to Si−Cl/Si−N bond exchange, as shown in Scheme 42.[398−400]

As the temperature is raised, both trimethylchlorosilane and ammonium chloride are volatilized, reducing the chlorine content of the system. As the polymerization reaction proceeds, the bulky trimethylsilyl groups along the silazane chain promote cyclization leading to cyclotetrasilazanes and cyclopentasilazanes. The authors pointed out that the number of cyclization and branching alternatives prevents identification of individual molecular structures in the growing preceramic polymer. A typical HPZ polymer contained (wt %) Si, 47.2; C, 23.0; N, 22.1; Cl, <0.1; and O, <0.2. After pyrolysis, the ^{29}Si NMR spectrum exhibited a broad signal centered at −46 ppm covering the region expected for silicon oxycarbide, oxynitride and carbonitride structures. The polymer was melt-spun and the green fibers cured by exposure to a multifunctional chlorosilane ($HSiCl_3$) at a temperature above the boiling point of the silane but below the softening point of the polymer. Pyrolysis at 1200 °C of the fibers under nitrogen provided a high ceramic yield (74%). Weight loss in the first stage of the pyrolysis (300-500 °C) led to an evolution of Me_3SiCl, NH_3, and volatile oligomers. The second stage (500−700 °C) included loss of methylsilanes, methane, and hydrogen. Only methane and hydrogen were lost above 700 °C. On the basis of NMR investigations, the authors found that the ceramic was amorphous as was also indi-

Scheme 42

$$HSiCl_3 + Me_3SiNHSiMe_3 \longrightarrow Me_3SiNHSiHCl_2 + Me_3SiCl$$

$$Me_3SiNHSiHCl_2 + Me_3SiNHSiMe_3 \longrightarrow (Me_3SiNH)_2SiHCl + Me_3SiCl$$

$$(Me_3SiNH)_2SiHCl + Me_3SiNHSiMe_3 \rightleftharpoons (Me_3SiNH)_3SiH + Me_3SiCl$$

$$2\,(Me_3SiNH)_2SiHCl \longrightarrow Me_3Si{-}NH{-}SiHCl{-}NH{-}SiHCl{-}NH{-}SiMe_3 + Me_3SiNHSiMe_3$$

etc.

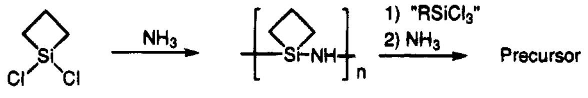
cated by XRD.[28] They concluded that silicon atoms are simultaneously bonded to carbon, nitrogen, and oxygen to give an amorphous silicon carbonitride ceramic.

b. Disproportionations Using Chlorodisilanes. As described above, a preceramic polymer was obtained from the reaction of mixtures of methylchlorodisilanes (issued from industrial "direct synthesis" residues) with an excess of HMDZ.[77,401–404] This precursor contains oligomeric species with the approximate composition $Me_{2.6}Si_2(NH)_{1.5}(NHSiMe_3)_{0.4}$.[405] Ceramic fibers were prepared by melt-spinning, curing, and pyrolysis of this precursor. A reaction scheme for the formation of polydisilazanes from a symmetrical tetrachlorodisilane as a model compound was developed.[406] It is worthy of note that, in this strategy, the methylene groups should insert into Si–Si bonds, *via* the Kumada rearrangement, therefore giving $Si-CH_2-Si-N$ linkages. Similarly, polymers were prepared from the ring-opening disproportionation of chlorinated disilanes and cyclic PSZs.[407]

4. Miscellaneous Reactions

Polysilacyclobutasilazanes (Scheme 43),[408,409] prepared according to a modified Nametkin's route,[146] were used for making polymers suitable for high-temperature applications.[410,411]

Scheme 43



"RSiCl3" = $HSiCl_3$, $MeSiCl_3$, $SiCl_4$, $Me_xSi_2Cl_{6-x}$ (x = 2 or 3)

Upon heating to 200–250 °C, the oligomers afforded cross-linked resins through ring-opening polymerization. The authors have shown that the cross-linking step is a combination of N–H addition across Si–C bonds and the ring-opening polymerization of the silacyclobutyl units. The pyrolysis of those polymers was investigated up to 1800 °C. Below 1200 °C, Si/C/N/O ceramics of various compositions were obtained in 60–80% yields. By 1800 °C, the residue was predominantly β-SiC by XRD (~50% yield).

Chloride-terminated poly(dimethylsilazanes) have been prepared by ring-opening polymerization of six- and/or eight-membered cyclosilazanes in the presence of $MeSiCl_3$. The Cl-terminated silazanes were ammonolyzed to give H_2N-terminated silazanes which could self-condense and were precursors to ceramics.[412]

In order to obtain processable Si/C/N ceramic precursors, a wide range of PSZs with various substituents, including vinyl groups, have also been investigated.[413–423] Their cross-linking has been studied by using a number of catalysts and radical initiators such as strong acids, bases, metal transition complexes, Lewis acids, polychlorosilanes, etc. Thus, PSZs obtained from the ammonolysis of dimethyldichlorosilane, or co-ammonolysis of dimethyldichlorosilane and methyltrichlorosilane, have been used for the preparation of ceramic materials, especially fibers.[21] Si–H-containing PSZs were also cross-linked using organoaluminum derivatives.[424,425] In addition, HMDZ[426] and 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane[427–429] have been investigated as ceramic precursors, and ceramic films have been reported from hexachlorodisilane.[430]

The high molecular weight linear polymers prepared by Soum and co-workers[348,349,431] by anionic or cationic ring-opening polymerization of cyclodisilazanes gave high char yields in the case of vinyl-substituted precursors. Treatment of PSZs, obtained from disilane residues, with $NaNH_2$ in liquid ammonia has led to useful preceramic polymers,[432] and PSs containing permethylsilazane and cyclodisilazane units were prepared by sodium polycondensation.[433] Also anionic equilibration of cyclodisilazanes, followed by condensation with functional organosilanes, provided silyl-bridged and coupled cyclosilazanes of high molecular weights which were converted to Si- and N-containing ceramics.[434,435]

