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Reviews

Preceramic Polymer Routes to Silicon Carbide

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Silicon carbide ceramic fibers derived from organometallic polymer precursors offer exceptional opportunities for the development of high-temperature ceramic and metal matrix composites. The literature concerned with processing SiC ceramic fibers from organometallic polymer precursors is located in diverse journals covering the fields of inorganic chemistry, polymer science, and materials and ceramics science and engineering. This review draws from the literature on precursor synthesis, precursor fiber processing, the pyrolytic transformation of precursor fibers to ceramic fibers, and the properties of the resultant ceramic fibers to provide a broad overview of current SiC precursor technology.

Introduction

The fabrication of high-modulus, refractory non-oxide ceramic fibers, especially silicon carbide (SiC), silicon nitride (Si_3N_4) and silicon–carbide–nitride (SiCN) fibers, has been the subject of intense research over the past 15 years.[1-21] In theory, it should be possible to fabricate, via preceramic polymer processing, $<$20-μm diameter, SiC, SiCN, Si_3N_4,[22,23] BN,[24] and TiB_2 fibers that offer high strength-to-weight ratios and exceptional thermal stability in harsh environments. Such fibers are expected to serve as superior reinforcing materials for ceramic and metal matrix composites (CMCs and MMCs).

In practice, non-oxide ceramic fibers produced from preceramic polymers have not exhibited tensile strengths and elastic moduli characteristic of the respective bulk ceramic materials. For example, state-of-the-art SiC ceramic fibers [Nicalon (Nippon Carbon Co.)[6] and Tyranno (Ube Ind.)[19] fibers], the only fibers available commercially in quantity, exhibit tensile strengths $\approx$2–2.5 GPa, elastic moduli $<$300 GPa and densities of 2.3–2.5 g/cm^3.[6,19] By comparison, SiC whiskers (single crystal, 0.3–1.0-μm diameter) exhibit tensile strengths of $\approx$8 GPa and elastic moduli of $\approx$580 GPa.[20] Hot pressed SiC (density = 3.2 g/cm^3) can have an elastic modulus of up to 450 GPa.[21] Furthermore, continuous SiC filaments produced by chemical vapor deposition (Textron) offer elastic moduli ($\approx$400 GPa), tensile strengths ($\approx$4 GPa) and densities ($\approx$3.0 g/cm^3) that come close to the bulk properties.[25]

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Unfortunately the Textron filaments, with diameters of 142 μm, are not true fibers. They consist of an inner core of carbon monofilament (33 μm diameter) covered by a 1.5-μm-thick layer of pyrolytic carbon which in turn is covered by *four* compositionally different layers of SiC and a final 1.5-μm-thick coating of carbon.[25] The 142-μm diameter means that the filaments are not flexible and cannot be woven. In turn, this means that the layup of uniformly filled preforms for MMCs or CMCs must be done by hand. Finally, they are much more susceptible to fracture because of higher bending stresses during handling (relative to fibers of <20 μm diameter) and higher flaw populations.

The purpose of this review is to provide a comprehensive overview of progress in SiC preceramic polymer processing of SiC fibers. The intent is to identify research directions that must be pursued, such that fiber characteristics will eventually approximate those of the bulk material. To be comprehensive, it is necessary to review efforts in chemical synthesis, polymer processing and ceramics processing. An attempt is made to provide a review for all three communities. Because of the rapidly with which new SiC precursor and fiber articles appear, and the extent of overlap of current publications (e.g., in Yajima-type precursors); it was necessary to choose selected, exemplary articles in specific areas rather than attempt to review every publication.

Background

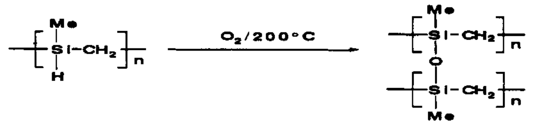
As will be discused, final ceramic fiber properties are dictated to a significant extent by the preceramic polymer (precursor) architecture. In turn, *acceptable* (useful) precursor architectures are defined primarily by specific polymer processing criteria, ceramics processing criteria and cost. *Accessible* precursor architectures are in turn dictated by the methods of chemical synthesis of the monomer units and the associated polymerization reactions. To date, only a limited number of useful synthetic routes have been devised because of these interlocking sets of criteria. In this section, we briefly define a "useful" preceramic according to specific polymer and ceramic processing criteria.

Criteria for Useful Preceramics. To be "useful" for fiber forming, a preceramic polymer must exhibit (1) controllable rheology, (2) latent reactivity, (3) controllable pyrolytic degradation, (4) high density and ceramic yield, and (5) high selectivity to desired ceramic product and microstructure.

Rheology. The type of fiber spinning method used (drawing or extrusion from solution or melt) engenders constraints on what is considered useful polymer rheology. It is commonly desirable to have non-Newtonian viscoelasticity such that during spinning, the polymer will flow readily without necking. Viscosity should be sufficiently high (at zero shear) such that once formed, the material will retain its new shape, be self-supporting, and not creep. Non-Newtonian viscoelastic behavior can be obtained either by using high molecular weight, chain entangled linear polymers or highly branched oligomers with a gellike nature. All spinnable preceramics developed to date are low molecular weight, highly branched, gellike oligomers {e.g., polycarbosilane (PCS), $-[MeHSiCH_2]_x-$, Me = CH_3}.[26] Detailed discussions on the correlation of rheology with "spinnability" are available in the literature.[27,28]

It is important to note here that very little concerning the technology of precursor polymer spinning has appeared in the literature, despite the critical nature of this part of ceramic fiber processing. In part, this is a consequence of industry protecting its technology and in part because each polymer system requires very specific parameters both for optimal spinnability and in the design of a spinning system to process that particular polymer. These parameters do not lend themselves to generalizations, except as described previously.[27,2]

Latent Reactivity. Once spun, the precursor fiber must retain some chemical reactivity that allows it to be rendered infusible. Otherwise, during pyrolysis, fiber integrity will be lost (e.g., by melting or creep) long before the chemical constituents are transformed into ceramic. Infusibility is commonly obtained through reactions that provide extensive cross-linking. Yajima polycarbosilanes are normally cross-linked by air oxidation:



$$-\!\left[\overset{Me}{\underset{H}{Si}}-CH_2\right]_n\!- \xrightarrow{O_2/200\,°C} \begin{array}{c} -\!\left[\overset{Me}{Si}-CH_2\right]_n\!- \\ | \\ O \\ | \\ -\!\left[\underset{Me}{Si}-CH_2\right]_n\!- \end{array} \qquad (1)$$

Pyrolytic Degradation. In current generation preceramics, the rates and mechanisms by which extraneous organic ligands are removed as gaseous products, during the pyrolytic transformation of the precursor fiber into the ceramic fiber must be carefully controlled to ensure uniform densification, to prevent retention of impurities, and/or the creation of gas generated flaws (e.g., pores). The processes involved can be likened to binder burnout in ceramic powder compacts.[29,30]

For example, if the pyrolytic degradation of $-[MeHSiCH_2]_x-$ were to proceed optimally then the overall process would be that shown in reaction 2.

$$-[MeHSiCH_2]_x- \xrightarrow{\Delta} xCH_4 + xH_2 + xSiC \qquad (2)$$

Unfortunately, almost half of the excess carbon [e.g., every other Me group] is retained in the final ceramic fiber (see below).

Ceramic Yield and Density Changes. The volume changes associated with pyrolytic conversion to ceramic materials must also be minimized, to maximize control of the (1) final fiber diameter, (2) porosity/voids, and (3) densification induced stresses. Therefore, it is important to formulate preceramics that contain the minimal amounts of extraneous ligands. This permits satisfaction of the above criteria and yet provides high weight percent conversions (ceramic yield) and maximum densification during conversion to ceramic product. Consequently, those preceramic polymers that require extraneous carbon containing ligands for spinnability, stability or because of monomer availability (cost) are likely to contain the minimum necessary—typically as methyl groups.

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Selectivity and Microstructure. The pyrolysis of $-[MeHSiNH]_x-$ leads to SiCN ceramics at temperatures of >600 °C; whereas, pyrolysis of isostructural $-[H_2SiNMe]_x-$ gives Si_3N_4 and free carbon.[31] Similar results are found for AlN precursors.[32] Thus, the architecture of the preceramic monomer unit can control selectivity to ceramic products and to some extent microstructure. Therefore, a major concern in choosing a precursor system for a target ceramic is the facility with which synthesis permits manipulation of the polymer architecture, independent of the chemical composition. This facility will permit chemically similar precursors to be made, if fine tuning is necessary, or grossly different precursors, if the first product is far from the target material. To date, only limited studies on structure/product correlations for SiC precursors have appeared.

Essentially all non-oxide ceramics produced to date are fully amorphous until they have been heated to temperatures exceeding $\approx$1100 °C, or under ammonia. The former treatment, when it does lead to crystallization, typically causes deterioration of mechanical properties and leads to formation of composite (segregated) materials.[20,33,34] The latter treatment provides an excellent route to Si_3N_4, BN, TiN, or AlN. However, it represents an extra processing step and cannot provide carbides.

At present, the only criterion of use in designing precursors that form useful (nano-) microstructures is simply to prepare precursors that are nearly stoichiometrically correct and that can be pyrolytically transformed to stoichiometrically pure, ceramic products. These products can be expected to crystallize. Thus, control of the pyrolysis conditions should provide control of the resulting microstructures. Recent work at Dow Corning (see below) indicates that removal of excess oxygen and carbon from PCS fibers by heating to temperatures where CO and SiO form thermodynamically (>1200 °C), when coupled with the introduction of boron provides a mechanism for obtaining dense, stoichiometrically correct, microcrystalline SiC fibers. Unfortunately, the general utility of this approach has yet to be determined.

The above, general criteria serve as a basis for the selection of candidate organometallic precursors potentially of use for processing both oxide and non-oxide ceramics. For specific materials, additional criteria can also play a role including ease of synthesis, purification, and stability toward air and moisture.

As we will see in the following sections, processability rather than product quality has been the primary motivation (to date) for many of the precursor development studies found in the literature. The first section presents a detailed overview of the synthetic methods that have been explored.

Precursor Chemistry

Five general synthetic routes have been used to develop SiC preceramic polymers. These include (1) dehalocoupling of chlorosilanes to form polysilanes which are then converted to polycarbosilanes (PCS), (2) ring-opening polymerization, (3) polycarbosilane syntheses via hydrosilylation, (4) polysilane syntheses by dehydrocoupling reactions, and (5) displacement and redistribution reactions of chlorosilanes. The dehalocoupling reactions have been studied most extensively.

Dehalocoupling. *Polycarbosilane* (*PCS*). PCS chemistry, as originally developed by Yajima, relies on two well-founded chemical reactions. The alkali metal promoted (Wurtz) dehalocoupling of chlorosilanes, reaction 3, and the Kumada rearrangement as exemplified by reaction 4.[35-37]

$$x(CH_3)_2SiCl_2 + 2xM \xrightarrow{\text{refluxing toluene}} -[(CH_3)_2Si]_x- + 2xMCl \quad (M = Li, Na) \qquad (3)$$

$$(CH_3)_3\,Si{-}Si(CH_3)_3 \xrightarrow{400\ °C} (CH_3)_3SiCH_2Si(CH_3)_2H \qquad (4)$$

Yajima et al.'s earliest papers[7] describe the preparation of PCS $\{-[MeHSiCH_2]_x-\}$ from dodecamethylcyclohexasilane, $-[(CH_3)_2Si]_6-$. This cyclic oligosilane is prepared via reaction 3 (M = Li) and then autoclaved under Ar at $\approx$400 °C to first force ring-opening polymerization and then subsequent rearrangements such as illustrated in reaction 4. Fractionation of the resulting ring-opened products provides a polymer with $M_n \approx 1500$ that was suggested to be primarily $-[MeHSiCH_2]_x-$, based on the IR spectrum.[7b] The ceramic yield was 60%.

The fractionated polymer could be either melt spun[8] or dry spun[7] from benzene solutions to form 10–20-μm-diameter precursor fibers. Pyrolysis of these fibers provided the first SiC fibers prepared from preceramic polymers. Unfortunately, there are several disadvantages to this preparative method. It is technically difficult to work with lithium metal and expensive, and the fractionation process is exceedingly time-consuming. In 1976, Yajima et al. published a new, simple and more economic method of preparing PCS wherein molten sodium (refluxing toluene) is used instead of Li.[9] The resulting polydimethylsilane (PDMS) is obtained in yields over 80%.[10]

Reaction 4, the Kumada rearrangement, is the critical step in the generation of PCS with superior processing properties. Consequently, considerable effort has been invested in optimizing the PDMS/PCS conversion process. In the most common method, PDMS is heated to 320 °C in flowing Ar, melted, refluxed for 5 h, and then heated to 470 °C to remove volatile materials.[9] The resulting PCS (PC-470) is obtained in a 50–55% yield and has a number average molecular weight M_n = 1500 Da.[38]

Polycarbosilane (*PC-B*). Efforts to improve the synthesis have focused on (1) increasing the yield, (2) lowering the reaction temperature, (3) lowering the reaction time, and (4) eliminating the need for an autoclave. Two alternative approaches have been explored. The first involves heating to 470 °C (rather than 320 °C) in an autoclave, which according to Okamura gives a 60% polymer yield.[38] However, the use of an autoclave makes the process technically difficult and increases the cost (but

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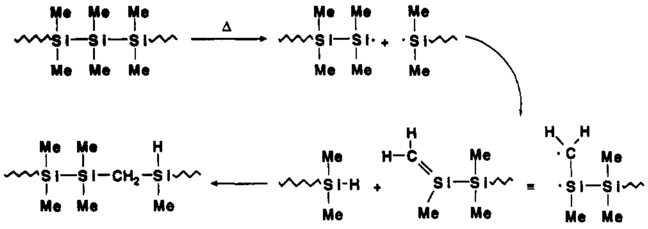
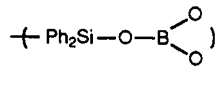
Scheme I. Kumada Rearrangement of Polysilanes to Polycarbosilanes



see Toreki et al. below). Alternately, several groups have explored the use of Lewis acid catalysts such as poly(borodiphenylsiloxane) (PBDPSO), prepared by reaction of boric acid with Ph_2SiCl_2, and normal pressures.[39] The general structure of PBDPSO is



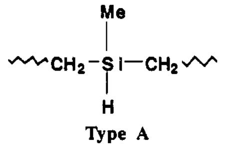
$$-\!\!\left(\, Ph_2Si{-}O{-}B\genfrac{}{}{0pt}{}{O}{O} \right)_n$$

PCS prepared using PBDPSO or related catalysts is called PC-B and 60% yields are typical.[38] Polymer molecular weights are in the range M_n = 1000–2000 Da. No ceramic yields are reported for the PC-Bs, but it is assumed that they are relatively high as both PC-470 and PC-B are produced on an industrial scale.[38]

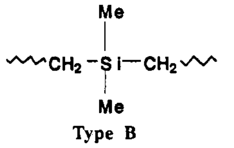
Characterization of PCS-470. The transformation of the PDMS polysilane backbone into a polycarbosilane backbone via the Kumada rearrangement[35–37] is assumed to occur via radical reactions.[10] The primary reaction (see Scheme I) involves pyrolytic cleavage of Si–Si bonds to form silylene and Si–H containing fragments, that subsequently react to give Si–CH_2–Si linkages. Ideally, total conversion should lead to the formation of polysilapropylene or PCS, $-[MeHSiCH_2]_x-$.

