JOURNAL OF
Materials
CHEMISTRY

Processing stoichiometric silicon carbide fibers from polymethylsilane. Part 1 Precursor fiber processing

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Received 8th July 1998, Accepted 9th September 1998

A highly branched form of polymethylsilane (PMS), $-[\mathrm{MeSiH}]_x[\mathrm{MeSi}]_y-$, has been synthsesized and successfully processed into infusible precursor fibers *ca.* 30–100 μm in diameter. These precursor fibers were converted into stoichiometric, nanocrystalline SiC fibers, 20–70 μm in diameter, by pyrolysis in an inert atmosphere at ramp rates up to 20 °C min^{-1} to 1000 °C. Precursor synthesis, fiber processing, fiber curing and pyrolytic processing are described. Bulk materials were characterized using TGA, DTA, chemical analysis, and XRD.

Introduction

In the 1970s, Yajima *et al.*[1–4] developed a polymer precursor route to thin (10–15 μm diameter) Si–C–O ceramic fibers that are basis of the Nicalon™ and Tyranno™ fibers now used in high performance composite materials. In this process, precursor fibers are first produced by melt-spinning polycarbosilane (PCS), $-[\mathrm{MeHSiCH_2}]_x-$. These precursor fibers are then air cured and pyrolytically transformed to ceramic fibers at *ca.* 1200 °C. Unfortunately, this approach has several drawbacks:[1–6] (1) PCS is produced from polydimethylsilane, $-[\mathrm{Me_2Si}]_x-$, *via* an expensive multistep synthesis; (2) the initial 1 : 2 Si : C ratio leads to excess C in the final product; (3) air curing used to provide polymer fiber infusibility introduces undesirably high oxygen contents; (4) the resulting non-stoichiometric, amorphous fibers offer mechanical properties inferior to bulk, polycrystalline, stoichiometric SiC, and (5) fiber application temperatures are limited to 1200 °C because the retained oxygen reacts with C and Si to form gaseous species at high temperatures. The release of gaseous species degrades fiber properties as pores form coincident with exaggerated grain growth leading to significant decreases in tensile strengths at >1200 °C.

To overcome these problems and achieve SiC literature mechanical properties, stoichiometric, dense and polycrystalline SiC fibers with diameters of *ca.* 15 μm must be made, preferably *via* a simple, inexpensive route. Recent efforts have targeted lowering oxygen and carbon contents to obtain near stoichiometric SiC fibers, as described below.

Toreki *et al.* have prepared Yajima PCS with $M_\mathrm{n} \approx 5$–10 kDa (*cf.* 1–2 kDa in the Yajima process).[5] These polymers do not melt on heating, but are soluble in organic solvents and form viscous solutions suitable for dry-spinning. The dry-spun precursor fibers are heated directly in an inert atmosphere to high temperature, without air-curing. SiC fibers produced by this method contain <2 wt.% oxygen and therefore have better thermal stability than Nicalon fibers. However, the initial 1 : 2 Si : C ratio still gives fibers with excess carbon. The Toreki fibers exhibit tensile strengths of *ca.* 1.8 GPa at 1000 °C, and 1.2 GPa after heating to >1500 °C in Ar. By comparison, Nicalon fibers heated to 1500 °C exhibit tensile strengths of only 0.3 GPa. Sacks *et al.* have improved on the original Toreki fibers to produce phase pure, SiC fibers with the appropriate properties, unfortunately the exact chemistry has not been described.[6]

An alternative approach designed to minimize oxygen contents was developed at Dow Corning. Dow Corning patents indicate that when Yajima PCS is cured in nitrogen dioxide (NO_2) infusibility can be obtained with the incorporation of only small amounts of oxygen.[7–9] The NO_2 treated fibers are then exposed to boron trichloride (BCl_3). The incorporation of boron permits pyrolytic processing to dense, substantially crystalline SiC fibers. Thermally stable, substantially polycrystalline SiC fibers can be formed from PCS with 3–5 wt.% boron and some titanium which binds with the excess boron to make TiB_2. The boron acts as a sintering aid to promote densification at temperatures >1400 °C. It is also required to retain fiber integrity. The resulting SiC fibers have O contents of <0.1 wt.% after heating to >1600 °C. Stoichiometric β-SiC fibers, as well as SiC fibers containing up to 20 wt.% excess carbon were produced. Fiber densities approach 3.1 g cm^{-3} (fully dense SiC ≈ 3.2 g cm^{-3}). Average tensile strengths of up to 3 GPa and elastic moduli of >420 GPa were obtained. These properties are closer to the properties of bulk SiC than any other precursor derived fibers reported so far. These fibers represent the state-of-the-art in SiC fiber processing but still require expensive, multistep processing.