As previously noted, a problem with the simple PSZs as precursors of Si_3N_4 is that the polymers are nitrogen-deficient, with respect to the Si/N stoichiometry of the ceramic. A possible way of redressing this nitrogen deficiency would be to incorporate some N–N bonds into the PSZs. Thus, in addition to the imidation and the modification of PHPSZ previously reported by Isoda *et al.*,[368] the synthesis of precursors from the condensation of hydrazine with chlorosilanes, such as methyldichlorosilane, dimethylchlorosilane, methylvinyldichlorosilane, and $SiCl_4$ has been reported.[436–438] Moreover, treatment of oligosilazanes $(SiMeH-NH)_n$ with hydrazine at 70 °C led to a resin exhibiting high char yield upon pyrolysis.[439]

To complete these miscellaneous reactions, one must mention that isocyanate-modified PSZs exhibiting a tailorable viscosity were developed as ceramic precursors.[440] They can be thermoset by heating with dicumyl peroxide, affording high char yield of SiC and Si_3N_4 upon pyrolysis under nitrogen.[441] In addition, ammonolysis of methyltriisocyanatosilane yielding poly(methylsilazanes), and subsequent thermal degradation of this polymer gave SiC and Si_3N_4 materials.[442]

5. PCSZs with Carbon in the Main Chain

Numerous silazane oligomers and polymers with hydrocarbon groups in the main chain have been

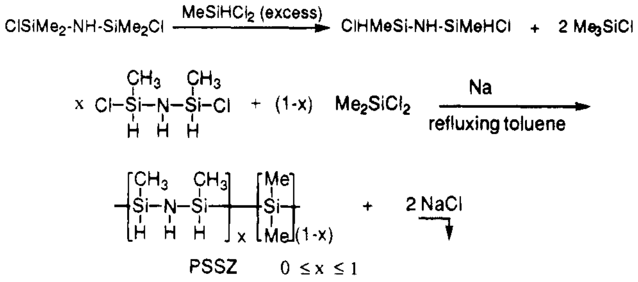
Table 7. Polycarbosilazanes (PCSZs) from Polysilasilazanes (PSSZs)

entry	x	yield (%)	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	volume of gas (mL·g^{-1})	char yield (%)	softening interval (°C)
1	0.10	47	24.0	8.9	63	65	160–170
2	0.25	65	2.8	2.1	78	49	120–140
3	0.50	78	5.3	2.8	52	45	90–100
4	0.50	71.5	19.2	8.5	72	61	170–190
5	0.75	75	35.0	16	50	58	160–170
6	1.0	59.5	12.0	6.8	19	60	140–150

reported,[347] but most of them should lead to ceramics containing a too large excess of elemental carbon. However, a few precursors possessing such structures have been designed for use in the preceramic polymer area.

a. The Copolymer Route to Precursors with Controlled Si/C/N Ratios. This strategy is based on the use of new oligomers, poly[(dimethylsilylene)-*co*-(1,3-dimethyl-1,3-dihydrogenodisilazane)]s (PSSZs). Owing to the presence of $-[(Me_2)SiSi(MeH)NH]-$ sequences in the main backbone, these starting materials were expected to afford novel polycarbosilazanes (PCSZs) upon thermolysis, *i.e.*, organosilicon polymers possessing $Si-CH_2-Si-N$ linkages *via* the Kumada rearrangement,[443-447] the copolymer strategy offering the control of the composition within the main backbone. PSSZ oligomers were synthesized according to the sodium copolycondensation of dimethyldichlorosilane with 1,3-dichloro-1,3-dimethyldisilazane, a novel monomer, as depicted in Scheme 44.[448,449]

Scheme 44



The as-obtained materials are gray, translucent oils possessing $\bar{M}_n$ values in the range 2100–6000 depending on the x values. Basically, they can be regarded as modified PDMSs containing randomly distributed $-(MeSiH-NH-SiHMe)-$ units. However, their microstructure is somewhat more complex since they also contain a small proportion of sequencies resulting from partial trisilylation of nitrogen atoms under nucleophilic conditions. The fact that they exhibit low viscosity for values of x lesser than 0.75 led the authors to infer that they contain no significant proportion of cage-like or condensed ring structures. As expected, their nitrogen content increases as a function of x, at least when $x \leq 0.75$. They possess a low residual chlorine content (about 1% weight), which was readily removed by a final treatment with ammonia. Upon heating under an inert atmosphere at atmospheric pressure, these copolymers provided solid precursors (Table 7).

Table 8. Elemental Analysis of PCSZ (at. %)

x	C (%)	Si (%)	H (%)	N (%)	O (%)
0.1	36.3	50.2	9.5	3.0	1.3
0.25	33.4	48.0	8.3	8.4	1.9
0.5	27.8	51.5	7.7	11.7	0.8
0.75	25.0	51.6	7.3	15.1	1.4
1.0	24.1	51.6	7.7	12.9	1.5

Table 9. Elemental Analysis of Ceramics (at. %)

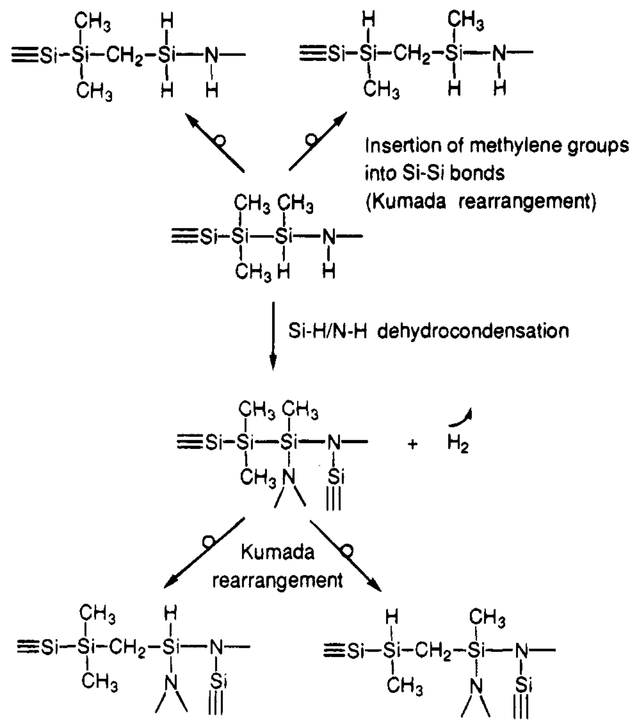
x	C (%)	Si (%)	N (%)	O (%)
0.25	42.0	40.0	16.0	2.0
0.5	38.0	42.5	18.0	1.5
0.75	33.0	43.0	22.0	2.0
1.0	33.0	42.0	23.0	2.0