The insertion of CH_2 groups into the Si–Si backbone coincident with the formation of Si–H bonds is demonstrated clearly in the IR spectrum of the resulting PC-470 by the appearance of new bands at 1020 and 1355 cm^{-1} (Si–CH_2–Si bending) and at 2100 cm^{-1} (νSi–H) and by UV spectra that indicate the disappearance of the σ–σ^* absorptions of the polysilane backbone.[10] However, the typical chemical analysis for PC-470 ($SiC_{1.77}O_{0.03}H_{3.7}$) is not that expected for $-[MeHSiCH_2]_x-$, SiC_2H_6.[10]

^{29}Si NMR experiments both on PCS in solution ($CDCl_3$)[14] and on PC-470 powders using magic angle spinning (MAS) techniques[40,41] indicate the presence of two different Si units: one corresponding to SiC_3H ($\delta \approx$ −17 ppm), where the Si atom is bonded to 3 C atoms and 1 H atom as in $-[MeHSiCH_2]_x-$, and one to SiC_4 ($\delta \approx 0$ ppm) where the Si atom is surrounded by 4 C atoms. PC-470 is thus a copolymer consisting of two types of monomer units:



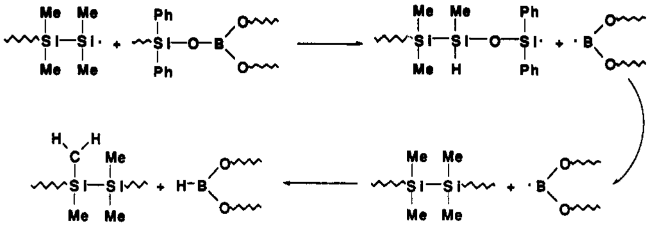
Type A



Type B

The presence of type B units is confirmed by the high ratio of C–H bonds to Si–H bonds (C–H/Si–H ≈ 11) as determined by ^{1}H liquid NMR.[10,41] An early solution ^{29}Si study found that the ratio of units A:B is almost 1:1.[14a] However, a recent MAS NMR study[41] on a commercial PCS (assumed to be PC-470) indicates that the ratio is closer to 1:2. These results suggest that the liquid ^{29}Si signal accounts for only a fraction of all of the Si sites. It is possible that some ^{29}Si centers may exhibit insufficient mobility to be detected by liquid NMR. This in turn suggests the existence of extensive cross-linking between the chains leading to a broad distribution of Si and C sites. The use of more accurate liquid NMR[14b] and MAS NMR (^{29}Si, ^{13}C, and ^{1}H)[41] experiments confirm the first structural model proposed by Yajima;[10] however, these data do not allow any refinement.

Scheme II. Boron-Catalyzed Rearrangement of Polysilanes to Polycarbosilanes



Characterization of PC-B. The preparation of PC-B using two different amounts of PBDPSO (3.2 and 5.5 wt %, PC-B3.2 and PC-B5.5) was examined in some detail.[11c,14] Chemical analyses reveal significant O contamination in the samples (O/Si ≈ 0.19–0.24), but very low B contents (B/Si ≤ 0.005). The main structural difference found between PC-B samples and PC-470 is the presence of Si–Si bonds in the PC–B backbone as determined by far-IR (broad band in the 350–400-cm^{-1} range), UV spectra (absorption around 235 nm), and ^{29}Si liquid NMR experiments (peak at ≈−34.5 ppm attributed to SiC_xSi_{4-x} units). The structure of PC-B can be described as consisting of three units SiC_4, SiC_3H, and SiC_xSi_{4-x}. The composition of the PC-B samples, based on NMR and IR data, was suggested to be: SiC_4 (0.40–0.44), SiC_3H (0.16–0.15) and SiC_xSi_{4-x} (0.53–0.47); however, the presence of Si–O bonds can be inferred from the high O contents.[11c]

The NMR data reported for PC-B samples exhibits very poor resolution because the peaks due to oxidized species such as $-O-Si(CH_3)_2-$ overlap with those attributable to SiC_4 and SiC_3H. The reported analysis of the various structural elements should thus be taken with caution because (1) the presence of siloxane bonds, even if mentioned, was neglected[14b] and (2) the liquid NMR signals are not likely to reflect all the Si sites in the cross-linked polymer for the reasons mentioned above.

The role of PBDPSO in the formation of PC-B, as proposed by Yajima et al.,[11c] is to enhance the formation of silapropylene radicals, produced via the pyrolytic cleavage of the Si–Si bonds. These reactions occur with formation of siloxane bridges and release of gaseous species containing B (Scheme II).

A recent paper discusses the role of PBDPSO[42] in PC-B synthesis and suggests that PBDPSO does not participate in the rearrangement of the silane backbone to a polycarbosilane backbone but rather enhances dehydrogenative coupling of Si–H bonds to form Si–Si cross-links.

Based on the above results, Dunogues et al. examined the effects of variations in the structure of the boron

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(42) Ishikawa, T.; Shibuya, M.; Yamamura, T. *J. Mater. Sci.* **1990**, *25*, 2809–2814.

catalyst on the type of PCS product.[43] They examined compounds such as $B(OR)_3$ where R = Me, Pr, $OSiMe_3$, $B(NEt_2)_3$, and $(Me_3Si)_2BNMe_2$. Thus, 0.5–1 g of catalyst was heated with 30 g of commercial PDMS at 380 or 400 °C for 6–20 h without using an autoclave. The recovered polymers exhibit M_n's ranging from 1800 Da [$B(NEt_2)_3$ run at 400 °C for 12 h] to 4500 Da [$(Me_3Si)_2BNMe_2$ run at 380 °C for 6 h]. The resulting products are reported to exhibit better long-term stability (shelf-life) than commercial PCS and somewhat better ceramic yields.[43]

High Molecular Weight PCS. Both PCS-470 and PC-B are of sufficiently low molecular weight ($M_n \approx 1$–2 kDa) that they melt on heating. Thus, the method of choice for producing precursor fibers is by melt spinning. Unfortunately, this leads to significant problems in curing as discussed below. To avoid such curing problems, Toreki et al. have sought to prepare PCS materials which do not melt but are soluble and can be wet or dry spun.[44,45] They find that thermal decomposition of polydimethylsilane (PDMS) in an autoclave provides access to relatively high molecular weight PCS (by comparison with PC-470) that does not melt but is soluble in organic solvents.

In their system, pyrolysis of PDMS for 1 h at 450 °C (1 atm of N_2) gives PCS with a molecular weight (vs polystyrene) of 1 kDa which melts and gives no ceramic product on heating to 1000 °C in N_2. However, heating for 24 h at 460 °C gives a polymer with a molecular weight of 3.7 kDa which foams but does not melt and gives a ceramic yield of 65%. Heating at 480 °C for 20 h gives a polymer with a molecular weight of 5 kDa which does not melt and gives a ceramic yield of 82%. If the temperature is reduced to 435 °C but the pressure is increased to 7 atm of N_2 and the heating time is 22 h, then the polymer produced has a molecular weight of 9.5 kDa; it foams slightly but does not melt on heating and gives a ceramic yield of 78%.

Although the resulting polymers are all soluble in toluene and chloroform, spectroscopic analyses were not undertaken. It was assumed that the chemical structure of the polymers is very similar to typical Yajima-PCS with some greater degree of branching and higher molecular weights.

Phenylmethylsilane–Dimethylsilane Copolymer (PSS). Poly(dimethylsilane), the precursor to PCS, is an insoluble, infusible, and therefore intractable polymer that remains a key problem in processing PCS. West et al. have developed a series of polysilane copolymers containing phenyl moieties that exhibit greatly enhanced solubility in common organic solvents.[46] The phenylmethylsilane–dimethylsilane copolymer, or "polysilastyrene" (PSS) has been used very successfully as a SiC precursor.[47,48] Like PDMS, the synthesis is also based on sodium-promoted Wurtz coupling of a 1:1 molar ratio of $PhMeSiCl_2$ to Me_2SiCl_2. The molecular weight distribution of the resultant polymer is bimodal, with maxima at $M_w \approx 15$ and ≈ 300 kDa. Following fractionation, the molecular weights (M_n) obtained can be as high as 150 000 Da. The fractionated, random copolymer is soluble in most organic solvents, except hexane and alcohols.

Polymethylsilane (PMS). The Schilling group at Union Carbide was one of the first groups to synthesize a polymethylsilane (PMS) SiC precursor.[49,50] The Schilling PMS precursor was one of three families of SiC precursors developed at Union Carbide, all of which contain Si–H and/or Si–($CH{=}CH_2$) groups to promote cross-linking during pyrolysis, to ensure high ceramic yields. As with the majority of polysilane precursors, they are prepared via dehalocoupling of chlorosilane monomers using either K or Na.[49–52]

The Schilling PMS precursor is prepared by reaction of $MeHSiCl_2$ with K in THF. The product is the polymer, $(MeSiH)_x(MeSi)_{1-x}$, where x varies depending on reaction conditions. The formation of MeSi groups indicates that dehalocoupling is accompanied by consumption of Si–H bonds.[49,50] For $x = 0.40$, the ceramic yield is 60% but the polymer is only partially soluble. For $x = 0.65$–0.85, the polymer is fluid and the ceramic yields are quite low, 15–20%.

Seyferth et al.[53,54] have also used dehalocoupling of $MeHSiCl_2$ with Na as a synthetic route to PMS [$(MeHSi)_x(MeSi)_{1-x}$]. If x is kept in the range of 0.65–0.85, then the products are soluble polymers. However, the corresponding ceramic yields are also quite low; from 15 to 20%, and the ceramic product contains a 25 wt % excess of Si that crystallizes at higher temperature.[53] To increase both the ceramic yield and the C content, these polymers were modified by hydrosilylation with organic or organosilicon compounds[54] such as divinylbenzene, polybutadiene, $[Me(CH_2{=}CH)SiNH]_3$, and $[Me(CH_2{=}CH)SiO]_m$ ($m = 4$–6). Hydrosilylation of $[Me(CH_2{=}CH)SiNH]_3$ with $-[(MeHSi)_x(MeSi)_{1-x}]-$ (where $x = 0.8$–0.9) using chloroplatinic acid (H_2PtCl_6) as catalyst leads to polymers exhibiting ceramic yields of 57–72% depending on the Si–H:$SiCH{=}CH_2$ ratio (8:1 to 1:1).

Seyferth et al. also explored the utility of metal promoted cross-linking as a means of improving the ceramic yields of PMS.[54] Mono- and polynuclear transition metal carbonyls are known to react thermally and photochemically with Si–H and Si–Si bonds to form complexes, intermediates, or transition states that involve species such as M–Si, Si–M–Si, or Si–M–M–Si. Reductive elimination of H_2 or redistribution of Si–Si bonds[55] provides a way to cross-link polymers. Unmodified $-(MeHSi)_x(MeSi)_{1-x}$, where $x = 0.65$, gives a 12% ceramic yield; however, photochemical irradiation of hexane solutions in the presence of catalytic amounts (2 wt %, 4 h) of $Ru_3(CO)_{12}$ provides a 55% ceramic yield. The solubility of the cross-linked polymer is not mentioned. The same treatment, applied to a commercial Nicalon PCS, gives a soluble polymer wherein 34% of the Si–H bonds were consumed as determined by ^1H NMR. TGA gave an 87% ceramic yield vs 55–60% for the uncured PCS on heating to 950 °C at 10 °C/min in Ar.

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(43) Duboudin, F.; Birot, M.; Babot, O.; Dunoguès, J.; Calas, R. *J. Organomet. Chem.* **1988**, *341*, 125–132.

(44) Toreki, W.; Batich, C. D.; Choi, G. J. *Am. Chem. Soc., Polym. Prepr.* **1991**, *32*, 584–585.

(45) (a) Toreki, W.; Batich, C. D.; Sacks, M. D.; Morrone, A. A. *Ceram. Eng. Sci. Proc.*, in press. (b) Morrone, A. A.; Toreki, W.; Batich, C. D. *Mater. Lett.* **1991**, *11*, 19–25. (c) Toreki, W., private communication, 1992.

(46) West, R. *J. Organomet. Chem.* **1986**, *33*, 327–346.

(47) West, R.; David, L. D.; Djurovich, P. I.; Yu, H.; Sinclair, R. *Ceram. Bull.* **1983**, *62*, 899–903.

(48) West, R. In *Ultrastructure Processing of Ceramics, Glasses and Composites*; Hench, L. L., Ulrich, D. R., Eds.; Wiley: New York, 1984; pp 235–244.

(49) Schilling, C. L.; Williams, T. C. *Am. Chem. Soc., Polym. Prepr.* **1984**, *25*, 1.

(50) Schilling Jr., C. L. *Brit. Polym. J.* **1986**, *18*, 355–358.

(51) Schilling Jr., C. L.; Wesson, J. P.; Williams, T. C. *Am. Ceram. Soc. Bull.* **1983**, *62*, 912–915.

(52) Schilling Jr., C. L. U.S. Patent 4,472,591, 1988.

(53) Seyferth, D.; Yu, Y.-F.; U.S. Patent 4,639,501, 1987.

(54) Seyferth, D.; Sobon, C. A.; Borm, J. *New J. Chem.* **1989**, *14*, 545–547.

(55) Laine, R. M. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Kluwer Academic: Dordrecht, Netherlands, 1990; Vol 7, pp 37–63.

The major problem for both of these precursor systems is chemical composition. PMS typically gives excess Si on high temperature pyrolysis, whereas Nicalon PCS gives excess C. When an appropriate mixture of the two polymers is irradiated in the presence of $Ru_3(CO)_{12}$, a moderately soluble solid results. The ceramic yield is 68%, but more important, the reported chemical composition corresponds to 99% SiC and only 1% C. No detailed analyses were performed on the pyrolyzed samples to confirm the formation of pure SiC.

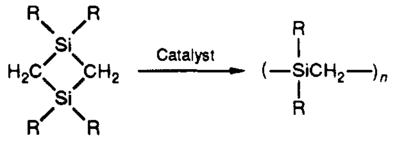
Polymethylsilanes can also be prepared via catalytic dehydrocoupling as described below.

Vinylic Poly(methylsilanes) (VPS). The second family of polymers developed at Union Carbide are vinylic polymethylsilanes (VPS) prepared by dehalocoupling of Me_xSiCl_{4-x} and $Me(CH_2{=}CH)SiCl_2$.[49-52] If Na in THF is used, the vinyl groups are preserved in the resulting polymer and provide cross-linking functionality for further polymer processing. The composition Me_3SiCl:Me_2SiCl_2:$Me(CH_2{=}CH)SiCl_2$ 0.85:0.3:1 provides ceramic yields of 50%. If $MeHSiCl_2$ is used instead of Me_2SiCl_2, the ceramic yield increases to 57.2% due to additional Si–H groups.[50] The use of K instead of Na causes MeHSi groups to disilylate the vinylic groups to produce tetrafunctionalized Si units; thereby destroying the opportunity to cross-link. Dehalocoupling of pure $Me(CH_2{=}CH)SiCl_2$ with molten sodium leads to insoluble polymers.

Copolymers and terpolymers were prepared with methylchlorosilanes, Me_xSiCl_{4-x} ($x = 1, 2, 3$), and $Me(CH_2{=}CH)SiCl_2$. The solubility of the resulting polymers varied from 20 to 60% depending on the initial compositions, but the reactions were not optimized.[51] The degree of solubility was found to be a function of the extent of cross-linking. The higher the content of Si–Cl bonds per silicon, the lower the solubility. These potassium derived vinylic polymers do not exhibit any UV absorptions commonly found in polysilanes with up to 20 consecutive Si–Si bonds. Si–Si bonds, although present, are likely to be isolated in a polycarbosilane backbone. The carbon portion of the backbone likely comes from incorporation of vinyl groups. The ceramic yields for the various compositions range from 17 to 44%. X-ray diffraction patterns of the pyrolytic products are similar to those obtained for Yajima's PCS.[51]

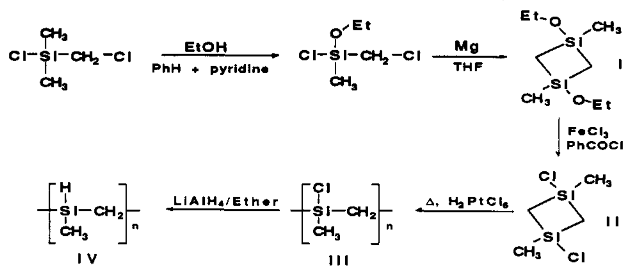
Methylchlorosilane/ene Copolymers. The third family of precursors developed at Union Carbide are the polysilahydrocarbons prepared by coupling monomeric chlorosilanes to alkenes such as styrene ($PhCH{=}CH_2$) or isoprene [$CH_2{=}C(Me)CH{=}CH_2$] using a K/THF mixture.[49,50] If a difunctional monomer such as Me_2SiCl_2 is used, the resulting polymers are linear with very low ceramic yields, <5%. If trifunctional monomers are introduced, the ceramic yields are much higher. When $MeSiCl_3$ is used in place of Me_2SiCl_2, the ceramic yields increase to 25–30%, and with $MeHSiCl_2$, copolymers with isoprene exhibit ceramic yields of almost 50%.