Clearly, precursor polymers with a Si : C ratio of 1 : 1 offer the best potential to obtain stoichiometric SiC fibers. Polymethylsilane (PMS), $-[\mathrm{MeSiH}]_x-$, with a 1 : 1 Si : C stoichiometry, offers the opportunity to meet this potential. Spinnable PMS, $-[\mathrm{MeSiH}]_x[\mathrm{MeSi}]_{1-x}$, was first synthesized by Seyferth *et al.*,[10,11] using dehalocoupling of $\mathrm{MeHSiCl_2}$ (Si : C = 1 : 1) with Na:

$$\mathrm{MeHSiCl_2} + \mathrm{Na} \rightarrow -[\mathrm{MeSiH}]_x[\mathrm{MeSi}]_{1-x}- + \mathrm{NaCl}_\downarrow \quad (1)$$

However, precursor fibers drawn from this polymer (M_n = 400–700 Da) gave black powders on pyrolysis in N_2, unless they were air cured prior to pyrolysis. Pyrolysis gave materials with excess Si (*ca.* 25 wt.%) and low ceramic yields (<30 wt.%). To increase yields and C contents, compounds with vinyl groups, *e.g.* $[\mathrm{Me(CH_2{=}CH)SiNH}]_3$ or $[\mathrm{Me(CH_2{=}CH)SiO}]_{4-6}$, were combined with this PMS. The improved ceramic yields were *ca.* 70 wt.%. No detailed analyses of fiber mechanical properties were reported.

PMS, $-[\mathrm{MeSiH}]_x-$, can also be synthesized *via* dehydrocoupling of $\mathrm{MeSiH_3}$, the Harrod reaction, using titanocene or zirconocene complexes, $\mathrm{Cp_2MMe_2}$ (M = Ti, Zr; Cp = C_5H_5), as catalysts:[12]

$$x\mathrm{MeSiH_3} \xrightarrow[\text{cyclohexene, 45–60 °C}]{0.2\text{ mol\% }\mathrm{Cp_2TiMe_2}} -[\mathrm{MeSiH}]_x- + 0.5x\mathrm{H_2} \quad (2)$$

Kobayashi *et al.* recently described a similar PMS synthesis using $\mathrm{(C_5Me_5)_2NdCH(SiMe_3)_2}$ as catalyst.[13] The synthesis is a one-step polymerization of $\mathrm{MeSiH_3}$, with *ca.* 90% conversion of monomer to PMS. Like Seyferth PMS, Harrod PMS offers access to nearly pure SiC upon pyrolysis.[14,15] The highly crosslinked, solid polymer does not melt on heating and gives ceramic yields of 70–80 wt.%. On heating to *ca.* 1000 °C in N_2, PMS provides near stoichiometric SiC ($SiC_{0.9}H_{0.2}O_{0.1}$), with nanosized β-SiC grains and 5–10 wt.% excess Si. This polymer offers the type of ceramic product desired for SiC fibers.

In related work, Hengge *et al.* used Cp_2MMe_2 to catalyze dehydropolymerization of disilanes:[16]

$$\mathrm{MeH_2SiSiH_2Me\ (neat)} \xrightarrow{\mathrm{Cp_2ZrMe_2}} \mathrm{H[MeSiH_{0.58}]_xH} \quad (3)$$

The low Si:H ratio is indicative of a highly crosslinked and intractable material. These polymers were reported to provide phase pure SiC, although the method of characterization was not described.

The target of the work reported here was to use Harrod PMS precursor to process stoichiometric SiC fibers. The advantages of using Harrod PMS are: a one step, high-yield synthesis; 1:1 Si:C ratio and high ceramic yields. Furthermore, the as-produced polymer is spinnable right from the polymerization solution. Unfortunately $MeSiH_3$, the polymerization catalysts, and the resulting polymer are quite pyrophoric. A nonpyrophoric PMS precursor built by reverse engineering of the precursor developed here will be described at a later date.[15]

The studies described below define parameters that must be considered/controlled in the overall process that leads to stoichiometric, dense SiC fibers. The following sections discuss: (1) synthesis of a spinnable, modified Harrod PMS; (2) fiber spinning; (3) fiber curing; (4) control of stoichiometry during pyrolysis, and (5) conversion of PMS fibers to dense ceramic fibers. Studies on the polymer-to-ceramic transformation process for bulk polymer, using ^{29}Si solid state NMR and FTIR, have been described.[14]

Experimental

1 General synthetic procedures

All air and moisture sensitive materials were handled using standard Schlenk techniques or in the argon atmosphere of a glove box, Vacuum Atmosphere Model No. MO40-2-Dri-Lab. All solvents were distilled in Ar–N_2 and degassed prior to use.