Under mild conditions (300–370 °C, 2–5 h), good yields of soluble and fusible PCSZs were obtained. When more severe conditions were used (470 °C, 4 h), or when x values were increased, insoluble and infusible products resulted. On the other hand, in the case of the thermolysis of *N*-methyl copolymers,[445,447] no substantial proportion of solid product was obtained, but oligomers were essentially formed, accompanied with evolution of a small amount of gas, even upon thermolysis under severe conditions (above 400 °C), at atmospheric pressure. This observation corroborates that the presence of both Si–H and N–H sites is necessary to achieve efficient cross-linking, as previously observed in the case of PSZs containing SiH-NH linkages. As they exhibit a good thermal stability even in the molten state, these PCSZs were used to prepare fibers. Physicochemical characterizations showed that important structural changes took place during the PSSZ/PCSZ conversion. Thus, IR spectra showed new absorption bands at 1350 (very weak) and 1040 (shoulder) cm^{-1} characteristic of the vibrations of $Si-CH_2-Si$ sequences, δ_{C-H} and ω_{Si-C}, respectively. For a given value of x, this feature is strongly dependent on the degree of conversion (temperature and duration of the thermolysis): only very weak bands can be seen in the case of a poorly converted material, whereas an appreciable increase in the intensity of these bands is observed for more transformed products. In addition, a marked decrease of bands at 3380 cm^{-1} (ν_{N-H}) and 1180 cm^{-1} (γ_{Si_2N-H}) is observed. These results as a whole show that the thermal conversion of PSSZ proceeds *via* Si–H/N–H condensations and hydrogen evolution at a temperature of about 280–300 °C, leading to the creation of Si_3N nodes, as reported in the case of PSZs. Besides this main pathway, insertion of methylene groups into Si–Si bonds, *i.e.*, the Kumada rearrangement, simultaneously takes place (Scheme 45).

Tables 8 and 9 clearly show the correlation between the x value and the nitrogen content of PCSZs and ceramics obtained after pyrolysis. The presence of oxygen was due to contamination.

This route allowed the preparation of small diameter silicon carbonitride fibers (15–18 μm) containing only a small excess of free carbon (5% at.). They

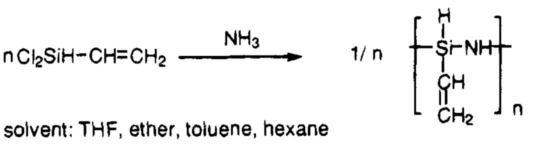
Scheme 45



remained amorphous up to 1400 °C, exhibiting good thermomechanical properties: Young's modulus E = 220 GPa (1600 °C); tensile strength σ_p = 2400 MPa (pyrolysis temperature 1200 °C), σ_p = 2000 MPa (pyrolysis temperature 1600 °C).[450-452] Interestingly, above 1400 °C, they gave β-SiC nanocrystals, whereas crystals of Si_3N_4 were never observed up to 1600 °C. Comparison of electron beam and oxygen-cured fibers showed that oxygen was detrimental to mechanical properties. However, these fibers progressively decomposed under argon from 1450 to 1600 °C with loss of nitrogen. In contrast with most of the other PSZ routes, giving carbon-containing silicon nitride, this method leads to nitrogen-containing silicon carbide.

b. Polyvinylsilazanes (PVSZ)s. In the context of the preparation of ceramic matrixes, PSZs containing vinyl groups are of particular interest because they offer the possibility of cross-linking *via* the polymerization of unsaturated groups or hydrosilylation without weight loss. For example, Seyferth and coworkers[371] have reported the use of PSZs resulting from the co-ammonolysis of methyldichlorosilane and methylvinyldichlorosilane or methylallyldichlorosilane for the preparation of ceramics. Similar products were also investigated by Lebrun *et al.*[414,415] while Corriu *et al.*[453,454] have reported the synthesis of a novel precursor of silicon carbonitride from the ammonolysis of vinyldichlorosilane (Scheme 46).

Scheme 46



$$n\,Cl_2SiH{-}CH{=}CH_2 \xrightarrow{NH_3} 1/n\,\left[\begin{matrix}H\\ |\\ {-}Si{-}NH{-}\\ |\\ CH\\ \|\\ CH_2\end{matrix}\right]_n$$

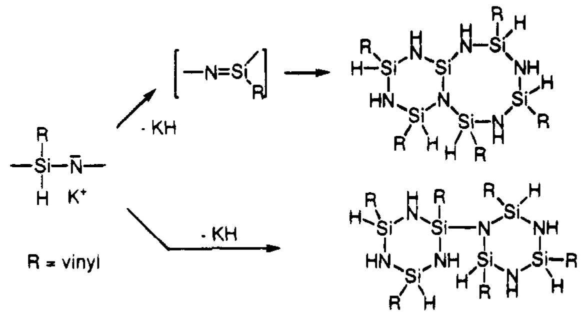
Low mass oligovinylsilazanes (OVSZs) were so obtained whatever the solvent was. They were not distilled because of the possibility of thermal cross-linking at relatively low temperature. In order to obtain high char yields on pyrolysis, OVSZs were cross-linked under various conditions and the conversion of these precursors has been thoroughly investigated:

(a) Thermal cross-linking occurred spontaneously at a relatively low temperature (*i.e.*, 110 °C) in the absence of a catalyst. ^1H NMR and ^{13}C NMR data were consistent with hydrosilylation reactions, occurring according to α- (major) and β-addition (minor) modes. On the other hand, transamination with release of ammonia is only a minor pathway during the thermal cross-linking at this temperature.

(b) In the presence of a platinum catalyst, OVSZs led in a few minutes to an insoluble, infusible solid.