Ring-Opening Polymerization. Ring-opening polymerization of various derivatives of 1,3-disilacyclobutane can be used for the preparation of several types of polycarbosilanes:[55]



Poly(silaethylene). A recent patent by Smith describes the formation of a linear poly(silaethylene) (R = H) by ring-opening polymerization of 1,3-disilacyclobutane using H_2PtCl_6 catalyst.[56] This polymer is reported to give 85% ceramic yields of pure SiC at temperatures as low as 900 °C, but only IR data are used as support for formation of crystalline SiC. As noted by Interrante et al.,[57] "since the Si–H bond is also activated by the transition-metal catalyst used, it seems doubtful that a linear polymer has been formed". The patent claims that the ring-opened polymer can be shaped and molded into various forms, and it can be spun and drawn into fibers. No more details are given concerning this preparation.

Scheme III. Synthesis of Poly(methylhydridocarbosilane)



The analogous permethyl derivative, 1,1,3,3-tetramethyl-1,3-disilacyclobutane (R = Me) can be readily polymerized to high molecular weight poly[(dimethylsilylene)methylene], M_n = 260 kDa.[57] This polymer is stable up to 450 °C, but as with most linear polycarbosilanes without latent functionality (Si–H or Si–$CH_2{=}CH$ bonds), it then decomposes rapidly to give a negligible ceramic yield.

Poly(silapropylene). Interrante et al. have also studied H_2PtCl_6-catalyzed ring-opening polymerization of disilacyclobutanes as a route to SiC precursors. 1,3-Dichloro-1,3-dimethyl-1,3-disilacyclobutane was chosen as the starting monomer because the Si–Cl bonds permit the introduction of various substituents.[57] Poly[(methylchlorosilylene)methylene], $-[MeClSiCH_2]_x-$ was prepared (see Scheme III) by polymerization under mild conditions and then reduced with $LiAlH_4$ to poly(silapropylene), $-[MeHSiCH_2]_x-$.[57] As shown in Scheme III, 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane (I), prepared by a Grignard reaction from (chloromethyl)methylethoxychlorosilane, reacts with $FeCl_3$/PhCOCl to give 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane (II). Ring-opening polymerization is run with 0.4 wt % chloroplatinic acid at 80 °C for 16 h. Reduction of the resulting poly[(methylchlorosilylene)methylene] (III) with $LiAlH_4$ provides an extremely viscous poly(silapropylene) (IV). NMR (^1H, ^{13}C, and ^{29}Si) experiments indicate that the polymer is linear and atactic. The molecular weights of poly(silapropylene) decrease with increasing amounts of catalyst. Two polymers were prepared with respective M_n = 6 and 35 kDa and corresponding M_w of 40 and 290 kDa.

The ceramic yields for these two precursors are quite low, 10 and 20%, respectively. A preliminary heat treatment of the polymer under nitrogen (400 °C) favors Si–H bond cross-linking reactions, leading to a 66% ceramic yield for the latter polymer. Broad XRD peaks due to β-SiC are reported for a sample heated to 1600 °C for 4 h. Note that the 35 000 Da polymer is completely linear and yet gives a high ceramic yield. This is atypical of preceramics polymers and is only possible because of the low-temperature cross-linking reaction.

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(56) Smith, T. L. U.S. Patent 4,631,179, Dec 1986.

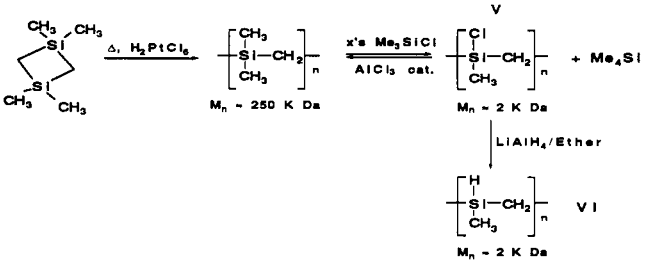
(57) (a) Wu, H.-J.; Interrante, L. V. *Chem. Mater.* **1989**, *1*, 564–568. (b) Wu, H.-J.; Interrante, L. V.; *Macromolecules* **1992**, *25*, 1840–1841.

Table I. Properties of Selected Derivatives of Poly(chloromethylsilaethylene)

starting polym	reaction	resultant product[a]		M_n (Da)	ceramic yield (%)
V	$2{\equiv}\text{Si—Cl} + 2\text{Na} \xrightarrow{-2\text{NaCl}}$	$\equiv$Si—Si$\equiv$	VIIs[a]	4250	11.4 VIIi[a] 77.6
V	$2{\equiv}\text{Si—Cl} + 2\text{K} \xrightarrow{-2\text{KCl}}$	$\equiv$Si—Si$\equiv$	VIIIs	4930	43.5 VIIIi 59.3
V	$\equiv\text{Si—Cl} + 2\text{Me}_2\text{NH} \xrightarrow{-\text{Me}_2\text{NH}_2\text{Cl}}$	$\equiv$Si—NMe$_2$	IX	2480	33.5
V	$\equiv\text{Si—Cl} + 2\text{MeNH}_2 \xrightarrow{-\text{MeNH}_3\text{Cl}}$	$\equiv$Si—NHMe	Xsa	3580	24.7
			Xsb[b]	3940	53.0
V	$2{\equiv}\text{Si—Cl} + 3\ \text{NH}_3 \xrightarrow{-2\text{NH}_4\text{Cl}}$	$\equiv$Si—NH—Si$\equiv$	XIs	4120	37.5
V	$2{\equiv}\text{Si—Cl} + \text{H}_2\text{O} \xrightarrow{-2\text{HCl}}$	$\equiv$Si—O—Si$\equiv$	XII	2960	54.3
VI	$2{\equiv}\text{Si—H} + \text{1,3-butadiene} \xrightarrow{\text{catal}}$	$\equiv$Si—[CH$_2$]$_4$—Si$\equiv$	XIII		14.0
VI	$2{\equiv}\text{Si—H} + \text{divinylbenzene} \xrightarrow{\text{catal}}$	[$\equiv$Si(CH$_2$)$_2$]$_2$C$_6$H$_4$	XIV		24.7

[a] s and i for soluble and insoluble fractions. [b] Experiment run without solvent.

Scheme IV. Transformation of Poly(dimethylsilaethylene) into PCS



By comparison, chloroplatinic acid-catalyzed ring-opening polymerization of the 1,1,3,3-tetrachloro-1,3-disilacyclobutane followed by treatment with LiAlH$_4$ gives pure, *unbranched*, poly(silaethylene) with $M_n \approx 12.3$ kDa and $M_w \approx 33$ kDa. This polymer gives very high (87% vs 91% calc) ceramic yields (1000 °C) of what appears to be very pure SiC (although no analysis is given). The purity is suggested by the fact that the β-SiC crystallites form at 1000 °C.

Poly(dimethylsilaethylene), $-[\text{Me}_2\text{SiCH}_2]_x-$. Dunogues et al. have used ring-opening polymerization of 1,1,3,3-tetramethylsilacyclobutane to get high molecular weight poly(dimethylsilaethylene) as a starting point to synthesize PCS model compounds and for use as a SiC precursor (see Scheme IV):[58] Chlorination of this polymer with Me$_3$SiCl and catalytic amounts of AlCl$_3$ leads to the rearrangements shown in Scheme IV.

The new polymer, V, is soluble in polar solvents but exhibits a large decrease in molecular weight due to AlCl$_3$ promoted formation of dimethylchlorosilyl end groups. Polysilapropylene, VI ($M_n \approx$ 2–2.2 kDa) was synthesized for the first time, by reduction of V with LiAlH$_4$.[59] NMR studies clearly demonstrate the linear nature of both polymers with ^{29}Si and ^{13}C NMR spectra exhibiting peaks due solely to the repeat and terminal groups. These results are quite consistent with the work reported by Interrante et al., as noted above.

As expected, polymers V and VI gave ceramic yields of 5% on heating to 1000 °C in Ar. However, derivitization of the Si–Cl or Si–H bonds in V and VI provides access to polymers with higher molecular weights and degrees of cross-linking.[60] The various preparations and their properties are summarized in Table I.

The ceramic yields are quite low for the soluble derivatives, most likely because of depolymerization reactions that lead to the formation of volatile cyclic species rather than branches and crosslinks. Cyclic volatiles are also produced when long chain hydrocarbons are introduced, which explains the poor ceramic yields for XIII and XIV. The higher ceramic yield for XII suggests that intermolecular condensation occurs in this case.

All the samples pyrolyzed at 1200 °C were reported to contain significant quantities of O (14–24 atom %).[61] Structural investigations were performed on selected samples using ESCA, XRD, and Raman. Features similar to those of Yajima pyrolyzed PCS are observed. These include (1) the presence of a silicon oxycarbide phase and graphitic C for the precursors VIIs, IX, X, and XI. At 1400 °C, the sample from polymer VIIs exhibits XRD patterns indicative of crystalline β-SiC with a 3-nm mean crystallite size. The samples from the nitrogen-based polymers are still amorphous at this temperature, suggesting that nitrogen inhibits crystallization.

Poly(dimethylsilaethylene), as prepared by ring-opening polymerization, is known to give inferior ceramic yields due primarily to its linear structure and lack of reactive groups. Seyferth et al.[62] describe the modification of poly(dimethylsilaethylene) by incorporating Si–H or Si–CH=CH$_2$ groups into the polymer. Efforts were then made to deprotonate the methylene bridges using strong bases. This reaction is known to be activated by the presence of adjacent methylsilyl groups. Metalation of a poly(dimethylsilene) ($M_n \approx 2020$ Da) at −78 °C was effected using a mixture of *n*-butyllithium and potassium *tert*-butoxide in THF. Chlorosilane was then added to introduce either Si–H groups (Me$_2$HSiCl) or Si–CH=CH$_2$ groups (Me$_2$SiClCH=CH$_2$). Metalation occurs approximately every fourth (Me)$_2$SiCH$_2$ residue. Unfortunately, the vinyl modified poly(dimethylsilaethylene) still gives

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(58) Bacqué, E.; Pillot, J. P.; Birot, M.; Dunoguès, J. *Macromolecules* **1988**, *21*, 30–34.

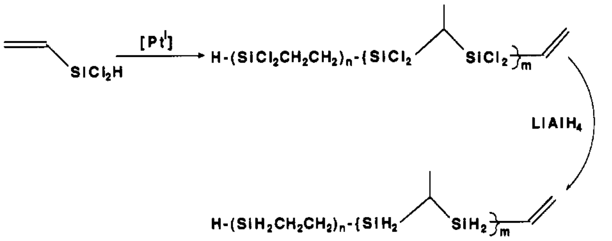
(59) Bacqué, E.; Pillot, J. P.; Birot, M.; Dunogès, J. *Macromolecules* **1988**, *21*, 34–38.

(60) Bacqué, E.; Pillot, J. P.; Birot, M.; Dunoguès, J.; Lapouyade, P.; Bouillon, E.; Pailler, R. *Chem. Mater.* **1991**, *3*, 348–355.

(61) Bouillon, E.; Pailler, R.; Naslain, R.; Bacqué, E.; Pillot, J. P.; Birot, M.; Dunoguès, J.; Huong, P. V. *Chem. Mater.* **1991**, *3*, 356–367.

(62) Seyferth, D.; Lang, H. *Organometallics* **1991**, *10*, 551–558.

Scheme V. Hydrosilylation in the Synthesis of Vinyl Endcapped Precursors



a very low ceramic yield, 2%, with a first weight loss between 80 and 240 °C, that is likely due to the cleavage of the organosilyl side groups. Attempts were also made to cross-link the Si–H groups of a Me_2HSi-modified poly(dimethylsilaethylene) with a similar polymer modified with $Si{-}CH{=}CH_2$ groups via hydrosilylation without significant success. It was concluded that hydrosilylative cross-linking was inefficient because of steric factors.

Several related modifications of poly(dimethylsilaethylene) using hydrosilylation as a key step were also tried. Hydrosilylation of Me_2HSi-modified poly(dimethylsilaethylene) with $[Me(CH_2{=}CH)SiNH]_3$, as per the PMS modification above, followed by radical-catalyzed [azobis(isobutyronitrile), AIBN] cross-linking provides a precursor polymer that gives ceramic yields of only 24%. Hydrosilylation of $Me_2(CH_2{=}CH)Si$-modified poly(dimethylsilaethylene) with $-[(MeSiH)_x(MeSi)_{1-x}]-$ ($x = 0.65$–0.85) followed by treatment with AIBN gives a copolymer with a 68% ceramic yield. The composition of the resulting ceramic was found to correspond to *an apparent ceramic composition* of 91 wt % SiC and only 9 wt % excess C. Variations in the molar ratio between the two polymers gave an even higher SiC content, 94 wt %. No detailed characterization of the polymers or their pyrolysis products has been published.

Hydrosilylation. Corriu et al. have explored hydrosilylation as a means of preparing polycarbosilanes without first starting with the synthesis of polysilanes. The starting monomer is vinyldichlorosilane, $SiH(CH_2{=}CH)Cl_2$, prepared by redistribution reactions.[63–65] Hydrosilylation reactions are conducted either with platinum on charcoal (Pt/C) or with chlorplatinic acid as a catalyst; see Scheme V.[64,65] The resulting chlorosilane polymer is reduced by $LiAlH_4$ to give poly(vinyl)silane with SiH_3 and $SiH_2(CH{=}CH_2)$ endcaps. The addition of $HSiCl_3$ or $(CH_2{=}CH)_2SiCl_2$ to the starting vinyldichlorosilane leads to polymers having the same endcap. Pendant vinyl groups have also been introduced, according to the reactions given in Scheme VI.

The molecular weights of these poly(vinyl)silanes are highly dependent on the nature of the solvent, and M_n can vary from 960 Da in hexane (64% yield) up to 5500 Da in chlorobenzene (78% yield). NMR characterization showed that hydrosilylation occurs mainly at the β-carbon leading to linear $-SiH_2{-}CH_2CH_2-$ units rather than at the α-carbon, which would give branched, $-SiH_2{-}CHMe-$ units.

Scheme VI. A Second Type of Precursor Prepared by Hydrosilylation

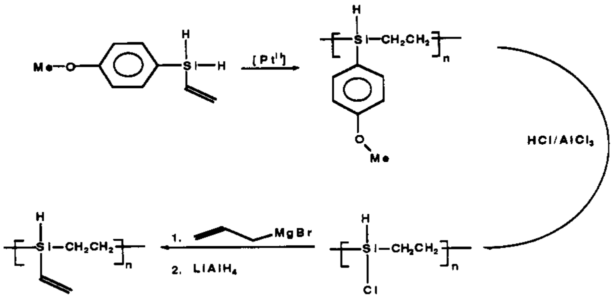


Table II. Properties of Selected Derivatives of Poly(vinylsilane)

polymer	SiH/Si–($CH{=}CH_2$)	DP_n	ceramic yield (%)
XV $H_3Si{-}(C_2H_4SiH_2)_n{-}(CH{=}CH_2)$	21	10	30
XVI $H_3Si{-}(C_2H_4SiH_2)_n{-}H$	∞	12	12
XVII $(CH_2{=}Ch){-}Si{-}(C_2H_4SiH_2)_n{-}(CH{=}CH_2)$	10	10	56
XVIII $-(-(CH_2{=}CH)Si(H)C_2H_4)_n-$	1	13	60
XIX 2.5 (XVI) + 1.0 (XVIII)	4.5		62

Pyrolysis of the various polymers was conducted under nitrogen up to 1400 °C. The ceramic yields do not vary much with the molecular weight of the starting polymer as shown in Table II.[65] However, the ceramic yields are considerably improved by the presence of terminal vinyl groups that allow hydrosilylation reactions to occur during the first stage of pyrolysis. This novel hydrosilylative curing step was identified by the observation of an exotherm at 200 °C in the DSC curves, and a strong decrease of the IR bands corresponding to $\nu Si{-}H$ or $\nu CH_2{=}CH-$, for all of the polymers except XVI, which has no vinyl groups.