Solvent purification. THF was distilled from sodium benzophenone ketyl. Hexane and toluene were distilled using the same procedure as used for THF with 10 g of tetraglyme added to improve the solubility of sodium benzophenone ketyl. Diethyl ether was distilled from sliced sodium (20 g/2L flask). Acetonitrile was distilled from calcium hydride in Ar (2 g/2 L solvent). Methanol and ethanol were distilled from activated magnesium (5 g Mg, 0.5 g I_2/L solvent). Small quantities of solvent (70 mL) were added first to initiate reaction. A vigorous reaction occurs and after 15 min, 1 L of solvent can be added.

Catalyst syntheses. Cp_2TiMe_2 or Cp_2ZrMe_2 were prepared by reaction of Cp_2TiCl_2 or Cp_2ZrCl_2 with MeLi according to published methods.[12] In general, *ca.* 100 mg of either Cp_2TiCl_2 or Cp_2ZrCl_2 (Strem Chemicals) were placed in a dry 50 mL Schlenk flash with a stir bar (in the drybox). Freshly distilled and deoxygenated hexane was added to this flask using a cannula. Approximately 1.5 mL of 1.4 M of MeLi (Aldrich) in either was added dropwise, and the solution was then filtered through Celite under Ar to remove the resulting LiCl precipitate. The filtrate was evaporated to dryness under vacuum and the product purified by sublimation at 100 °C at 10^{-2} Torr.

Preparation of methylsilane ($MeSiH_3$): CAUTION, this material can burn on contact with air. Commercial $MeSiH_3$ contains sufficient chlorosilane impurities to deactivate the catalyst and further purification before polymerization was necessary. Consequently, two procedures were developed to produce pure $MeSiH_3$: (A) by reacting $MeSiCl_3$ with $LiAlH_4$ using ethylenediamine (en) as the purification agent, and (B) as a by-product of the catalytic redistribution of polymethylhydridosiloxane, –$[MeHSiO]_x$–, as described below.

Method A. $MeSiCl_3$ (Aldrich) was refluxed over Mg turnings and distilled under N_2 to eliminate impurities. Ethylenediamine was stirred over CaH_2 overnight and distilled under N_2. All solvents and reagent liquids were transferred *via* cannulae under N_2. $LiAlH_4$ reduction of $MeSiCl_3$ was run in a flame dried three-necked, 1 L flask. Dry THF (500 mL) was added and the flask was then taken inside the drybox. $LiAlH_4$ (24 g, 0.6 mol), an addition funnel and a condenser were added to the flask, the assembly was removed from the drybox, connected to a Schlenk line and pressure equalized with an N_2 flush. The condenser was cooled to −46 °C with a liquid N_2–MeCN slush. The outlet of the condenser was connected to a 200 mL, thick walled, Pyrex trap charged with 30–50 mL of ethylenediamine (en) and cooled with liquid N_2.

$MeSiCl_3$ (80 mL) was then transferred to the addition funnel and added dropwise to the reaction flask with magnetic stirring. The $MeSiH_3$ gas that evolved and some $MeSiHCl_2$ and $MeSiH_2Cl$ were collected in the en trap over 1–2 h. After addition, the reaction was stirred for 30 min as it warmed to room temperature and was then heated slowly. Vigorous gas evolution was observed at temperatures as low as −20 °C. By employing a stepwise increase in reaction temperature (10 °C steps from 10 to 50 °C), foaming was controlled and the chemical yield maximized. During reaction, the condenser was maintained at −46 °C to condense THF and partially reacted volatiles, *e.g.* $MeSiHCl_2$ and $MeSiH_2Cl$. The level of the trap bath must be high enough to prevent the excape of $MeSiH_3$ out of the bubbler (w/Firestone valve), but low enough to prevent clogging with frozen silane. Slight positive N_2 pressure prevents backflow of silanes into the Schlenk line. The reaction was heated at 50 °C for 4 h. During the last 0.5 h, no further gas evolved for the reaction scale described here. Pure $MeSiH_3$ was obtained by trap-to-trap distillation into an evacuated weighed metal cylinder cooled with liquid N_2. The transfer requires *ca.* 2 h and provides 85–95% yields.