(c) The KH-catalyzed Si–H/N–H dehydrocondensation afforded an insoluble PSZ. Interestingly, the vinyl groups remain inert under these conditions. A proposal for a mechanism involving the possible formation of silaimines is depicted in Scheme 47.[453]

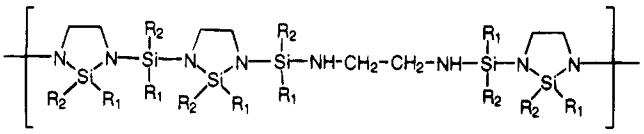
Scheme 47



By comparison of ^{29}Si NMR chemical shifts of a cross-linked PVSZ with those of various cyclodisilazanes, Corriu *et al.*[453] have found that no downfield signal assigned to strained cyclodisilazane is present, since the chemical shifts (−24, −32 ppm) are quite close to those of the starting OVSZ. This means that no four-membered Si_2N_2 structure was formed from KH-catalyzed dehydrocondensation or that they cannot be accurately observed by ^{29}Si-NMR spectroscopy in such complex structures.[385] Pyrolysis of the KH cross-linked precursors afforded high char yields (>80%). However, the fact that a good ceramic yield (59%) was obtained even in the case of non-cross-linked OVSZ shows that thermal cross-linking readily occurs in these cases. The effect of a platinum catalyst on the microtexture of the Si/C/N ceramics has been investigated by high-resolution TEM[455] and multinuclear magnetic resonance.[456] The local environments of all the atoms were identified and the different sites quantified. At 1400 °C, the material is composed of a silicon carbonitride phase and a free carbon phase: polymerization or hydrosilylation of vinyl groups are responsible for the carbon retention. Another interest of the vinyldichlorosilane route is the possibility to reverse the order of ammonolysis and hydrosilylation reactions.

c. Ethylene-Bridged Precursors. PSZs with Si–CH_2–CH_2–Si–N linkages have been described many years ago.[347,457,458] Mariam *et al.*[459-462] have reported the synthesis of oligomers from the polycondensation of ethylene diamine with methydichlorosilane and dimethyldichlorosilane and their use as ceramic precursors. They showed that the structure of these oligomers was constituted of cyclic and acyclic segments (Scheme 48) whose respective percentages play an important role on char yields.

Scheme 48



$R_1 = CH_3$; $R_2 = H, CH_3, -CH{=}CH_2$

In addition to applications as Si/C/N ceramic precursors, the authors found some of these types of oligomers allowed various chemical modifications.[461,462]

d. Miscellaneous Reactions. Precursors of Si/C/N ceramics were obtained by KH polymerization of PCSZs resulting from the ammonolysis of a mixture of $MeSiHCl_2$ and $Cl_2MeSi(CH_2)_4SiMeCl_2$.[463] PCSZ precursors have been prepared by action of chlorinated disilanes with various diamines, leading to SiC-containing ceramics upon pyrolysis.[464] Ethylene-bridged chlorosilazane precursors of ceramic fibers have also been prepared from disproportionation involving oligosilazanes and polychlorosilanes $R-SiCl_2-CH_2CH_2SiCl_2-R$ at 30−300 °C.[465,466] Moreover, "hybrid" precursors containing Si−C and Si−N in the main chain have recently been reported.[467]

D. Structural/Compositional Effects

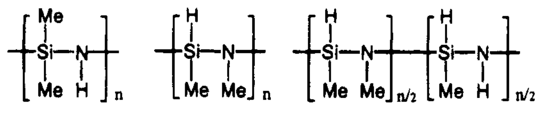
1. Precursors Where Silicon Is Bonded Only to Nitrogen

To have a better understanding of the precursor-to-ceramic conversion, Interrante *et al.*[468] have studied the condensation−polymerization of tetrakis(ethylamino)silane, $Si(NHEt)_4$. Because the silicon is bonded only to nitrogen, this compound was expected to be a potential source of pure silicon nitride that does not require pyrolysis under ammonia. Its thermal polymerization was studied in detail by means of a variety of physicochemical techniques and various cyclosilazanes, including cyclodisilazanes, were characterized. However, carbon was not entirely lost since pyrolysis under nitrogen yielded a carbonitride which remained amorphous up to 1500 °C. When this amorphous solid was heated to 1500 °C under argon, N_2 was lost, yielding nanocrystalline β-SiC with carbon and some α-SiC; however, on heating to 1600 °C under nitrogen, a mixture of α-Si_3N_4 and carbon with minor amount of β-SiC was obtained, presumably due to the repression of the loss of N_2 from the ceramic under these conditions.

2. PSZ and PCSZ Models

a. Si- and (or) N-Methylated PSZ Models. In early investigations, Arkles[469] examined the direct pyrolysis of cyclic and oligomeric model PSZs possessing $-(SiMe_2-NH)-$ or $-(SiMeH-NMe)-$ linkages and, alternatively, a PSZs with both units (Scheme 49). The precursors obtained from catalytic reequilibration at 225−300 °C of the cyclic compounds were formulated in terms of linear models.

Scheme 49

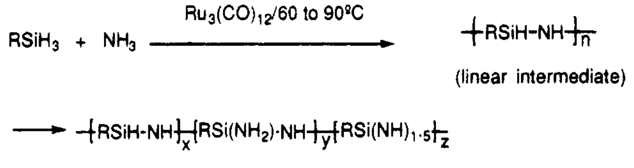


18 **19** **20**

Low ceramic yields were obtained in the case of **18** (5−10%), **19** (15−20%); however, it was higher for **20** (50−55%). This is in good agreement with our work[450] concerning PSSZ copolymers. In any case, Arkles showed that the oligomers eliminated at the beginning of the pyrolysis and the non volatile residue possessed similar compositions. The PSZ **19** appeared to undergo conversion at lower temperatures than PSZ **18** and in higher yields. Although it seems difficult to draw conclusions regarding the poor char yields, Arkles suggested that this was due to the low bond dissociation energy of the $N-CH_3$ bond *vs* the $Si-CH_3$ bond, providing an additional site for partial reticulation during the pyrolysis. Also, the strong yield enhancement in the case of **20** was logically explained by the ability of the relatively basic nitrogen to react with silicon hydride, generating hydrogen. As previously pointed out, these results are consistent with the observation that *N*-Me-substituted PSZs containing Si−H bonds exhibit a certain stability compare to PSZs containing N−H and Si−H bonds, although they are somewhat reactive at high temperature.[356,470]

Laine and Blum *et al.*[52,55,154] have investigated the pyrolytic behavior of various types of silicon- and nitrogen-substituted PSZs prepared *via* catalyzed dehydrocondensation and conclude (i) as expected, pyrolysis of poly(dimethylsilazane) ($\bar{M}_n$ = 2000, $\bar{M}_w$ = 9600) yields negligible amounts of ceramic products. Because the polymeric fraction is a nonvolatile residue, the polymer volatility cannot account for the low ceramic yield; such a behavior is explained only by cleavage of Si−N bonds, accompanied by parallel Si−C splitting that starts above 450 °C and (ii) monosubstituted silane involved in the catalytic dehydrocoupling with ammonia provides an additional reactive site, allowing for the formation of three-dimensional polymers (Scheme 50).