Unfortunately, the introduction of a large number of vinyl groups dramatically increases the carbon content as shown by the chemical analyses of polymers XV, XVIII, and XIX following pyrolysis to 1400 °C, which give respectively $SiC_{1.19}O_{0.02}$, $SiC_{3.21}O_{0.06}$, and $SiC_{1.41}O_{0.14}$.

Hydrosilylation of PCS. Baney et al. have developed a method of rendering PCS infusible prior to pyrolysis based on hydrosilylation.[66] PCS, which typically contains 0.1–5.0 wt % Si–H bonds, is mixed with a hydrosilylation catalyst and an unsaturated compound such as a polyolefin, vinylsilane, or vinylsiloxane. Commercial PCS from Nippon Carbon Co. was mixed in toluene with either polyisoprene or *cis*-polybutadiene (4 wt %), and a catalyst such as tris(triphenylphosphine)rhodium(I) chloride, bis(diethylsulfide)platinum(II) chloride, or chloroplatinic acid, H_2PtCl_6 (0.06–0.14%). Fibers of various compositions, as well as ones from pure PCS solution, were drawn from the toluene solution and cured in Ar at 388 °C for 12 h. The pure PCS fibers melt during the heat treatment. The modified PCS fibers are rendered infusible and converted into ceramics after pyrolysis to 1200 °C. The ceramic yields ranged from 67 to 73%, and the oxygen content is as low as 2–3 wt %. The problem with these preparations is the significant amount of C introduced into already C rich PCS. No further characterization of these materials has been forthcoming.

Dehydrocoupling of Silanes. The serious drawbacks to dehalocoupling are (1) the reaction is biphasic (metal and chlorosilane), (2) highly reactive alkali metals are used, (3) there are purification problems associated with removing salt byproducts from the product polymers, and (4) the product polymers often need to be endcapped. The dehydrocoupling process shown in reaction 5 provides a

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(63) Boury, B.; Carpenter, L.; Corriu, R. J. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 785–787.

(64) Boury, B.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Planeix, J. M.; Vioux, A. *Organometallics* **1991**, *10*, 1457–1461.

(65) Boury, B.; Corriu, R. J. P.; Douglas, W. E. *Chem. Mater.* **1991**, *3*, 487–489.

(66) Baney, R. H.; Burns, G. T. European Patent, 0,251,67S, 1987.

means of avoiding these problems, although, it has its own drawbacks.

$$x\mathrm{RSiH_3} \xrightarrow{\text{catalyst}} x\mathrm{H_2} + -[\mathrm{RSiH}]_x- \qquad (5)$$

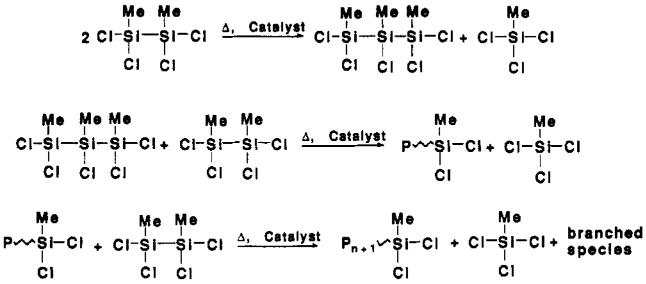
Polymethylsilane (PMS). Numerous catalysts have been found effective for promoting oligomerization and polymerization as illustrated by reaction 5. Two recent reviews cover much of what has been published on the subject.[55,67] To date, the best catalysts found for reaction 5 are the dicyclopentadienyl dimethyl metallocenes: $\mathrm{Cp_2MMe_2}$ where, M = Ti, Zr, and Hf or simple derivatives of these complexes. Methylsilane ($\mathrm{MeSiH_3}$) provides access to one of the better SiC precursor polymers: polymethylsilane ($-[\mathrm{MeSiH}]_x-$), although there is a brief note on the use of ethyl- and vinylsilane as the initial monomer.[68-72]

A typical reaction is run at 60 °C, under approximately 10 atm of $\mathrm{MeSiH_3}$, in toluene–cyclohexene solution with 0.2 mol % catalyst (based on total moles $\mathrm{MeSiH_3}$ used). The byproduct hydrogen is consumed coincidentally by "Ti"-catalyzed hydrogenation of cyclohexene to cyclohexane. This minimizes pressure buildup. The reaction is normally run for 6–9 days and results in an 80–90% yield of toluene- and cyclohexane-soluble polymer. The longer the reaction time, the higher the molecular weight of the product and the higher the viscosity. Molecular weights of M_n = 1.2 kDa (DP = 25–30) can be obtained although HPLC molecular weight profiles indicate fractions with molecular weights up to 10 kDa (versus a polystyrene standard). Upon removal of solvent, the catalyst remains active and can cause gelation; however, a slight over pressure of $\mathrm{H_2}$ prevents further cross-linking. The resulting polymer has sufficient rheology to permit processing and gives relatively good ceramic yields (70–75%, 900 °C) of relatively pure SiC (typical chemical analysis = $\mathrm{Si_1C_{0.9}H_{0.2}O_{0.1}}$).[71]

The drawbacks to this process are that $\mathrm{MeSiH_3}$ is difficult to work with because of its flammability and the resulting polymer (with catalyst) is also flammable. Thus, standard precautions are necessary to handle the system until conversion to ceramic product is complete. However, as noted above, oxygen is detrimental to the behavior of all SiC fibers; therefore, maintaining an oxygen free environment during processing is prerequisite to obtaining superior SiC fibers (one exception is boron treated PCS, see below).

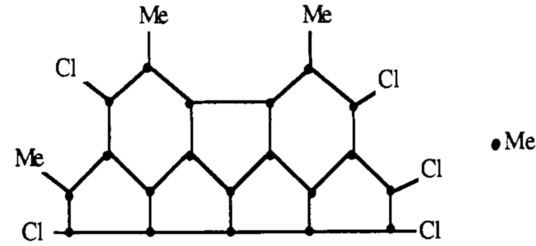
Redistribution and Substitution Reactions. *MPS Polymers.* Another class of polysilanes, developed at Dow Corning, is prepared by the catalytic redistribution of Si–Si and Si–Cl bonds of disilanes as illustrated in Scheme VII.[73]

Scheme VII. Redistribution Reactions as a Route to Spinnable Polymers



This new synthetic route avoids the dehalogenative coupling reaction commonly used to produce polysilanes. Another advantage of this preparation is that it uses a mixture of disilane byproducts from the "direct process" for the synthesis of methylchlorosilanes. The approximate composition of this mixture is 55% $\mathrm{(MeCl_2Si)_2}$, 35% $\mathrm{Me_2ClSiSiMeCl_2}$, and 10% $\mathrm{[Me_2ClSi]_2}$. Catalysts used are usually quaternary phosphonium and ammonium halides.

The disilane mixture undergoes catalytic redistribution when heated (with 1 wt % $t\text{-}\mathrm{Bu_4PCl}$) slowly from 90 to 250 °C over several hours. This provides a 20% conversion to methylchloropolysilane. Monosilanes are distilled off as well as $\mathrm{[(CH_3)_2ClSi]_2}$, which does not seem to react. The resulting yellow pyrophoric polymer is toluene soluble material. Chemical analysis, assuming no Si–Me bond redistribution, suggests a polymer composition of $\mathrm{(MeSi{\equiv})_{5.7}(Me_2Si{=})_1(Cl)_{1.9}}$. This corresponds to a highly branched polysilane with an average of 2.65 Si–Si bonds per Si. The following structure has been proposed based on five and six member rings:



The presence of Si–Cl bonds permits various chemical modifications to this precursor,[74-79] to improve polymer processability. Reactions with Grignard reagents such as $\mathrm{CH_3MgCl}$ or $\mathrm{C_6H_5MgBr}$ give alkylated or arylated polymers.[75] Alkoxylated polymers are obtained by reaction with various alcohols (e.g., MeOH, EtOH, phenol, ...).[76] Si–H bonds can be introduced by reduction of the Si–Cl bonds with $\mathrm{LiAlH_4}$.[77] Aminosilanes can be formed from reaction of the polymer with amines.[78] Reaction with hexamethyldisiloxane introduces trimethylsiloxy groups, $\mathrm{-OSi(CH_3)_3}$, bonded to the polysilane backbone.[79]

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(67) Corey, J. Y. In *Advances in Silicon Chemistry*; JAI Press: London, 1991; Vol. 1, pp 327–387.

(68) Mu, Y.; Harrod, J. F. In *Inorganic and Organometallic Oligomers and Polymers*; IUPAC 33rd Symposium on Macromolecules; Harrod, J. F., Laine, R. M., Eds.; Kluwer: Dordrecht, Netherlands, 1991; pp 23–36.

(69) Zhang, Z.-F.; Mu, Y.; Laine, R. M.; Babonneau, F.; Harrod, J. F.; Rahn, J. A. In *Inorganic and Organometallic Oligomers and Polymers*; IUPAC 33rd Symposium on Macromolecules; Harrod, J. F., Laine, R. M., Eds.; Kluwer: Dordrecht, Netherlands, 1991; pp 127–146.

(70) Harrod, J. F. In *Inorganic and Organometallic Polymers with Special Properties*; NATO ASI Ser. E: Appl. Sci. Vol. 206; Laine, R. M., Ed.; Kluwer: Dordrecht, Netherlands, 1991; pp 87–98.

(71) Zhang, Z.-F.; Babonneau, F.; Laine, R. M.; Mu, Y.; Harrod, J. F.; Rahn., J. A. *J. Am. Ceram. Soc.* **1991**, *74*, 670–73.

(72) Masnovi, J.; Bu, X.-Y.; Conroy, P.; Andrist, A. H.; Hurwitz, F. I.; Miller, D. In *Better Ceramics Through Chemistry IV*; *Mater. Res. Sym. Proc.*; Zelinski, B. J., Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh 1990; Vol. 180, pp 779–783.

(73) Baney, R. H.; Gaul, J. H.; Hilty, T. K. *Organometallics* **1983**, *2*, 859–863.

(74) Baney, R. H.; Gaul Jr., J. H.; Hilty, T. K. In *Emergent Process Methods for High Technology Ceramics*; Davis, R. F., Palmour III, H., Porter, R. L., Eds.; Plenum Press: Materials Science Research, 1982; Vol. 17, pp 253–262.

(75) Baney, R. H.; Gaul, J. H. U.S. Patent 4,298,559, Nov 1981.

(76) Baney, R. H.; Gaul, J. H. U.S. Patent 4,298,558, Nov 1981; Re. 31,447, issued Nov. 1983.

(77) Baney, R. H.; Gaul, J. H. U.S. Patent 4,310,482, Jan 1982.

(78) Baney, R. H.; Gaul, J. H. U.S. Patent 4,314,956, Feb 1982.

(79) Baney, R. H.; Gaul, J. H. U.S. Patent 4,310,481, Jan 1982.

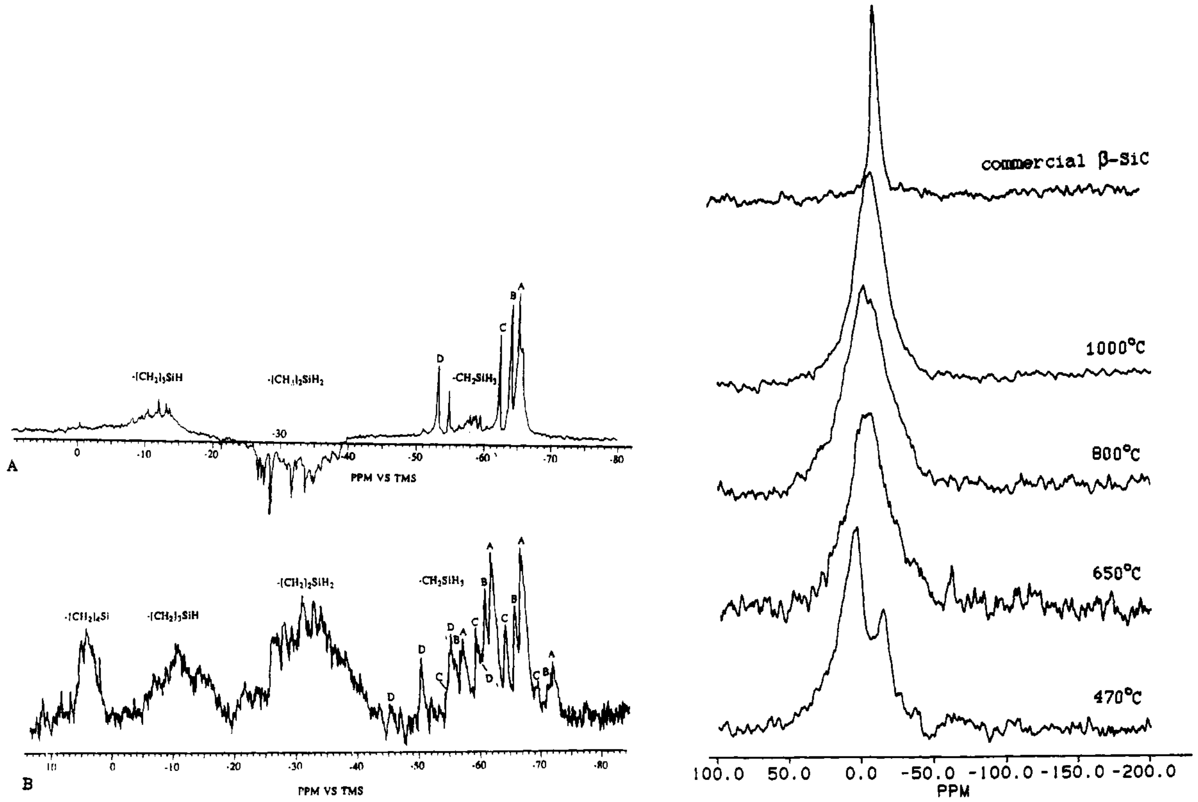


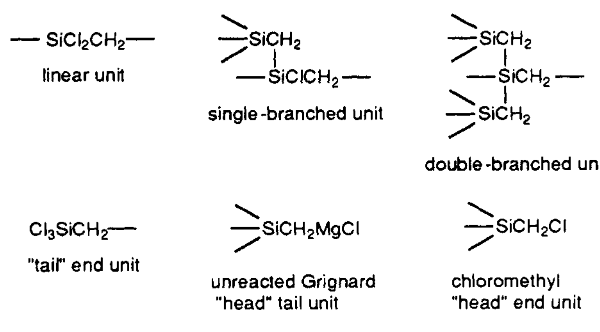
Figure 1. ^{29}Si NMR study of the chemical evolution of highly branched PCS on pyrolytic transformation to SiC. Left: solution DEPT NMR (multiplicity of 1.5) with proton decoupling (A) and proton coupling (B), letters indicate sets of quartets ($^1H_{Si-H} \approx 200$ Hz) from SiH_3 endgroups. Right: solid-state MAS ^{29}Si NMR of polymer heated at 10 °C/min to 1000 °C in N_2.

Vinyl groups have also been introduced by reaction of the mixture of methylchlorodisilanes with phenylvinyldichlorosilane using t-Bu_4PCl as catalyst.[80] The composition of one particular polymer, in terms of Si units, was found to be approximately: 7% $[(C_6H_5)(CH_2{=}CH)Si]$, 16% $[Me_2Si]$, and 78% $[MeSi]$. The polymer also contained 26 wt % Cl. These were reacted with CH_3MgCl to convert the polymer to a CH_3-endblocked polysilane. The ceramic yield for this type of polymers is ≈45–50%.