Method B. Reaction was carried out in a dry 2 L, three-necked flash using previously published methods.[17] Initially, 750–900 mL of freshly distilled toluene was added to the flask. A five fold volume of toluene to –$[MeHSiO]_x$– ($M_n \approx 2000$ Da, from Hüls) is required to avoid gelation as redistribution occurs. Then, 150 ml of –$[MeHSiO]_x$– was placed in a dry 250 mL Schlenk flask and degassed by sparging Ar through the oligomer for 1 h. The degassed –$[MeHSiO]_x$– was transferred to the 2 L flask and 5–10 mL of hexane containing 20–40 mg of Cp_2TiMe_2 was added dropwise under Ar. Initiation of the redistribution reaction is slow and can require 0.5–2 h depending on adventitious impurities. Reaction commences when the solution turns royal blue.[17] Redistribution to –$[MeSiO_{1.5}]_x$– occurs concurrent with release of $MeSiH_3$, which can be trapped without using en. The collection time for this reaction is 48–72 h.

2 Polymer synthesis

Polymerization of $MeSiH_3$. This reaction was performed in a 400 mL Parr reactor equipped with magnetic stirrer. The catalyst [Cp_2TiMe_2 or Cp_2ZrMe_2, 327 mg] was dissolved in distilled cyclohexene (80 g) and added to the Parr reactor under Ar–N_2. The reactor was then sealed, cooled with liquid N_2 and evacuated. $MeSiH_3$ was then transferred under vacuum from the metal container (see above) by condensing into the cooled reactor. The resulting solution was warmed to 55 ± 1 °C in a thermostatted oil bath.

Dehydrocoupling occurs with concurrent production of H_2. However, the catalyst also promotes rapid hydrogenation of cyclohexene to cyclohexane. Thus, the reaction was followed by decreases in $MeSiH_3$ pressure with time. The rate of pressure decrease exhibits a linear, first order dependence on initial $MeSiH_3$ pressure. Heating was ceased when the rate of the pressure decrease was < 2 psi h^{-1} [*ca.* 25 h (1 psi $\approx 6.895 \times 10^3$ Pa)] as rapid gelation occurs beyond this point. Unreacted $MeSiH_3$ (with some H_2 and N_2) was transferred back to the attached metal cylinder cooled with liquid N_2. By mass difference, 25 g of $MeSiH_3$ were found to react, giving a 90% yield of PMS. The PMS concentration was *ca.* 0.2 g mL^{-1}. The molecular weight (M_n) was *ca.* 1200 Da.[12,14] This PMS was characterized by NMR, FTIR, TGA and DSC as described below.

Increasing PMS molecular weight. The reaction vessel from above, containing *ca.* 25 g PMS was taken into the dry box and the residual gases vented. A sample (*ca.* 5 ml) was transferred in the dry box to a sealed, 50 ml Schenk flask and heated under Ar at 60 °C until gelation occurred. Gelation times were typically 7–12 h. The remaining polymer solution was then transferred into Schlenk flasks in the dry box. The sealed flasks were removed from the dry box and heated at 60 °C (Ar) to increase the molecular weight (MW). Heating was stopped after a period equivalent to 80–90% of the gel time and the solutions were stored below 0 °C.

Star-branched polymers *via* vinyl modification. To further increase the MW to improve spinnability, and to provide functionality for self-curing, PMS was modified by reaction with tetravinylsilane (TVS), $Si(CH{=}CH_2)_4$, 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane [$SiMe(CH{=}CH_2)NH]_3$, or dimethyldivinylsilane $SiMe_2(CH{=}CH_2)_2$. 5–20 wt.% of these compounds were added to PMS solutions brought to 80–90% of their gelation time. The weight percentage added was based on: ($MeSiH_3$reacted + additive) = 100 wt.%. For example, 48.8 g (1.06 mol) $MeSiH_3$ was polymerized to give 214 ml (PMS + solvent) solution. Therefore, a 30 ml portion of this solution consumed 6.84 g (0.15 mol) $MeSiH_3$. Addition of 0.36 g (2.6 mmol), 0.76 g (5.6 mmol), or 1.71 g (12.5 mmol) TVS to a 30 mL portion of PMS solution results in 5, 10 and 20 wt.% vinylsilane-PMS solutions respectively.