Scheme 50



The increase in latent reactivity of the resulting polymer containing Si−H, N−H, and NH_2 functional groups led to a controlled degree of cross-linking during the pyrolysis. Interestingly, they have shown that the ceramics obtained from oligo- and poly(*N*-methylsilazane)s possess about the same composition, *i.e.*, 83% Si_3N_4 and 17% carbon by weight. They concluded that the composition of the ceramic product appeared to be defined by the monomer unit $-(H_2SiNMe)_x-$ and was independent from the molecular weight or viscoelastic properties.

In addition to liquid and solid state NMR characterizations, FTIR spectroscopy has emerged as a

Table 10. Ammonolysis and Hydrazinolysis of Chlorosilanes

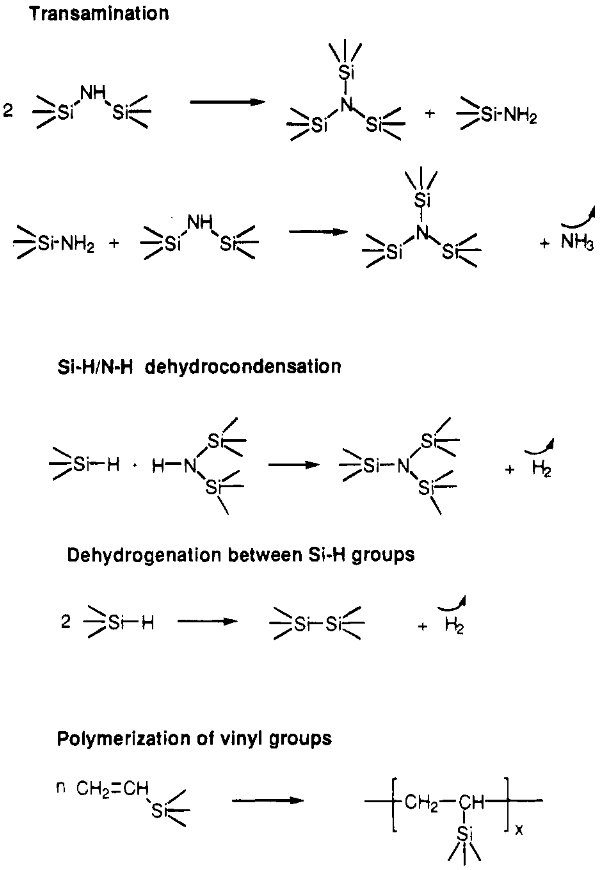
$(CH_3)_2SiCl_2$	ND_3
$(CH_3)_2SiCl_2$	CH_3NH_2
$(CH_3)_2SiCl_2$	$H_2NCH_2CH_2NH_2$
CH_3SiHCl_2	$H_2NCH_2CH_2NH_2$
$SiCl_4$	H_2NNH_2
CH_3SiHCl_2	H_2NNH_2
$(CH_3)_2SiCl_2$	H_2NNH_2
$(CH_3)_2SiCl_2/CH_3SiHCl_2$ (1/4, 1/1, 1/3)	H_2NNH_2

powerful method for studying the pyrolysis mechanisms enabling one to observe the various structural changes that occur during the pyrolysis.[55,471,472] For example, Mariam *et al.*[473] have investigated the pyrolysis of a series of precursors resulting from the ammonolysis and hydrazinolysis of various chlorosilanes (Table 10). They concluded that NH, NH_2, and SiH groups were affected first, leaving most likely Si_3N_4/SiC materials and perhaps elemental carbon. From the precursor depicted in Scheme 48 ($R_1 = CH_3$, R_2 = vinyl), they obtained a ceramic whose formula $Si_{5.5}C_{10}N_{5.2}O_1$ showed that considerable loss of carbon occurred during the pyrolysis.[474]

On the assumption that reactions of pendent substituents occurred independently from backbone cleavage, Burns *et al.*[475] have investigated the effect of changing the alkyl group on the polymer pyrolysis and the ceramic properties. To test the assumption of radical mechanisms, two series of R groups were considered. In the first series (R = methyl, ethyl, isopropyl, phenyl, benzyl, allyl, and *tert*-butyl), the R group was varied so that homolytic cleavage of the Si–C bond during pyrolysis would produce a silyl radical and a methyl, a primary or secondary carbon, a phenyl, a benzylic, an allylic or a tertiary carbon radical, respectively. In the second series (R = ethyl, propyl, isobutyl, 3-butenyl, 2-phenethyl, and 2-methylphenethyl), the R group was varied such as the α-C-C bond cleavage would produce an $\equiv SiC^\bullet$ radical and a methyl, a primary, a secondary, an allylic, a benzylic, or a secondary benzylic carbon radical. As far as the adjacent groups are concerned in the pyrolytic degradation, the following conclusions were drawn from these investigations: (i) silsesquiazanes thermally degrade by a two-step radical mechanism involving an initial silicon–carbon bond cleavage followed by a β-elimination of a hydrogen radical; (ii) saturated alkyl groups contribute approximately the same amount of carbon to a ceramic char, whatever their structure is; in others words, adjacent hydrocarbon groups are lost during the pyrolysis to a large extent; (iii) unsaturated substituents result in a higher carbon content, and the number of carbon atoms of unsaturated groups influences the carbon ratio in the resulting ceramic; and (iv) the stability to oxidation of an amorphous Si–C–N ceramic char is a function of surface area and carbon content in accordance with percolation theory predictions.

b. PVSZ Models. To gain more insight into mechanisms of thermal cross-linking of these preceramic polymers, Corriu *et al.*[476,477] have investigated the thermal behavior of a series of OVSZ model compounds in which each functionality (vinyl, Si–H, or N–H) was successively replaced by a nonreactive methyl group. The following polymers were studied: $-(SiViH-NH)_n-$, $-(SiViH-NMe)_n-$, $-(SiMeH-NH)_n-$, $-(SiViMe-NH)_n-$, $-(SiMeH-NMe)_n-$, $-(SiViH-NH)_x-$, $-(SiMe_2-NH)_y-$, $-(SiViH-NH)_x-(SiMeH-NH)_y-$ (n, x, and y varying according to the nature of the PSZ). The influence of these structural changes on the thermal reactivity of the PSZs during the curing step at low temperature (120 °C) and during the subsequent pyrolysis were examined. The more likely processes are given in Scheme 51.