Highly Branched PCS. Interrante et al. have explored an alternate route to a highly branched hydridopolycarbosilane by Grignard coupling of chloromethyl trichlorosilane, followed by reduction with $LiAlH_4$:[81]

$$Cl_3SiCH_2Cl \xrightarrow{Mg/Et_2O/reflux\ 5D} -[Cl_2SiCH_2]_x- \xrightarrow{LiAlH_4/H_2O/HCl} -[H_2SiCH_2]_x- \quad (6)$$

Theoretical average formulas for the resulting polymers should be $-[SiCl_2CH_2]_x-$ and $-[SiH_2CH_2]_x-$, but the actual structures are much more complex. IR and multinuclear NMR indicate the presence of the following units in the chloropolycarbosilane, resulting almost exclusively from head-to-tail (Si–C) coupling:



The extensive branching of the polymer at silicon is due to the trifunctionality of the original Cl_3Si groups. The average formula for the polymer is $-[SiH_{1.85}Et_{0.15}CH_2]_x-$. The ethyl groups derive from cleavage of the diethyl ether solvent with concomitant formation of EtCl which is incorporated via a Grignard reaction. A typical M_w found for the polymer is 745 Da. The polymer is *reasonably air stable*; although, it gradually cross-links with loss of H_2 over a period of months. If the polymer is heated at rates of 10 °C/min to 1000 °C, then the ceramic yields vary from 58 to 76%. Apparently, volatilization of low molecular weight species competes successfully with cross-linking. If holds are instituted at 80 °C and again at 200 °C, then ceramic yields of ≈80% are obtained. This is close to the theoretical yield of 83% expected if the polymer stoichiometry indicated above converts completely to SiC.

At 1000 °C, XRD spectra indicate the formation of poorly crystalline β-SiC. Solid-state ^{13}C NMR studies reveal a peak centered at ≈18 ppm typical of silicon carbide and a very broad peak just above the noise level in the 100–200 ppm region that *may* indicate the presence of graphitic or amorphous carbon. The presence of carbon cannot be confirmed by TGA studies run in air where there is only a slight weight gain on heating to 1000 °C. The ^{29}Si NMR (Figure 1) confirms the presence of SiC giving a single peak at approximately 20 ppm.

Polysilylacetylenes. Barton et al. and several other groups have prepared a family of SiC precursors based on silylacetylene or disilylacetylene polymers.[82] Dilithio-

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(80) Haluska, L. A. U.S. Patent 4,546,163, 1985.

(81) Whitmarsh, C. K.; Interrante, L. V. *Organometallics* **1991**, *10*, 1336–1344.

(82) (a) Ijadi-Maghsoodi, S.; Pang, Y.; Barton, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 955–965. (b) Corriu, R. J. P.; Gerbier, Ph.; Guérin, C.; Henner, B.; Jean, A.; Kuhlmann, Th.; Garnier, F.; Yassar, A. *Organometallics*, in press.

acetylene, LiC≡CLi, prepared from $CHCl_2CH_2Cl$ and *n*-BuLi in THF (−78 °C), can be reacted with a variety of dichlorosilanes ($RR'SiCl_2$, R, R′ = Me or Ph) or 1,2-dichlorodisilanes ($ClMe_2Si-SiMe_2Cl$) to give high yields (>90%) of processable polymers. Following removal of oligomers and cyclics, polymers with molecular weights (M_w) of 20–70 kDa are recovered. The softening points are between 120–175 °C for the silylene–acetylene polymers and 70–100 °C for the disilylene–acetylene polymers.

The ceramic yields for the two types of polymers are on average 80% and 60% respectively. The main weight loss occurs in the 400–800 °C range, with loss of methane for methyl derivatives and/or benzene for phenyl derivatives. Above 800 °C, XRD patterns reveal the standard diffraction peaks for β-SiC. However, as expected, the final ceramic products contain free C as shown by ESCA. The polymer that provides the highest SiC content (by chemical analysis) is the dimethylsilylene–acetylene, $-[Me_2Si-C{\equiv}C]_x-$, polymer. The lowest SiC contents are obtained with the diphenylsilylene–acetylene, $-[Ph_2Si-C{\equiv}C]_x-$, and the tetramethyldisilylene–acetylene, $-[Me_2SiMe_2Si-C{\equiv}C]_x-$, polymers.

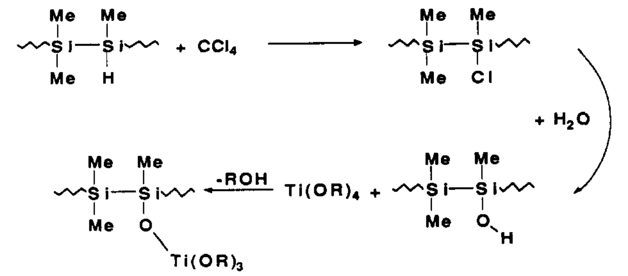
Fibers are drawn easily from the melt but need to be cross-linked before pyrolysis. Barton et al. find that exposing the fibers to triflic acid vapor (CF_3SO_2OH) replaces some phenyl groups with triflate groups. Hydrolysis of the triflates provides silanol groups that form siloxane cross-links. No further characterization or description of the pyrolysis chemistry and fiber properties have been published.

Titanium-Modified PC. To improve the high-temperature properties of PCS fibers, Yajima et al. prepared a new precursor, poly(titanocarbosilane) (PTC), by introducing titanium into a PCS-based polymer.[16–18] The presence of Ti in the silicon carbide network should help in retaining the amorphous state of the ceramic at a higher temperature. PCS prepared by thermolysis of PDMS with a few percent of PBDSO (PC-B) is refluxed with $Ti(OR)_4$ (where R = *i*-Pr or *i*-Bu) in xylene (Ti/Si ≈ 0.15). Removal of the solvent, followed by heating to 220 °C results in polymerization leading to a polymer with $M_n \approx 1.7$ kDa.

The proposed mechanism for the formation of PTC is via reaction of Si–H bonds with Ti–OR bonds to form Si–O–Ti bridges. IR spectra reveal the presence of such bonds as evidenced by an intense band at 920 cm^{-1}. On further heat treatment above 200 °C, these bands disappear as the Si–O–Ti linkages disproportionate to O–Ti–O and O–Si–O containing species.[17,18] MAS NMR studies on PTC prepared from a commercial PCS demonstrate that the local environment at the Si atoms does not change during the reflux. ^{29}Si MAS NMR clearly shows the consumption of Si–H bonds and the formation of Si–O bonds during the polymerization process with a new peak appearing at ≈10 ppm due to SiC_3O units. However, according to ^{13}C MAS NMR data, the Si–O bonds seem to be related to the formation of Si–OR rather than Si–O–Ti bonds.[83] Ti K-edge absorption studies (XANES and EXAFS) show that the titanium environment is close to that found in TiO_2-based particles.[84] Clearly, there is a need for more detailed studies on the precursor materials formed during the low-temperature reactions.

Song et al.[18] have approached the synthesis of Ti modified PCS via chlorine modified PCS. Their method, shown in Scheme VIII, relies on the chemical transformation of PCS Si–H bonds to Si–OH bonds which subsequently react with $Ti(OR)_4$ by a condensation process to form the desired Si–O–Ti linkages. Feng et al. have recently prepared PTC polymers via Scheme VIII with Ti/Si ratios of 0.07 and 0.15 and successfully made a series of modified ceramic fibers as discussed below.[85]

Scheme VIII. Synthesis of a Titanium-Modified PCS



Precursor Processing

Pyrolysis of Bulk PC-470 and PC-B under Ar. Pyrolysis of PC-470 in Ar gives typical ceramic yields of ≈60%. Under identical conditions, PC-B gives ceramic yields of ≈65–70%.[13,14a] According to TG-DTA and gas evolution curves, the pyrolysis process can be divided into 6 stages:

(1) Below 400 °C, low molecular weight polycarbosilanes are removed.

(2) Between 400 and 550 °C, the molecular weights of PCS increase via two different processes. In PC-470, the weakest bonds in the polymer, the Si–H bonds, are consumed as shown by IR[14a] and ^{29}Si MAS NMR.[41,86] The MAS NMR study shows no evidence for the formation of Si–Si bonds. Thus, it was concluded that Si–H bonds condense with $Si-CH_3$ groups leading to $Si-CH_2-Si$ linkages. *In contrast*, both Si–H bonds and $Si-CH_2-Si$ bonds increase in the PC-B samples treated similarly, due to the transformation of the polysilane moieties into polycarbosilane moieties.[14]

(3) The third stage, from 550 to 850 °C corresponds to transformation into an inorganic material with the elimination of Si–H, $Si-CH_3$, and $Si-CH_2-Si$ moieties, as characterized by an endotherm in the DTA, and loss of H_2 and CH_4. The ^{29}Si MAS NMR spectra of fired PC-470 samples exhibit one single peak assigned to SiC_4 units.[86] This peak shifts and broadens with continuing increases in temperature, beginning at 0 ppm in unfired PC-470 and moving to −8 ppm in PC-470 fired at 840 °C. These changes are associated with the crosslinking reactions that occur around the C atoms. The increase in linewidth is due to an increase in the distribution of Si sites; almost all the Si sites are surrounded by 4 C atoms but the nature of the C atoms changes as the decomposition proceeds with increasing time and temperature. The conversion of the polymeric network into an inorganic SiC network can be illustrated as shown in Scheme IX.[86] At 700 °C, additional, competing decomposition processes lead to the formation of C=C double bonds as a prelude to the formation of a free carbon phase and dangling C bonds (radicals).[41] At 800 °C, the material appears as an

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[83] Babonneau, F.; Livage, J.; Soraru, G. D.; Carturan, G.; Mackenzie, J. D. *New J. Chem.* **1990**, *14*, 539–544.

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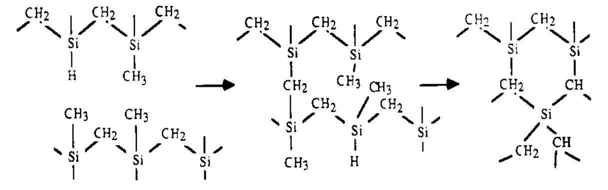
Scheme IX. Suggested Mechanism for Conversion of PCS to Ceramic Product



amorphous material by both XRD[14] and TEM.[87] Chemical analysis ($SiC_{1.6}H_{0.65}$), suggests that the 800 °C material can be described as an hydrogenated SiC with an average of two CH groups per Si atom and excess carbon.[86]

(4) The fourth stage of the pyrolysis occurs between 850 and 1000 °C and is characterized by minimal weight loss and no gas evolution peak. This stage is considered transitional.

(5) The fifth stage, between 1000 and 1200 °C marks the onset of crystallization. At 1000 °C, the XRD pattern is indicative of β-SiC with crystallite sizes around 2 nm. The crystallite size is slightly larger for PC-470 as compared to PC-B. TEM confirms the presence of β-SiC crystals of 2 nm size; however, the sample appears heterogeneous as some amorphous ($\approx$20%) SiC-like particles are also observed along with the presence of aromatic carbon layers, two or three piled up to form basic structural units (BSU).[87,88] During this stage, H_2 evolution continues (by mass spectrometry) and represents the final stage in conversion of PCS to an inorganic network via dehydrogenation reactions.[14] ^{29}Si MAS NMR also shows a decrease in the linewidth due to ordering/crystallization of SiC.[86,89] At 1200 °C, all the Si atoms appear to have a local environment expected for crystalline β-SiC according to the chemical shift value, −16 ppm. At this temperature, EXAFS patterns also exhibit features due to a crystalline structure similar to β-SiC[90] *out to the eighth nearest neighbor distance from Si.* From the number of second-neighbor atoms extracted from the fitting procedure, the crystallite size was estimated to be ca. 2 nm, in quite good agreement with the XRD results which give a 2.5-nm crystallite size.[14,41] TEM shows the disappearance of the amorphous phase and the association of BSUs edge-to-edge to form oriented rims of free graphitic carbon around the SiC crystals.[88] At 1300 °C, chemical analysis for PC-470 gives $SiC_{1.40}H_{0.0.46}O_{0.035}$ and for the PC-Bs, $SiC_{1.48}H_{0.139}O_{0.145}$ (PC-B3.2) and $SiC_{1.57}H_{0.051}O_{0.145}B_{0.006}$ (PC-B5.5).

(6) The last stage of the pyrolysis process occurs above 1200 °C and corresponds to crystal growth occurring with loss of CO due to the reaction of Si–O bonds with excess C.[14] However, even at 1500 °C, XRD patterns are not well defined; most likely as a consequence of the presence of excess carbon and grain sizes ranging from 5 to 13 nm, depending on the sample. The identification of the silicon carbide phase was done more accurately by ^{29}Si MAS NMR because the data for an increasing number of polytypes are now available in literature.[91-93] In PC-470 heated above 1500 °C, the main peak at −16.3 ppm is assigned to β-SiC (see Figure 6 below). The two peaks at −20 and −25 ppm correspond to the presence of Si sites found in some α-polytypes.[41] However, the identification of the cubic polytype, 3C by ^{29}Si MAS NMR is still under investigation since a range of shifts from −16 to −19 ppm have been reported. A recent study suggests that the peak at $\approx$−16 ppm is characteristic of well ordered β-SiC.[94]

High Molecular Weight PCS Fibers. Toluene solutions (approximately 50 wt % polymer) of various molecular weight PCS polymers, produced by autoclaving PDMS (see above),[44] were extruded through a small orifice (30–70-μm diameter) using nitrogen pressure and wound on a spinning glass drum. The fibers prepared from a PCS with a molecular weight of $\approx$2 kDa (PCS-2000) were easily spun but melted upon pyrolysis and gave little ceramic product. The PCS-5000 polymer was more difficult to spin but provided precursor fibers that survived pyrolysis; albeit these fibers shriveled somewhat and tended to mat on heating to 1000 °C. The PCS-9500 polymer was very difficult to spin; however, these fibers maintained their shape relatively well on pyrolysis to 1000 °C. Unfortunately, the PCS-9500 precursor fibers were quite brittle.

The major problem in spinning the high molecular weight polymers arises as a consequence of instability of the polymer solutions leading to polymer precipitation as solvent is removed to adjust viscosities. This problem was solved by blending PCS-5000 with small amounts of a vinylic polysilazane (to aid in curing).[45] The polysilazane acts as a plasticizer to enhance spinnability.

Using unspecified PCS-5000/vinylpolysilazane blends, Toreki et al. were able to process ceramic fibers with diameters ranging from 10–60 μm following pyrolysis to 1000 °C. Scanning auger analysis of these fibers indicates that much lower oxygen and carbon contents are obtained using the appropriate blend. These results were reported to have been confirmed by XRD, FTIR, and chemical analysis; although, no data are reported. Neutron activation analysis showed typical oxygen contents of approximately 1.6% where Nicalon analyzes for 15%. The oxygen content of the starting PDMS derived polymer is <0.5%. The nitrogen content from the polysilazane component is reported to be very low, but no quantitative data are provided. Microstructural analyses by SEM and TEM of the 1000 °C fibers indicate that they are amorphous. On heating to temperatures >1200 °C β-SiC will crystallize as determined by XRD. The fiber mechanical properties are described in the section on materials properties.

Titanium-Modified PCS. The PTC ceramic yield is higher than for PCS, >70% vs 50–55%.[16a] The material remains amorphous on heating to 1200 °C and crystallizes at higher temperatures into a mixture of β-silicon carbide and TiC. The pyrolytic evolution of PTC has been followed by ^{29}Si MAS NMR,[95] XPS[96] and Ti K-edge absorption

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[87] Monthioux, M.; Oberlin, A.; Bouillon, E. *Composites Sci. Technol.* **1990**, *37*, 21–35.

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[89] Babonneau, F. In *Inorganic and Organometallic Polymers with Special Properties*; NATO ASI Ser. E: Appl. Sci. Laine, R. M., Ed.; Kluwer: Dordrecht, Netherlands, 1991; Vol. 206, pp 347–358.

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[93] Apperley, D. C.; Harris, R. K.; Marshall, G. L.; Thompson, D. P. *J. Am. Ceram. Soc.* **1991**, *74*, 777–782.

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[95] Babonneau, F.; Soraru, G. D.; Mackenzie, J. D. *J. Mater. Sci.* **1990**, *25*, 3664–3670.