After adding the vinyl compounds, the PMS solutions were again heated at 60 °C (Ar, 12–24 h) to form branched, vinyl-modified PMS (discussed below). After vinylsilane modification, the resulting PMS solution is stable and can be stored at room temperature for > 3 d. Most research focused on TVS modified PMS solutions (TVS-PMS), to avoid incorporating N into the resulting SiC fibers.

Boron modified TVS-PMS. Boron was incorporated into PMS by hydroboration of the residual vinyl groups in TVS-PMS, resulting in B- and TVS-modified PMS (B-TVS-PMS). Several B additives were tested including $Me_2S{\cdot}BH_3$, $THF{\cdot}BH_3$, $NH_3{\cdot}BH_3$, $Me_3N{\cdot}BH_3$ and $C_4H_9N_2{\cdot}BH_3$. Only $Me_2S{\cdot}BH_3$ reacted with TVS-PMS to provide clear, spinnable solutions.

The amount of $Me_2S{\cdot}BH_3$ added was determined by assuming that: (1) no B loss occurs during further processing, and (2) all the Si combines with all the C to form pure SiC after pyrolysis. An example of the synthesis of a successful spinning solution includes: 10 wt.% of TVS (0.8 g, 6 mmol), 3 wt.% $Me_2S{\cdot}BH_3$ (0.24 g, 3.2 mmol), and 87 wt.% reacted $MeSiH_3$ (7 g, 150 mmol), which gives a molar ratio of $Si:C:B \approx 1:1.3:0.015$. Based on the above assumptions, the final B concentration in the SiC product would be 0.4 wt.%. Note that this amount of boron makes no changes in the behaviour of TVS-PMS on pyrolysis to temperatures of 1000 °C. Consequently, the various discussions below do not consider its presence or absence during pyrolysis. The effects of B addition are only important when fibers are processed above 1000 °C. This will be the subject of a following paper.

3 Precursor fiber spinning

Attempts made to melt-draw fibers at 80 °C were not successful as melting Harrod PMS rapidly leads to crosslinking and an intractable material. Thus, efforts focused on dry-spinning.

Dry-spinning (fiber extrusion). All vinylsilane modified PMS solutions were dry-spinnable when concentrated to 0.6–0.8 g mL^{-1} from 0.15–0.25 g mL^{-1}. The resulting solutions were placed in an extruder (Fig. 1) mounted inside an Ar dry box. Typically, 3–5 ml of viscous solution were loaded into the extruder chamber, and fibers were then extruded by applying 100–500 psi Ar pressure to force the polymer through a 140 mm diameter spinneret. These extruded fibers continuously self-draw at 20–40 cm below the spinneret. Longer fibers could not be drawn due to dry box height limitations. Precursor fibers with 70–120 µm diameter collected across a square wooden framework with a spacing of *ca.* 10 cm. The fiber diameters are not uniform because of the crude spinning system. In some cases, thin 30 µm diameter fibers were obtained. The extruded fibers were dried for at least 5 h prior to pyrolysis.

4 Curing

Unmodified Harrod PMS fibers melts on heating. To avoid melting, efforts were made to cure precursor fibers. The methods examined included: (1) low temperature thermal cures; (2) curing with traces of ammonia; (3) curing with γ-irradiation, and (4) curing by incorporating reactive functionality. Only the last method, based on bringing the polymer close to its gelation point and then adding thermally reactive

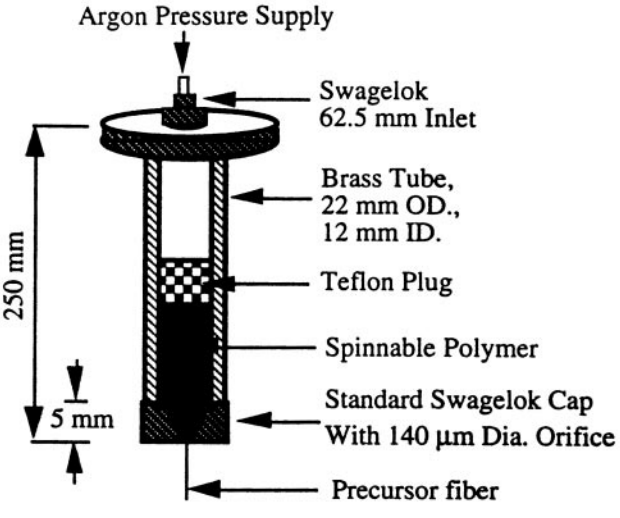


Fig. 1 Schematic diagram of a pressure extruder made from standard swagelock fittings.

vinyl functionality really worked. In this instance, no intermediate curing stages or green fiber pretreatments were necessary as the fibers cured even with heat ramp rates up to 20 °C min^{-1}.