Scheme 51



Corriu has drawn up the following order in reactivity at 120 °C: hydrosilylation > SiH/NH dehydrocondensation > polyaddition of vinylic groups ~ dehydrocoupling of SiH bonds. However, even though solids were obtained, IR spectroscopy showed the presence of unreacted Si–H, vinylic, and N–H functions which indicates that cross-linking was far from completion. During the pyrolysis, the main cause for weight loss was assigned to depolymerizations, probably due to transamination and disproportionation reactions. Thus, the small amount of volatile silanes such as $MeSiH_3$ could be assigned to disproportionations of minor importance. When methyl groups on nitrogen prevent transaminations, the loss of oligomers during pyrolysis may be ascribed only to disproportionations. Very likely, hydrogen evolved at low temperature (330 °C) was due to Si–H/N–H condensations. On the other hand, formation of Si–Si bonds appeared unlikely (or Si–Si bonds are not stable at this temperature). So, the only cause of nitrogen loss should be the transamination.

The silicon carbonitrides obtained from poly(methylsilazane)s remained amorphous up to 1400 °C. Characterization suggests that the ceramics obtained

Table 11. Yields, Weight-Average Molecular Mass, Polymolecularity, and Char Yields (CY) of Polycarbosilazane Models

PCSZ	R^1	R^2	yield (%)	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	CY (%)
PCSZ I	H	H	84	3700	2.45	19
PCSZ II	H	Me	95	4800	3.3	4.5
PCSZ III	Me	H	20	850	1.10	2.5

Table 12. Thermolysis of PCSZ I

run	volume of evolved gas (mL·g^{-1})	soluble PCSZ (yield, %)	insoluble PCSZ (yield, %)
1	61	55	0
2	94	56	5
3	97	65	11
4	112	11	44

Table 13. GPC Results, Char Yields (CY), and Softening Temperatures of Soluble Cross-Linked Materials Obtained from PCSZ I

run	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	CY (%)	melting interval (°C)
1	48,000	5.6	38	80–90
2	78,800	5.3	52	140–150
3	21,510	7	65	180–190
4	2950	2.5	24	<25

Table 14. Cross-Linking of 1,1,3,3-Tetramethyldisilazane at 540 °C in an Autoclave

run	time (h)	final pressure (bar)	soluble PCSZ yield (%)
1	24	3.5	65
2	48	4	75
3[a]	24	3.5	71

[a] Run performed in the presence of $Ru_3(CO)_{12}$ (0.1% by weight).

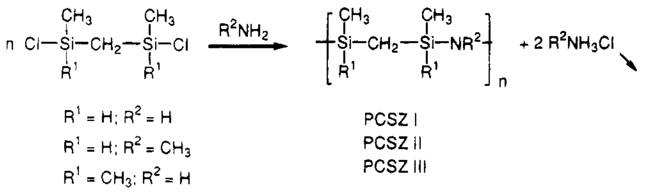
Table 15. Weight-Average Molecular Mass, Polymolecularity, Softening Intervals, and Char Yields of Polycarbosilazanes Obtained from 1,1,3,3-Tetramethyldisilazane

run	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	softening interval (°C)	CY (%)
1	1450	1.1	< 25	10
2	10,200	5.1	140–150	43
3	1800	1.3	< 25	16.5

at 1200–1400 °C consist of various SiC_xN_{4-x} tetrahedra and free carbon which would hinder the crystallization of Si_3N_4 and SiC. In addition, Goursat *et al.*[478,479] have studied the conversion of a solid copolymer $-(ViSiHNH)_x-(MeSiHNH)_y-$ into a ceramic in the 20–1450 °C temperature range. The char yield, ceramic composition, and gaseous evolution were found to directly depend on the heating rate, pyrolysis atmosphere, and duration of the pyrolysis. The various pathways have been discussed in terms of transamination reactions and radical mechanisms. These authors have also studied the pyrolysis of various PSZs under nitrogen. The overall transformation involves three steps, and the observed porosity was attributed to oligomer release.

c. *PCSZ Models.* PCSZ models (Scheme 52) were synthesized by ammonolysis (PCSZ I and PCSZ III) and aminolysis (PCSZ II) of the corresponding 1,3-dichloro-1,3-disilapentanes.[480]

Scheme 52



Direct pyrolysis of the as-obtained PCSZs resulted only in poor char yields (Table 11), showing that splitting of the CH_2-Si-N backbone and formation of gases and oligomers occurred more rapidly than thermal cross-linking whatever the substituents at silicon and nitrogen were.

Interestingly, heating PCSZ I at 350–400 °C in a quartz vessel under inert gas at atmospheric pressure readily resulted in solid PCSZs, besides a small fraction of distillable low-boiling compounds and a gas evolution. Yields of the as-obtained fusible precursors depend on the evolved gas volume (Table 12). The main gaseous component was hydrogen while CH_3SiH_3, $(CH_3)_2SiH_2$, and methane also were formed.[242,480]

On-line pyrolysis/mass spectrometry revealed that hydrogen was the first gas evolved, the evolution starting at 280 °C with a maximum at 420 °C. A second hydrogen release, with a maximum at 600 °C, probably resulted from the ceramization pathway. It must be emphasized that no ammonia evolution was detected, showing that no transamination took place. Otherwise, under similar conditions, the PCSZ II exhibited a quite different behavior since no reaction occurred within the same temperature range; heating this compound at higher temperature only resulted in a slight gas evolution and low-boiling oligomers, while no solid (cross-linked) material could be obtained. Owing to the formation of oligomeric products, the refluxing temperature progressively decreased, showing that the cleavage of the backbone occurred without substantial cross-linking. Heating PCSZ III at 500 °C in an autoclave for several hours resulted in no substantial amount of volatile product, and the starting PCSZ was recovered unchanged. Soluble cross-linked PCSZs obtained from PCSZ I exhibited a marked increase in average molecular weight and polydispersity values with respect to the starting material. Also, char yields were considerably higher (Table 13). A good correlation between softening temperature ranges and ceramic yields exists. The latter closely depend on the cross-linking degree but not on the molecular weights.[242,480]

IR spectra revealed that the N–H absorption band at 3375 cm^{-1} totally disappeared while the Si–H band at 2117 cm^{-1} underwent a strong decrease. ^{29}Si NMR spectra showed that new structural units were created, exhibiting signals in the range of −7.5 to 2 ppm ($\mathit{Si}C_3N$ and $\mathit{Si}C_2N_2$ nuclei).