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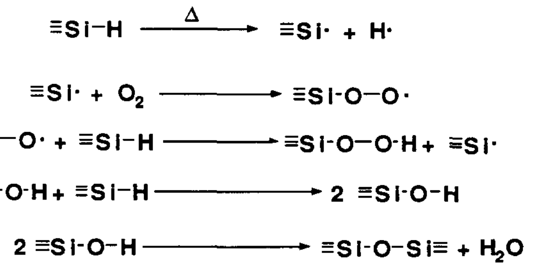
Scheme X. Oxidative Cross-Linking of PCS by Radical Mechanisms



(XANES and EXAFS).[84] In the 500–800 °C temperature range, Si–O bonds are formed as shown by the presence of peaks due to $SiC_{4-x}O_x$ units in the NMR spectra. Above 800 °C, both XPS, Ti K-edge XANES, and EXAFS show the formation of TiC particles. Above 1000 °C, Si–O species reorganize with subsequent formation of β-SiC crystallites as heating continues to 1200 °C. Crystallization is actually delayed compared to PCS, but once initiated, crystal growth is faster. The problem is that even though Ti is introduced to prevent crystallization, oxygen is introduced simultaneously via the titanium alkoxide and reacts at high temperature to form CO and favor crystal growth as seen for oxygen cured PCS.

Oxygen-Cured PCS Fibers. PCS precursor fibers can be processed by melt-spinning the polymer at 300–350 °C. To avoid further melting during pyrolytic transformation to a ceramic fiber, a curing step is performed wherein the fiber is heated in air for 30 min at 190 °C for PC-470 and ≈100 °C for PC-B.[13,97] Chemical analyses following curing gives O/Si molar ratios of ≈0.2 for PC-470 and ≈0.7 for PC-B. Oxidation of Si–H and Si–CH_3 bonds occurs with the formation of Si–OH, Si–O–Si, and C=O groups as shown by IR,[13,15] XPS,[98] and ^{29}Si MAS NMR.[13,40] Mechanisms have been proposed based on infrared data.[13] For PC-470, Si–H bonds are oxidized rather than C–H bonds and the reactions in Scheme X can be assumed.

PC-B oxidizes at much lower temperatures (even at RT) apparently by formation of silyl radicals:

$$\equiv\mathrm{Si}^{\bullet} + \mathrm{O}_2 \rightarrow \equiv\mathrm{Si{-}O{-}O}^{\bullet}$$

The mechanism whereby these radicals form is not clear; although in the PC-B case the SiC_xSi_{4-x} units are a likely source as they contain easily cleaved Si–Si bonds.

Pyrolysis of the cured PCS fibers provides ceramic yields of 80–85%, 15–20% higher than for uncured PCS, which correlates directly with the presence of oxygen cross-links. The precursor fibers undergo transformation from polymer to ceramic at 500–800 °C. Oxygen is retained during this process as shown by the persistence of peaks due to SiC_xO_{4-x} species in the XPS curve.[98] The presence of oxygen strongly modifies the crystallization kinetics by inhibiting crystal growth. Thus, attempts to study crystallization kinetics in fibers (by XRD)[97] and monofilaments (by TEM)[98] were thwarted by very poor diffraction patterns (crystallite sizes <2 nm). The crystallite sizes are suggested to be related to the molecular size of the original precursor.[97]

The TEM studies also revealed the presence of a 5-nm-thick layer of free carbon at the surface of the filament with the BSUs parallel to this surface. Formation of C_6-ring structures occurs during the polymer-to-ceramic conversion process as shown by Raman experiments.[99] In the Raman spectra, the carbon doublet at ca. 1350 and 1600 cm^{-1}, indicative of graphitic structures, is already present at 800 °C. From the relative intensities of the two lines, the average crystal size in the a plane was estimated to be less than 5 nm at 1200 °C. The presence of a free layer of carbon on these fibers is beneficial in promoting smooth fiber pullout from a wide variety of matrices.[100]

Above 1200 °C, loss of CO[97] and possibly SiO[98] occurs and is characteristic of cured samples. The chemical composition of a PCS fiber heated to 1400 °C ($SiC_{2.2}O_{0.07}$) shows a strong decrease in the O content and an increase in the C content. Coincident with these changes in composition, the fiber diameter is observed to shrink from 16 to 13 μm with a corresponding weight loss of 34%.[98] Rapid growth of β-SiC crystallites occurs simultaneously as revealed by XRD[97] and TEM[98] (crystallite sizes ≈7 nm at 1400 °C). At this temperature, TEM studies indicate the presence of a 40-nm-thick layer of isotropic turbostratic carbon covered with a 5-nm-thick film of carbon with BSUs oriented parallel to the filament surface. All of these changes have detrimental effects on the fiber properties as discussed below.

Nitrogen Dioxide/BCl_3 Cured PCS Fibers. A recent patent by Rabe et al. discusses the advantages of curing with NO_2 instead of oxygen.[101] It appears that brief treatments of PCS (from Nippon Carbon Co.) significantly reduce the time required to cure the PCS fibers and also reduce the total oxygen content retained in the fired fiber. The rate of curing and degree of oxygen retention are directly proportional to the exposure time (constant NO_2 concentration) and exposure temperature. Thus, heating at 25 °C for 30 min with a 3 vol% concentration of NO_2 gave a fired fiber (1200 °C) oxygen content of 5.6% as opposed to the 10–15% levels found for air cured fibers as described above. Alternately, heating at 125 °C for 5 min with a 3 vol% concentration of NO_2 gave a fired fiber (1200 °C) oxygen content of 5.1%. What is most important about this process is that if the resulting NO_2 cured fiber is then heat treated with as little as 5% BCl_3 over a 25–140 °C temperature range, then the fibers can be heated to temperatures of *1800 °C, to produce fibers that are essentially oxygen free.*

The boron treatment engenders unique properties to the PCS precursor fiber; properties that have not been observed in any other SiC precursor fibers described to-date. These properties permit curing the fiber and pyrolyzing it to obtain an essentially pure SiC fiber. The introduction of a boron component surmounts the problems of CO and SiO loss during high-temperature processing of PCS-derived ceramic fibers. Typically, the loss of these species coincides with the formation of porous, weak ceramic fibers at higher temperatures and the crystallization of large β-SiC grains. The boron apparently promotes densification of the fiber during CO/SiO evolution and permits recovery of fully dense fibers (>3.1 g/cm^3) with less than 0.1% oxygen when the fibers are heated in Ar to temperatures above 1200 °C.

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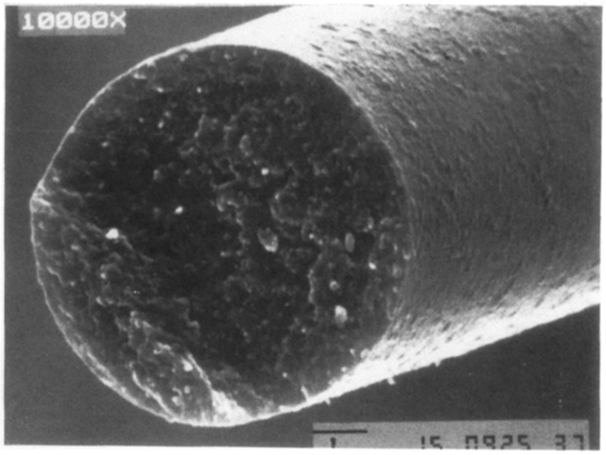


Figure 2. Scanning electron microscope image of fully dense, stoichiometric SiC fiber (1-μm bar). Produced by oxidative curing of PCS fibers followed by boron doping and pyrolysis to high temperatures (σ = 2.6 GPa, E = 450 GPa).

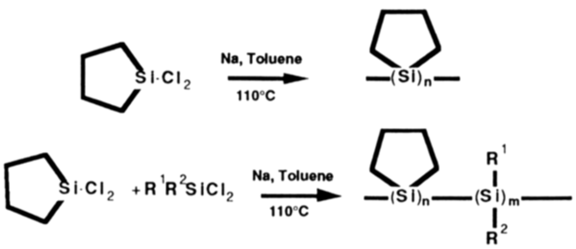
SEM studies on the fibers (see Figure 2) reveal a densification process that results in an outer ring, 1–2 μm thick, containing SiC crystallites with average grain sizes of 0.5 μm.[102] In the interior of the fiber, the grains are considerably smaller with average sizes running about 0.04 μm. If precursor fibers with large excesses of carbon are used, then TEM studies reveal the presence of graphitelike structures between the SiC grains.[102]

Given that boron is known to function as a sintering aid for SiC densification, its application here for improving the processability of SiC precursors seems quite logical and suggests that other applications of boron in processing SiC preceramics for non-fiber applications should be not only facile, but necessary to obtaining superior mechanical properties as discussed below.

Phenylmethylsilane–Dimethylsilane Copolymer (PSS). Although PSS offers improved processability over PDMS, the lack of Si–H bonds in these polymers renders the crosslinking process difficult, which leads to low ceramic yields. However PSS is UV sensitive, and this provides access to infusible intermediates. It also means that PSS must be protected from exposure to light. Cross-linking is obtained by UV irradiation at 330 nm, which photolytically cleaves Si–Si bonds. PSS can be cast into films, spun into fibers, and it has been used to infiltrate porous silicon nitride.[103] The in situ thermal decomposition of the polymer leads to the formation of silicon carbide particles that considerably improve the room temperature strength of the infiltrated body.[103] IR and GC-MS studies indicate that pyrolytic decomposition (following cross-linking) is similar to PCS, leading to the formation of Si–H and Si–CH_2–Si bonds in the earlier pyrolysis stages. Typical ceramic yields obtained by TGA are of the order of 30% at 800 °C.

Several efforts were made to improve the cross-linking behavior of PSS via other routes including the use of either γ-ray irradiation or a free radical initiator.[104] Thus, PSS cross-linked by dicumyl peroxide showed a ceramic yield of 67 vs 20 wt % for un-cross-linked PSS.

Scheme XI. Synthesis of Heterocycle-Containing Polysilane Copolymers



The West group has developed several new cross-linking systems for polysilanes.[105] A five-member heterocyclic ring containing Si (Scheme XI) can be introduced as a comonomer. This moiety permits oxidative cross-linking at low temperatures (80 °C). Copolymers containing Si–H bonds in phenylsilylene units (PhSiH) were also prepared and the polymer was cross-linked via hydrosilylation reactions, e.g., with trivinylphenylsilane. Alternately, side chains containing C=C bonds were incorporated in the polysilane backbone to induce susceptibility to cross-linking via UV radiation or heat treatment. Polysilanes were also mixed with polyunsaturated compounds and crosslinked by photolytic or thermal generation of radicals using an initiator. Unfortunately, there are no literature reports that evaluate these cross-linkable polymer systems as SiC precursors. However, it is likely that the carbon-rich organic group introduced for cross-linking purposes will provide ceramic products with excessive amounts of carbon following pyrolysis.

PSS fibers were hand drawn from a sample with $M_n \approx$ 12 kDa and photolytically cross-linked. On heating to 1100 °C the solid precursor fibers formed hollow ceramic fibers. The opacity of polysilastyrenes is such that cross-linking can be achieved only to depths of 10–20 μm and the un-cross-linked material depolymerizes during heat treatment.[106,107] On pyrolysis, the precursor fibers exhibit an 85% weight loss and a 40% shrinkage in length. The products are reported to be amorphous; although no detailed characterization has been published.

A recent study describes the role of polysilane composition (homo-, co-, and terpolymers) on ceramic yield.[108] Me_2SiCl_2, $PhMeSiCl_2$, $C_6H_{13}MeSiCl_2$, $CH_2{=}CHMeSiCl_2$, and $(CH_2{=}CHCH_2)MeSiCl_2$ were used as precursor monomers. Ceramic yields increase when methyl groups are replaced by phenyl, vinyl, or allyl groups. For example, the 1:9 $CH_2{=}CHMeSi/PhMeSi$ copolymer gives the best ceramic yields, 39 wt %. Chemical analysis shows excess amounts of carbon for all of the recovered ceramic products. An IR study of the pyrolysis process reveals formation of Si–H bonds above 400 °C; these polysilanes appear to decompose via carbosilane intermediates prior to formation of SiC/C composite materials.

Pyrolysis of VPS. The pyrolysis chemistry of VPS has been characterized by Interrante et al.[109] The translucent, viscous liquid provided by Union Carbide was

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Scheme XII. Copolymer Components in VPS

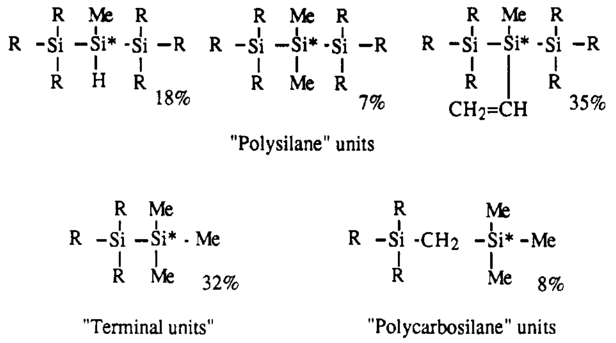

Table III. Ceramic Yields for Selected Derivatives of $(\mathrm{MeSi}{\equiv})_{5.7}(\mathrm{Me_2Si}{=})_{1.0}(\mathrm{R})_{1.9}$ Methylpolysilanes

modification R	ceramic yield at 1200 °C (%)	SiC crystallite size (nm) (Firing Temperature (°C))	ref
none	60–80	1–2 (1200)	110
$-\mathrm{CH_3}$	52–67		75
$-\mathrm{C_6H_5}$	37		75
-OR	52–73	3–4 (1200)	76
-H	78–90	6–16 (1600)	77
$-\mathrm{O{-}Si(CH_3)_3}$	40	3 (1555)	79
$-\mathrm{NHCH_3}$	63	18 (1600)	78
-NH(n-Bu)	17–53	6–73 (1600)	78

prepared by reacting a mixture of $\mathrm{Me_3SiCl}$, $\mathrm{Me_2SiCl_2}$, and $\mathrm{Me(CH_2{=}CH)SiCl_2}$ in a 0.85:0.3:1 ratio with Na in THF. Multinuclear NMR experiments (^{1}H, ^{13}C, and ^{29}Si) show the presence of several Si units and the composition given in Scheme XII is proposed. The polymer exhibits a ≈60% ceramic yield on heating in a TGA to 1000 °C under Ar. Weight loss occurs in two stages. Below 300 °C, thermosetting occurs and is characterized by a small weight loss and an exotherm in the DTA. Cross-linking occurs via polymerization of the vinyl groups, as shown by IR and solid-state NMR. Some Si–H bonds also react at this stage by hydrosilylation or through formation of Si-Si bonds and loss of H_2. The second stage occurs in the 300–750 °C range and is characterized by a 40% weight loss. The IR bands and NMR peaks due to Si–H bonds increase, and evidence for the simultaneous formation of $\mathrm{Si{-}CH_2{-}Si}$ bridges is found in the IR (band at 1046 cm^{-1}) and ^{13}C MAS NMR ($\delta = 10$ ppm). The latter observation indicates that rearrangement to a polycarbosilane occurs; a process that appears common to most polymethylsilane precursors.

The ^{29}Si MAS NMR at 400 °C consists primarily of a peak characteristic of $\mathrm{SiC_4}$ sites. With further heating, this peak shifts progressively to a value close to those characteristic of crystalline SiC ($\delta = -14$ ppm at 1000 °C). Above 400 °C, the NMR peaks broaden as the polymer is converted to a ceramic. ^{13}C MAS NMR reveals the presence of graphitic carbon at 650 °C. Elemental analysis of the sample heated to 1000 °C gives a Si/C ratio of 0.58 showing a 17 wt % excess of C. XRD reveals the presence of 2–3-nm size β-SiC crystallites.