5 Pyrolysis

Precursor fibers were pyrolyzed in Ar to transform them into ceramic fibers. All pyrolysis steps below 1400 °C were carried out in a single zone, Lindberg tube furnace (model No. 58114, Watertown, WI) or a Thermolyne high temperature tube furnace (type 54500, Dubuque, IA). Both tube furnaces are equipped with Eurotherm temperature controllers (model No. 818P, Northing, England). The heating rates used were 5–20 °C min^{-1}. Thinner fibers were cured at 20 °C min^{-1} without loss of fiber integrity.

Pyrolyses above 1400 °C were run in an Astro high temperature furnace (Model 1000). All samples pyrolyzed to >1400 °C were first pyrolyzed to $\geqslant 1000$ °C in a Lindberg furnace, under Ar. Samples were transferred to the Astro high temperature furnace under ambient conditions. The Astro furnace consists of a Eurotherm temperature controller (model No. 818P, Northing, England), a vacuum pump, and an Ar–N$_2$ supply. Two vacuum/Ar fill cycles were applied before starting heat-treatment to ensure elimination of O$_2$/moisture in the furnace. Samples were then heated above 1400 °C at 20–30 °C min^{-1} under flowing Ar.

6 Materials characterization

Thermogravimetric analyses (TGA). TGA studies of PMS precursor were carried out using a Hi-Res TGA 2950 Thermogravimetric TA Instruments Thermal Analyst 2200. Samples of 10–30 mg (chunks) were removed from the drybox and quickly placed in a Pt pan in air. The time required to load the samples was 3–5 min. Samples were then heated (10 °C min^{-1}) to 1000 °C in Ar (60 cm^3 min^{-1}).

Differential thermal analyses (DTA). DTA experiments were conducted on a DSC 2910 differential scanning calorimeter, with a 1600 °C DTA cell, TA Instruments Thermal Analyst 2200. Samples (10–15 mg) were removed from the drybox and quickly loaded in a Pt pan in air. The loading time was 3–5 min. Samples were heated at 5 °C min^{-1} to 1000 °C in Ar (50 cm^3 min^{-1}). Calcined alumina (Aluminum Co. of America) was used as the reference material.

NMR characterization. All solution spectra were run in CDCl$_3$ and recorded on a Bruker AM 360 MHz instrument at room temperature unless otherwise noted. Residual CHCl$_3$ was used as an internal reference. ^{1}H, ^{13}C and ^{29}Si NMR spectra were obtained with the spectrometer operating at 360, 90.6 and 71.5 MHz, respectively. Spin rates of 20 and 14 rps were used for 5 mm and 10 mm tubes respectively. ^{1}H NMR spectra were obtained using a 4000 Hz spectral width, an acquisition time of 4.096 s and 32 K data points. ^{13}C NMR spectra were obtained using a 20 000 Hz spectral width, an acquisition time of 0.8192 s and 32 K data points. ^{29}Si NMR spectra were obtained using an inverse gated technique, a 20 000 Hz spectral width, an acquisition time of 0.819 s, a delay between pulses of 5–10 s and 32 K data points.

Chemical analyses. Elemental analyses for selected pyrolyzed samples were performed by Galbraith Laboratories of Knoxville, TN.

X-Ray diffraction (XRD). XRD powder patterns were obtained using a Rigaku Rotating Anode Goniometer (Rigaku Denki Co. Ltd., Tokyo, Japan). Powder samples (100–200 mg) were ground in an alumina mortar and pestle, packed in a glass specimen holder, and placed in the goniometer. Scans were 5–80° 2θ in 0.01° increments with a 2° 2θ min^{-1} scan speed. Cu-Kα ($\lambda = 1.54$ Å) radiation was used.

Scanning electron microscopy (SEM). Micrographs were taken on a HITACHI S-800 microscope. SEM samples were prepared by breaking fibers into small segments and mounting them on the edge of an aluminum stub using double stick tape. Samples were sputter coated with a layer of Au/Pd to enhance their conductivity. Micrographs of fresh fracture surfaces were recorded to evaluate fiber microstructure.