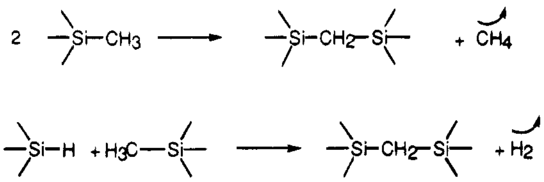
The high-temperature behavior of a simpler model, 1,1,3,3-tetramethyldisilazane was also examined. Heating this monomer at 540 °C in an autoclave resulted in the formation of solid, soluble precursors (Table 14). Run 3 shows that no appreciable effect of the metal complex was observed.

The GPC results, softening temperature ranges, and char yields of cross-linked materials obtained in runs 1–3 are given in Table 15. In this case also, IR spectra of cross-linked materials showed the complete disappearance of the ν_{N-H} absorption band at 3340 cm^{-1} and the γ_{Si_2NH} band at 1180 cm^{-1}.

Si−CH$_2$−Si bridges were formed since bands were observed at 1352 cm^{-1} $\delta_{CH_2Si_2}$ and 1040 cm^{-1} $\omega_{CH_2Si_2}$, along with an appreciable weakening of the ν_{Si-H} at 2120 cm^{-1}. Thus, observations concerning the PCSZ I and 1,1,3,3-tetramethyldisilazane are consistent with the fact that the conversion involves thermal Si−H/N−H condensations, leading to Si$_3$N nodes and hydrogen evolution (Scheme 53). Moreover, processes such as those involved in the formation of silicon carbide from polycarbosilanes probably occur above 500 °C (Scheme 54).[242,480]

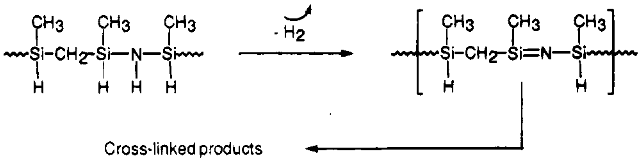
Scheme 53

Scheme 54



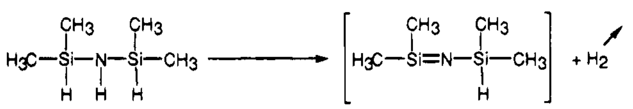
From a mechanistic point of view, it is apparent that the respective behaviors of the PCSZs I and II upon thermolysis are not completely consistent with the homolytic cleavage of the Si−H bond, which would result in hydrogen formation by attack of ≡Si−H and ≡C−H bonds. Thus, the PCSZs I and II do not afford comparable hydrogen evolution when they are treated under the same conditions, as it could be expected from a radical mechanism. Otherwise, the intermediate formation of transient organosilicon species such as silaimines and silylenes (or silenes) emerges as a plausible pathway to account for the whole phenomena and the hydrogen evolution.[153] Thus, in the case of the PCSZ I, the formation of silaimines, resulting from 1,2-hydrogen elimination in the first step, could explain the observed facile reaction and hydrogen evolution (Scheme 55).

Scheme 55



This assumption is in good agreement with other results concerning the pyrolysis of PSZs.[477] Indeed, it has been shown that stable sterically protected silaimines exist.[481−483] Moreover, the formation of silaimines resulting from Si−N cleavages had previously been postulated to account for ring contractions observed in the thermolysis of PSZs.[484] Therefore, it might be suggested that macromolecular chain-substituted silaimines are formed during the thermolysis of these PCSZs. Very likely, these intermediate silaimines would be extremely reactive under these thermal conditions. They would subsequently insert into Si−H, Si−N, and N−H bonds as soon as they were created, leading to the observed trisilylated nitrogen sites, or giving dimerization or polymerization reactions. To account for the formation of polymers in the case of 1,1,3,3-tetramethyldisilazane, a similar mechanism could be assumed (Scheme 56).

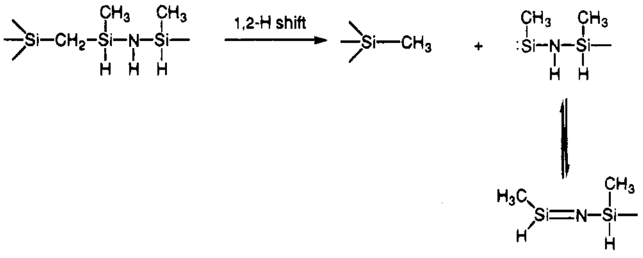
Scheme 56



It must be emphasized that small model molecules require higher temperatures (above 500 °C) to obtain high conversion rates. Consequently, at these temperatures, transient silaimines, silylenes (see below), and silyl radicals could simultaneously be formed.[242,480]

Similarly, silylenes could result from Si−C bond cleavage with 1,2-hydrogen migration, explaining simultaneously the evolution of gaseous silanes and the formation of oligomers (Scheme 57).

Scheme 57

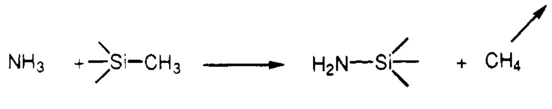


The formation of transient silylenes with subsequent insertion in an Si−H bond was assumed to account for the hydrogen evolution and thermal cross-linking of PCSs containing SiH$_2$ groups at relatively low temperature (380 °C), as mentioned in the SiC section.[249] Regarding the required, calculated high activation energy to isomerize simple models such as H$_2$Si=NH to H(H$_2$N)Si:,[485] it seems more likely that aminosilylenes could be directly formed (and not necessarily *via* silaimines) since these two species possess relatively close ground energy levels.