Pyrolysis of MPS Derivatives. The various modified versions of MPS, $(\mathrm{MeSi}{\equiv})_{5.7}(\mathrm{Me_2Si}{=})_{1.0}(\mathrm{Cl})_{1.9}[(\mathrm{MeSi}{\equiv})_{5.7}(\mathrm{Me_2Si}{=})_{1.0}(\mathrm{R})_{1.9}]$ have been assessed as to their ceramic yields and the size of the resulting SiC crystallites. These data are summarized in Table III. Unfortunately, no data are provided as to the exact processing conditions that provided the results summarized in Table III.

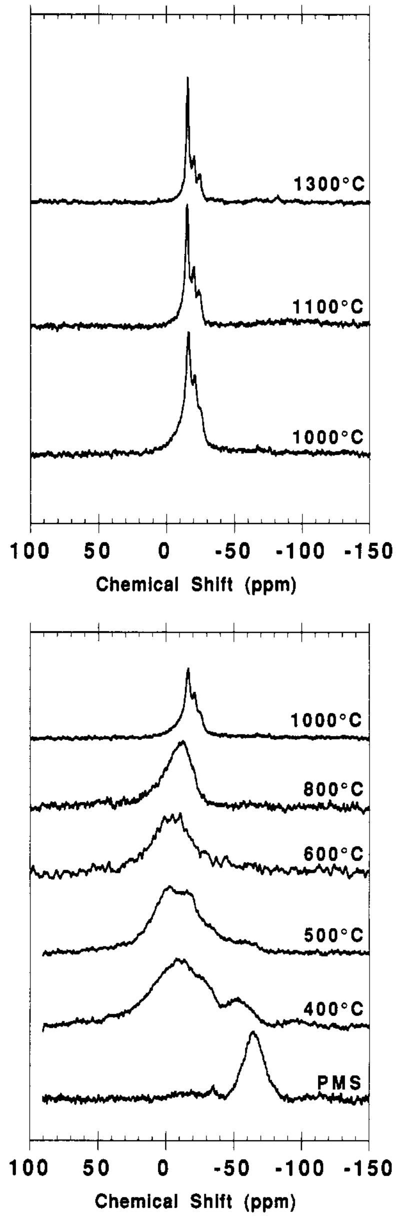

Figure 3. ^{29}Si MAS NMR study of the chemical evolution of PMS during pyrolytic transformation to SiC. 1.0-g samples of PMS heated at 1 °C/min to temperature in N_2 and held at respective temperatures for 1 h. The 400 and 500 °C spectra were obtained using cross-polarization techniques.

Pyrolysis of PMS. Detailed studies on poly(methylsilane) produced via dehalocoupling have not been forthcoming; although chemical and XRD analyses of the final ceramic products suggest that a mixture of SiC and metallic Si have been produced. Detailed studies on the pyrolytic behavior of PMS, $-[\mathrm{MeSiH}]_x-$, produced by dehydrocoupling indicate strong similarities to other polysilanes.[69,71]

As shown in the ^{29}Si MAS NMR (Figure 3A), the original polysilane [singlets at −64 ppm (major peak from chain) and −34 ppm (terminal groups)] are transformed at approximately 400 °C to polycarbosilane ($-\mathrm{H_2SiCH_2}-$) as evidenced by a singlet at −10 ppm. This change is corroborated by the FTIR results (Figure 4) which clearly show the $\mathrm{Si{-}CH_2{-}Si}$ bending vibration (1350 cm^{-1}).[71]

On heating to 1000 °C, the −10 ppm peak sharpens into two narrow, peaks at −15.4 and −19.4 ppm. These peaks, which do not change on further heating to 1300 °C (Figure 3B), correspond to β-SiC with a small amount of α-SiC. If the same sample is heated at 900 °C for selected times,

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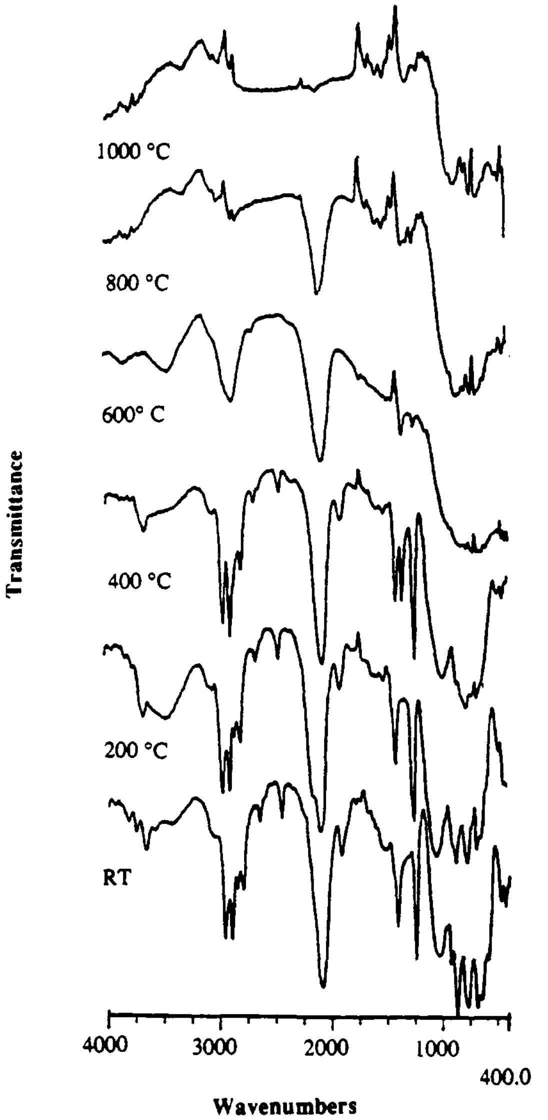

Figure 4. Diffuse reflectance Fourier transform infrared (DRIFT) study of the chemical evolution of poly(methylsilane) on pyrolytic transformation to β-SiC. Polymer heated at 10 °C/min to 1000 °C in N_2. Samples held at respective temperatures for 1 h.

a similar narrowing occurs (Figure 5). The presence of Si metal in small quantities (3–4%) is found in the 1300 °C ^{29}Si MAS NMR.

No evidence for the formation of SiO_x species is found in any of the NMR analyses, despite chemical analyses that indicate its presence. The latter result may arise during handling of the analytical samples. Thus, unlike PMS produced by dehalocoupling, PMS produced by dehydrocoupling gives near stoichiometric materials. Figure 6 compares the ^{29}Si MAS NMR of a commercial sample of β-SiC with that of PMS heated at 1000 °C and a bulk sample of PCS-470, obtained from Dow Corning, which was heated to 1500 °C.

One can conclude, on the basis of the comparison made in Figure 6, that even at 1000 °C the PMS-derived sample is highly crystalline. The high degree of crystallinity is confirmed by XRD. X-ray line-broadening studies indicate that the average crystallite sizes found are ≈4 nm at 1100 °C, 6 nm at 1300 °C and 11 nm at 1500 °C.[71] Figure 7 shows a set of transmission electron micrographs for samples of bulk PMS heated to 1100 and to 1300 °C. The accompanying small area diffraction studies illustrate the very fine nature of the β-SiC crystallites at 1100 °C and the growth in crystallite size on heating to 1300 °C.

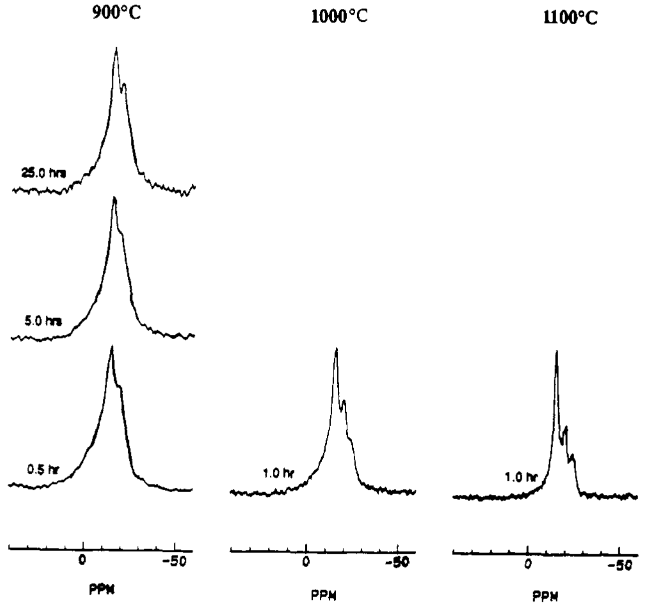

Figure 5. ^{29}Si MAS NMR study of crystallization of β-SiC from pyrolyzed PMS as a function of selected heating times at 900 °C and selected temperatures. 1.0-g samples of PMS heated at 1 °C/min in N_2 to 400 °C and then at 5 °C/min to 900, 1000, or 1100 °C and held for selected times.

Materials Properties

The expected and found materials properties of ceramic fibers in general have recently been reviewed by several authors.[2,20,33,34] The following discussion is meant to provide an in-depth description of the properties, advantages, and failings of SiC based fibers.

Nicalon. A wide variety of analytical techniques have been applied to characterize the structural properties of commercial Nicalon fibers including: XRD, SAXS, WAXS, TEM, EXAFS, MAS NMR, XPS, Raman, and ESR.[111-116] The oxygen content usually ranges from 10 to 15 wt %. Fiber microstructure has been determined by TEM[112] to consist of very small SiC crystallites (<3 nm) interspersed with free, *graphitic* carbon particles of less than 1 nm in size. The BSU units tend to lie parallel to the SiC crystallites. The presence of graphitic carbon was demonstrated both by ^{13}C MAS NMR[111,115] and by Raman spectroscopy.[114] Raman estimation of the average carbon crystallite size gives a value of ≈4 nm.

^{29}Si MAS NMR[111,114,115] and XPS[111,113,114] were used to establish the presence of SiC_xO_{4-x} units ($1 \le x \le 4$) and the mole percentages of the various units.[115] Thus, 40–50% of all Si atoms are surrounded by 4 C atoms, ≈6% of the Si atoms are surrounded by 4 O atoms with the remaining fraction of Si atoms *(40–50%)* existing as oxycarbide species.

Nicalon fiber densities range from 2.20 to 2.55 g/cm^3, lower than the theoretical value calculated based on the volume additivity rule, assuming the presence of SiO_2, SiC, and C in the fiber. SAXS and WAXS experiments[116] indicate the presence of nanometer-scale voids (1–2-nm

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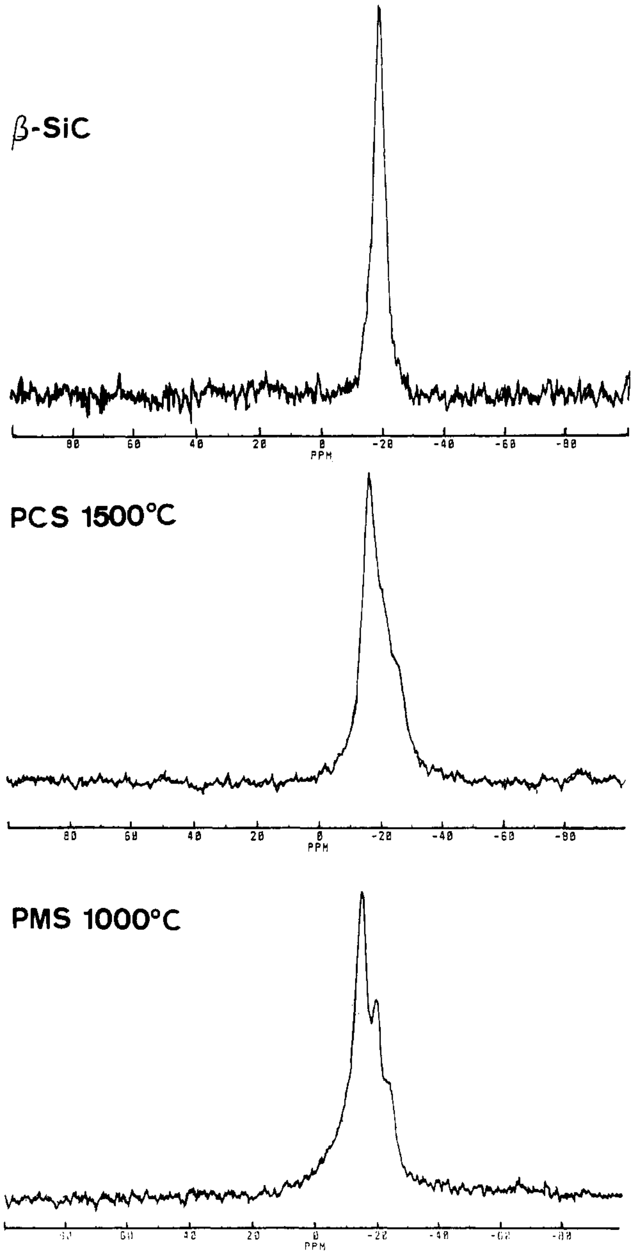

Figure 6. ^{29}Si MAS NMR comparison of linewidths of commercial β-SiC, PCS heated to 1500 °C, and PMS heated to 1000 °C. A bulk sample of commercial PCS (presumed to be PCS-470) was obtained from Dow Corning and pyrolyzed in N_2 to 1500 °C.

diameter) that represent 6–17% of the volume fraction of the sample. Structural models[111,114] have been proposed that describe the system as "a glassy silicon oxycarbide" in which extremely small SiC and graphitic crystallites exist as minor phases in a continuous Si–C–O major phase.

Nicalon fibers with diameters of 10–20 μm exhibit tensile strengths ≥2.3 GPa and elastic moduli of ≈200 GPa.[38,114] The mechanical properties dramatically decrease when the fibers are heat-treated above 1200 °C (tensile strength 0.56 GPa, young's modulus ≈100 GPa at >1500 °C).[9,13,15,34,38] These changes can be ascribed to the extensive structural modifications that occur as a consequence of the evolution of CO and SiO gases coincident with rapid crystallization of β-SiC as noted above.[117,118] Calculations of the partial pressures of CO and SiO that occur during high-temperature heat treatment of the fibers confirm the experimentally observed instabilities.[119] These calculations indicate that improvements in thermal stability would result through the reduction or elimination of oxygen and excess carbon. Furthermore, these studies suggest that replacing the excess carbon with excess silicon could improve thermal stability by 200–400 °C.[119]

Several groups have attempted to improve the mechanical properties of the fibers by using γ-ray or electron irradiation instead of oxidation to promote curing (cross-linking) in the precursor fiber.[38,120,121] Electron irradiation is expected to favor the cross-linking of the polymer via the formation of Si–Si bonds from Si–H bonds. The mechanical properties of fibers are found to increase with increasing irradiation dose, reaching values similar to those reported (at ambient temperature) for oxygen-cured fibers (Tensile strength 2.5–2.6 GPa, elastic modulus 220–250 *at 1400–1800 °C*, for a 10-MGy dose) but with very low oxygen contents.[120,121] These tensile strengths and elastic moduli are among the best reported to date for SiC/C composite fibers and the high temperature stability attests to the fact that the long standing problems with oxygen have been eliminated.

The microstructure of these fibers at 1200 °C was found (by small area electron diffraction studies) to consist primarily of β-SiC and presumably amorphous carbon, because at 1500 °C, similar diffraction studies indicate the formation of graphitic carbon. The surface of the fibers remains (by SEM) very smooth even after heating to 1500 °C. Moreover, Auger depth profile analyses show essentially no change in composition as one penetrates the surface of these fibers with carbon being in excess of Si by about 40% as in the standard Nicalon fibers.

High Molecular Weight PCS. Toreki et al.[44,45c] have prepared a series of ceramic fibers based on an unspecified blend of high molecular weight (5 kDa) PCS with vinylpolysilazane (molecular weight not reported). The mechanical properties of ceramic fibers with diameters ranging from ≈10 to 40 μm were evaluated using an Instron (1-in. gauge length) at room temperature before and following a set of aging studies. The average tensile strength of these fibers, as a function of fiber diameter, was determined to be between 1.3 and 3.0 GPa as the fiber diameter varies between 40 and 10 μm. Average tensile strengths were up to 3.2 GPa after 1000 °C pyrolysis (11-μm diameter).

On aging in nitrogen for 0.5–1 h at selected temperatures, over the range of 1000–1700 °C, the tensile strengths for one specific fiber composition (not defined) were found to diminish *linearly* from approximately 2 GPa at 1000 °C to 1 GPa at 1700 °C. Similarly, the average elastic modulus varied from approximately 230 GPa at 1000 °C to 260 GPa at 1700 °C. Other, unspecified compositions were found to give tensile strengths as high as 5 GPa. The increase in elastic modulus at higher temperatures is somewhat surprising but may occur if some silicon carbide nitride species are converted to SiC and N_2 to give a more homogeneous and/or denser fiber. Alternately, the for-

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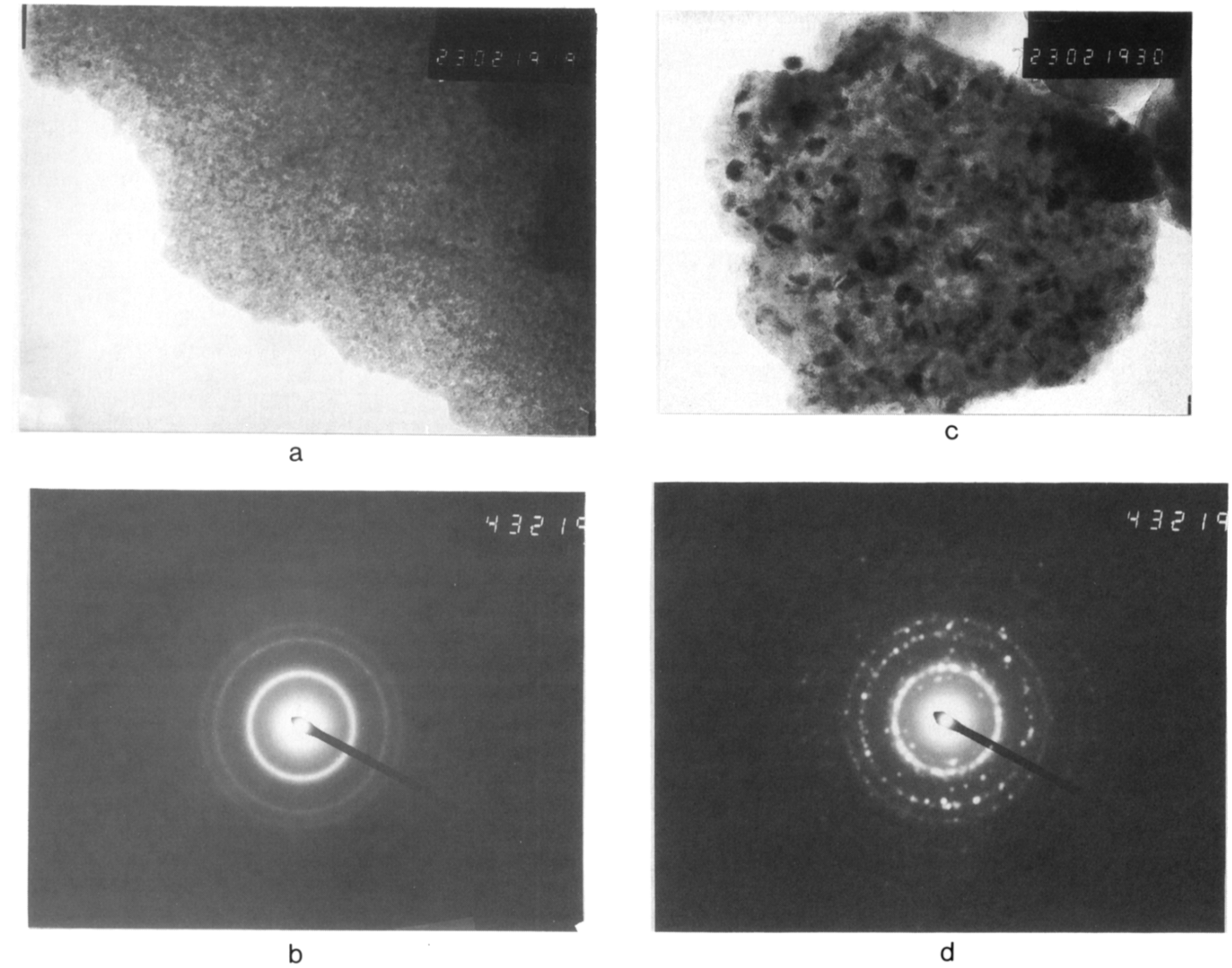

Figure 7. Transmission electron micrographs and corresponding small-area diffraction patterns for samples of bulk PMS heated to 1100 or 1300 °C in N_2. (a) TEM at 1100 °C, magnification 230 000×. (b) Small area electron diffraction pattern at 1100 °C. (c) TEM at 1300 °C, magnification 230 000×. (d) Small area electron diffraction pattern at 1300 °C.

mation of very small β-SiC crystallites may provide the observed improvements.

The conclusions are that the high molecular weight PCS derived fibers are as good as Nicalon and offer much better high-temperature stability as a consequence of their low oxygen content. The effects of any nitrogen-containing species and processing on the microstructural properties of these fibers may play key roles in their further development.

Titanium-Modified PCS. PTC fibers are also prepared by melt-spinning[16,17] followed by air curing. The mechanical properties are reported to be maximal at 1300–1400 °C, exhibiting elastic moduli of ≈220 GPa and tensile strengths of ≈3 GPa with fiber densities of 2.35 g/cm^3.[19] At 1300 °C, the fibers are mainly amorphous with crystallite sizes less than 2 nm. Fibers prepared from PTC and containing 1.5–4 wt % Ti are marketed by Ube Ind. under the trade name Tyranno. A study performed on the commercial fibers[122] confirms the manufacturers specifications: a narrow distribution of diameters with a mean of 8.5 μm, an elastic modulus of ≈170 GPa and tensile strengths ≥3 GPa. However, heat treatment at 1300 °C leads to severe degradation of the mechanical properties and a thermal stability even inferior to Nicalon.[18,122]

In recent studies by Feng et al.,[18] efforts were made to understand the effects of postprocessing heat treatments on fiber properties. Initially prepared fibers (see above) exhibited tensile strengths as high as 2 GPa and elastic moduli as high as 140 GPa. Heating in an oxygen flow over the range of 900–1200 °C resulted in complete conversion of the PCS–Ti fiber to a transparent and colorless SiO_2–TiO_2 fiber with a concomitant loss in the

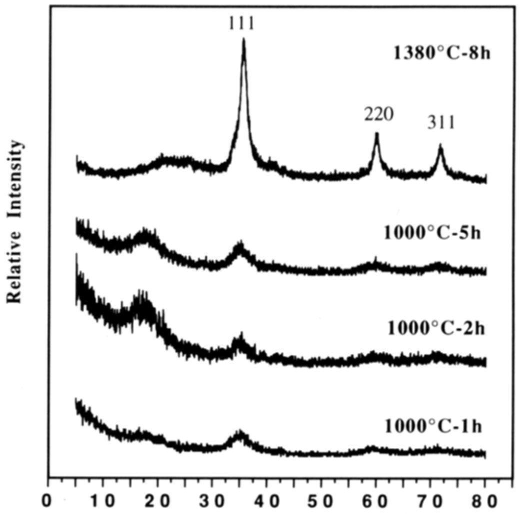

Figure 8. Crystallization of β-SiC from pyrolyzed PMS as a function of heating time and temperature. Precursor fibers heated at 1–10 °C/min to 1000 °C in N_2 and held for selected times. The 1380 °C pattern was obtained following heating 1000 °C fibers to 1380 °C in Ar for 24 h.

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Table IV. Common Ceramic Fibers and Their Properties[129]

fiber composition	source	ρ (g/cm^3)	av diam (μm)	tensile strength (GPa)	elastic modulus (GPa)	comments
carbon	Toray Ind.	1.81	6.5	2.7	392	
boron	Textron	2.5	140	3.6	400	filaments, CVD on tungsten
Nextel	3M	3.1	12	1.6	150	type 440, silica alumina
fiber FP	DuPont	3.95	20	1.4	390	
SiC bulk		3.2			450	hot-pressed
SiC whisker			0.3–1.0	$\approx$8	580	gas-phase synthesis
SiC	Textron	3.0	142	4	400	filaments, CVD
$SiC_{1.40}H_{.046}O_{.035}$	Nippon Carbon	2.5	15	2.8	200–220	PCS-470, composition at 1300 °C
SiTiC	Ube Ind.	2.35	8.5	3	180–220	Tyranno fibers
SiC	Dow Corning	2.70	10–20	1.7	220	MPS
SiC	Dow Corning	3.1	10–20	2.6	450	boron sintering aid
$SiC_{1.8}O_{0.0x}$	Univ of Florida		10–40	1–3	175	strength/modulus measured at 1000 °C, oxygen content $\approx$1.6 mol % by neutron activation analysis
SiC_x	Tohoku Univ		12	2.6	220–250	strength/moduli measured at 1400–1800 °C
SiC	Univ of Michigan	2.3–2.55	60–120			from PMS polymer
Si_3N_4 bulk					320	hot pressed
Si_3N_4 whisker						
Si_3N_4	Tonen	2.5	10	2.5	200–220	
SiCN	Dow Corning	2.55	10–15	3.1	260	HPZ
SiCN	Rhône Poulenc	2.4	15	1.8	220	

fiber mechanical properties (tensile strengths of $\approx$0.5 GPa and elastic moduli of $\approx$50 GPa). Likewise, pyrolysis of the same fibers in a flow of NH_3 leads to what the authors describe as a Si–Ti–O–N fiber material which exhibited tensile strengths of up to 0.8 GPa and elastic modulus of up to 125 GPa). The trivalent nature of nitrogen appears to be responsible for the different mechanical properties of the two fibers. In the latter fiber, TiN is produced as the only recognizable crystalline product. Its crystallization can be correlated to a loss in fiber strength.

Boron-Modified PCS. The introduction of sufficient quantities of boron to a precursor polymer that was not identified permits processing of essentially pure SiC fibers with densities in excess of 3.1 g/cm^3.[101,102] In principle, these fibers should exhibit the properties of bulk SiC and approach the properties of SiC whiskers. The fibers do indeed exhibit properties superior to Nicalon and Tyranno fibers, with average tensile strengths of up to 2.6 GPa and elastic moduli >450 GPa. Furthermore, aging at temperatures between 1600 and 1800 °C in Ar causes only limited loss of strength as opposed to other fibers.

Fracture toughness (K_{1c}) for these fibers was determined to be about 3 MPa m$^{1/2}$ as compared with average values of 2 MPa m$^{1/2}$ for Nicalon.[102] The difference here derives from the nanocrystalline nature of these fibers as opposed to the glassy nature of Nicalon and Tyranno fibers. In addition, dilatometry over the range 20–1300 °C indicates a CTE of 5.1×10^{-6}/°C.

Fibers aged in dry air at 1370 °C for 12 h retained approximately 70% of their original strength. The aging process causes the formation of an approximately 1-μm-thick SiO_2 layer on the fiber surface. The fibers tend to crack where SiO_2 formation is excessive.[102]

At present, these very promising fibers and processing methodology must be considered as being in the experimental stage, as the longest intact fibers produced to date run 10 cm in length.[102]

VPS Properties. VPS is recommended by the manufacturer "for manufacturing fiber-reinforced ceramic composites, for impregnating C/C composites to protect them from oxidation, and for molding or extruding ceramics to net shape".[123] Interrante et al. used VPS together with organoaluminum amides to prepare silicon carbide/aluminum nitride composites.[124] Unfortunately, there are no detailed studies on the mechanical properties of ceramic shapes made from VPS.

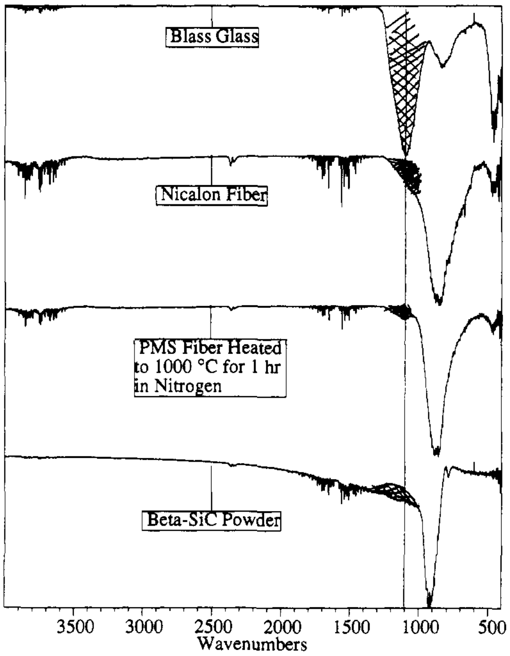

Figure 9. DRIFT comparison of silicon oxycarbide (black glass), commercial β-SiC, Nicalon, and PMS (1000 °C). Crosshatched area indicates Si–O stretching vibrations centered at approximately 1080 cm^{-1}.

MPS Fibers. Methylpolysilanes (MPS) prepared by redistribution of methylchlorodisilanes and modified by reaction with varied amounts of alkyl- or phenylmagnesium halides permits access to processable polymers with a wide variety of Si:C ratios.[125] Elemental analyses range from 52 to 75% for Si and 24 to 47% for C depending on the starting polymer. Fibers were melt-spun from many of these derivatives, then cured, and pyrolyzed in an inert atmosphere to 1000–1400 °C. The resulting ceramic MPS fibers exhibit high thermal stability with very low weight loss, only 3% on heating above 1400 °C *in air*. The commercially available, ceramics grade Nicalon fiber exhibits a 18% weight loss under the same conditions.

These results can be related to the different O contents, 2% *in the MPS fiber and* 11% *in the Nicalon fiber*. The chemical structure of the fiber was established by IR, MAS NMR, and XRD. The presence of a strong band at 840 cm^{-1} in the IR, a ^{29}Si peak at −14 ppm and a ^{13}C peak at 21 ppm in the MAS NMR are indicative of a silicon carbide phase. The ^{29}Si MAS NMR spectra also indicate the presence of Si–O bonds (as SiC_3O and SiC_2O_2 units) and the ^{13}C MAS NMR spectra (weak peak at ≈140 ppm) reveal the presence of graphitic carbon. XRD was used to show that 50 wt % of the material is nanocrystalline β-SiC with crystallites sizes averaging 2 nm. For the sample heated to 1200 °C, SAXS shows nm sized pores that represent a 10% volume fraction of the fiber material. Fibers with diameters in the 10–20-μm range exhibit tensile strengths of 1.7 GPa and elastic moduli of 210 GPa.

PMS Fibers. Preliminary studies on PMS derived fibers prepared by dry-spinning PMS from toluene–hexane solutions, followed by heating to 1000 °C in N_2 at 1–10 °C/min leads to ceramic fibers, 60–120 μm in diameter, with densities of 2.3 g/cm^3.[126] The crystallization of β-SiC occurs at 1000 °C with slight increases in crystallite size with extended heating, in accord with the bulk studies,[71] as shown in Figure 8. DRIFT spectra indicate that the fibers exhibit the same chemical transformations as seen in the bulk phase (see Figure 4). Heating fibers in Ar or N_2 above 1300 °C results in further densification to 2.5–2.6 g/cm^3.[127] Coincidentally, crystallization is also enhanced as seen in Figure 8.

The oxygen content is currently unknown; however, Figure 9 shows a comparison of silicon oxycarbide (black glass, 1000 °C),[31] commercial β-SiC, Nicalon, and PMS (1000 °C) with the νSi–O band crosshatched. These spectra suggest that only small amounts of oxygen are present in the PMS derived fibers; however, DRIFTS data can be deceiving.[128] Furthermore, it is important to note that the Si–O band seen in the PMS fibers at 1000 °C is not seen in bulk PMS heated to 1000 °C (Figure 4). Therefore, the oxygen present in the fibers is a consequence of processing and not the original synthesis.

Summary of Fiber Properties. Table IV represents an attempt to list the various properties of the SiC fibers cited in the literature.[129]

Based on the recent work at Dow Corning, the potential exists to prepare pure, nanocrystalline continuous SiC fibers with properties that match those of bulk SiC.

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