Finally, this work shows that Si−CH$_2$−Si−N building blocks are very likely preserved during the thermal cross-linking, leading to a preceramic polymer possessing a framework of Si−C−Si−N sequences, on the condition that Si−H and N−H bonds are present.[242,480]

d. Pyrolyses under Reactive Atmospheres. As previously emphasized for the PCSs, the pyrolysis atmosphere should play a crucial role on the mechanisms and the final composition of the materials. It has been mentioned in Section III.D.1 that pyrolyses of organosilicon polymers performed under different atmospheres (nitrogen or argon) led to ceramics with different compositions. Even though nitrogen may act as a nitridating reagent at high temperatures (above 1000 °C), it is clear that ammonia is far more reactive. Thus, Seyferth has shown that, in the case of the precursors obtained by KH dehydrocondensation (Section III.C.1.b), pyrolyses performed under nitrogen and forming gases resulted in similar products. Conversely, ammonia is an effective agent for the nitridation of the same precursor.[486] In the pyrolysis/nitridation route under ammonia atmosphere, carbon is first lost as methane and HCN from 750 °C[192] whereas hydrogen is lost from NH and NH_2 groups at higher temperature. Thus, nitrogen replaces carbon (both carbide and free carbon) as NH or NH_2 groups. Results of ^{29}Si NMR spectroscopy show that the nitridation of PCS fibers begins at 400–500 °C and is almost complete at 700 °C.[192] Although the mechanisms by which hydrocarbon groups are removed have not been completely elucidated, the nitridation has been explained as a nucleophilic displacement of carbon by NH_3 (Scheme 58).[487]

Scheme 58



This is consistent with the work of Seyferth *et al.* who have postulated that amino functions are formed in the solid and are progressively lost above 900 °C.[486] The efficiency of carbon removal is partially dependent on the initial cross-linking degree, but the nature of hydrocarbon groups seems to have only a slight effect.[488]

Interrante *et al.*[489] have investigated the ammonia-induced pyrolytic conversion of a vinylic PS and postulated in that case a different mechanism: ammonia provides the nitrogen which is incorporated into the originally N-free polysilane and would trap the free radicals which are formed during the decomposition of the polymer. In the first stage, the vinyl groups produce the thermal cross-linking of the polymer. Then, incorporation of nitrogen with associated loss of carbon occurs at 300–650 °C, as shown by elemental analyses and physicochemical characterizations.

E. Conclusions

As for the SiC preceramic polymers, the examples described in this section show that the structure of the Si_3N_4 and Si/C/N precursors is of paramount importance in the formation of ceramic materials. Linear polymers without latent reactivity are unfavorable preceramics, as corroborated by several reports on the pyrolysis of polydimethylsilazane and various PSZ models. This latent reactivity results from Si–H and N–H motifs capable to produce convenient cross-linking *via* Si–H/N–H dehydrocondensation reactions, or from vinyl groups leading to olefinic polymerization or hydrosilylation. The presence of a cross-linked structure or the capability of a polymer to further cross-link at low temperature thwarts the thermolytic retroversion reaction, frequently encountered in organosilicon chemistry, and is responsible for the evolution of volatile cyclic and linear oligomers from the polymer skeleton. Conversely, the retroversion reaction is promoted by the polymer flexibility at temperatures ranging from 200 to 450 °C, and it is clear that it competes kinetically with the cross-linking process.

The main chain structure of a given precursor and building of the network are of considerable importance. So, the chemical structure of monomeric units appear to control the final ceramic compositions. Thus, elemental analyses of ceramic products derived from many oligomers having different molecular weights and limited structural changes reveal almost identical chemical compositions, regardless of the polymerization degree. Conversely, more or less devolatilized precursors give similar ceramic compositions.

It is worthy of note that PSZs are precursors of silicon nitride, while PCSZs in which carbon is present in the main chain are most frequently precursors of silicon carbide. This means that the atoms present in the main chain remain in the ceramic; therefore, in copolymer strategies involving PSSZs, the nitrogen ratio in the ceramic can be controlled.

Although they influence namely the polymer properties and polymerization reactions, alkyl pendent groups bonded to silicon are partially eliminated during the pyrolysis. Therefore, they, are of relatively minor importance. However, when these pendent groups are phenyl or vinyl (or other unsaturated groups), they provide a significant free carbon enrichment of the final ceramic. In addition, in the case of *N*-Me PSZs obtained from the transition metal dehydrocoupling, carbon appeared to be retained in the final ceramic. However, it must be noted that, as for SiC precursors, removal of carbon has recently been observed when PSZs were pyrolyzed under a hydrogen atmosphere.[490]

Another general feature is that the presence of nitrogen delays the crystallization of silicon carbide in the ex-PCSZ ceramics. Nevertheless, above 1400 °C, the release of nitrogen from the ceramic (except under a nitrogen atmosphere) limits the potentialities of Si/C/N materials. Finally, in Si/C/N as in SiC-based ceramics, oxygen is not desirable while the role of a small percentage of free carbon has not been clearly determined.

From a mechanistic point of view, very little is known about the various transient moieties which are responsible for the pyrolysis transformations. Low valency species (silenes, silylenes, and silaimines) explain the observed results, but homolytic cleavages compete as the temperature increases. In addition, the presence of impurities such as chloride ions might promote cleavage and rearrangement of bonds at silicon or disproportionation reactions during pyrolysis. Further studies under inert and reactive atmospheres should bring out more complete information on pyrolysis mechanisms.

IV. General Conclusions

As the actually available fibers are essentially made *via* the Yajima strategy, the general conclusion is that given in Section II.A.6. Investigations are becoming more and more oriented toward materials free from oxygen and containing a relatively low, but well-controlled, amount of free carbon, with an homogeneous distribution. In addition, heteroelements, not only boron or titanium, are frequently introduced to prepare "doped" fibers. Finally, to make fibers which could be used up to 2000 °C, the need of novel or improved syntheses of metallic oxides might give rise to further intensive investigation. Since metal oxide fibers which must be involved in CMC materials for use up to 2000 °C still need long and intensive investigations to become viable, SiC-based and to a lesser extent Si/C/N- and Si_3N_4-based ceramics remain promising materials, at least for the next 10 years.

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