Results and discussion

1 Modification of PMS

Harrod PMS typically has $M_n = 1000$–2000 Da.[12] NMR spectra provide some information on polymer structure.[4,14] The PMS ^{1}H NMR (Fig. 2) shows only two broad PMS resonances for Si–H (3.87 ppm) and C–H (0.39 ppm); the remainder result from residual cyclohexene, cyclohexane and C$_6$D$_6$. The ^{13}C NMR shows one broad Si–CH$_3$ peak at 9.7 ppm. The ^{29}Si MAS spectrum exhibits resonances at -34.0 and -63.0 ppm,

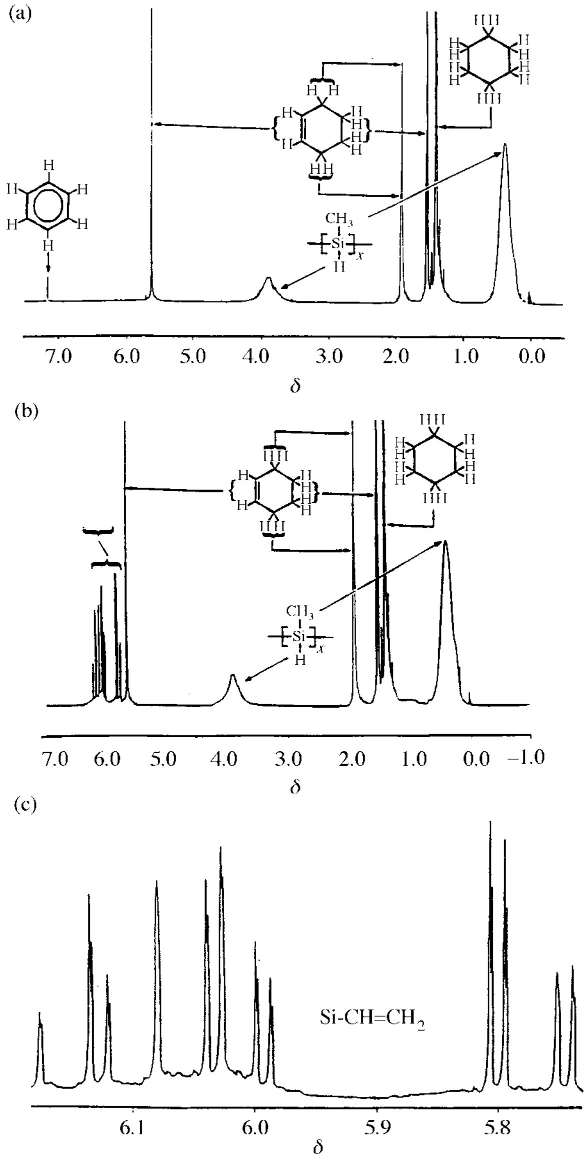
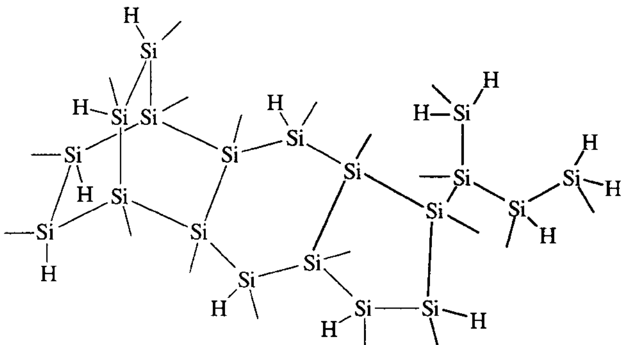


Fig. 2 (a) ^{1}H NMR of polymethylsilane polymer synthesized *via* the Harrod procedure. (b) ^{1}H NMR of 20 wt.% TVS-PMS. (c) Vinyl region of (b) expanded.

corresponding to –MeSiH– units and –MeSiH$_2$ groups respectively.[14]

The broad resonances indicate that the magnetic environments around H and C are not unique, suggesting branching. The ≡Si–CH$_3$: Si–H integration ratio in the ^{1}H NMR spectrum is 4.5:1 rather than 3:1, supporting a branched structure containing cyclics. Assuming $M_n = 1$–1.2 kDa, we can propose an idealized PMS composition as shown in Fig. 3. In related studies that will be described in a following paper,[15] we have identified (by mass spectral analysis) branched cyclics similar to:

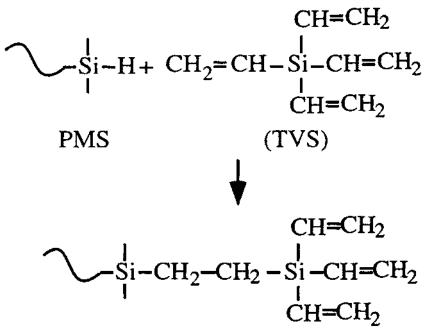


$C_{19}H_{70}Si_{19}$
832.4 Da
$SiC\underline{H}_3{:}Si\underline{H} = 4.4{:}1$

The composition shown in Fig. 3 is proposed based on the structure shown above.[15]

The implication is that dehydrocoupling occurs at both chain terminating –MeSiH$_2$ and backbone –MeSiH– groups. The formation of one tertiary Si for every three silicons suggests that the reactivity of the internal Si–H groups is almost as high as found for the chain ends. However, dehydrocyclization is likely much favored over chain growth because it is a unimolecular process whereas the latter is bimolecular. The implication is that the chain termini (–MeSiH$_2$ groups) are much more reactive than internal Si–H groups as previously suggested by Harrod *et al.*[12,14]

The low MW polymer obtained from the Harrod procedure is an obstacle to fiber spinning. It is difficult to increase MW by simply extending the dehydropolymerization reaction time because gelation occurs readily. However, stable PMS solutions can be obtained by vinyl modification of Harrod PMS. Vinylsilanes react with PMS *via* reaction (4). Hydrosilylation occurs thermally at 150–200 °C;[10,18] however, in our system it occurs at <60 °C most likely aided by a Cp$_2$ZrMe$_2$ derived catalyst.



$$\sim\!\mathrm{Si{-}H} + \mathrm{CH_2{=}CH{-}Si(CH{=}CH_2)_3} \longrightarrow \sim\!\mathrm{Si{-}CH_2{-}CH_2{-}Si(CH{=}CH_2)_3}$$

Vinyl-modified (capped) PMS (4)

The ^{1}H NMR spectrum shows no significant change in the Si–H : Si–CH$_3$ ratio on adding TVS,[19] suggesting that only a small percentage of the Si–H bonds (*e.g.* –MeSiH$_2$ groups) react. If terminal –MeSiH$_2$ groups are the most reactive Si–H sites[12] then TVS most likely reacts with these groups to form vinyl-capped PMS. This implies that MeSiH$_2$ groups also cause gelation. Thus, endcapping should reduce or eliminate gelation. Indeed, following reaction with vinylsilanes, the system is stable at ambient for days to weeks without gelation.

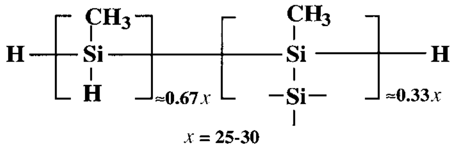
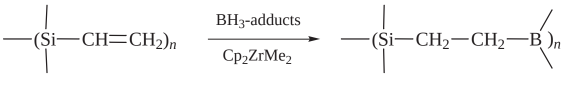


Fig. 3 Idealized molecular structure for PMS.

Because one TVS can react with up to four PMS molecules to form a star-branched polymer, the MW of PMS could increase as much as fourfold as suggested in Fig. 4. Initial efforts to produce high quality SiC fibers from TVS-PMS were unsuccessful because the desired final microstructure was not obtained, as discussed below. Thus efforts were made to introduce boron to the precursor synthesis.

Small amounts of B are known to aid SiC densification during sintering.[20–24] Several B containing organosilicon polymers have been synthesized.[25–27] Riccitiello and coworkers[25,26] and Riedel *et al.*[27] describe reacting BH$_3$ adducts with vinyl modified poly(diorganosilane)s to form B containing polymers. TVS-PMS is an end-functionalized oligomethylsilane (Fig. 4). However, the vinyl groups in TVS-PMS can also react with BH$_3$ adducts, especially in the presence of catalysts, as in the TVS-PMS solution:



$$-(\mathrm{Si{-}CH{=}CH_2})_n \xrightarrow[\mathrm{Cp_2ZrMe_2}]{\mathrm{BH_3\text{-}adducts}} -(\mathrm{Si{-}CH_2{-}CH_2{-}B})_n \qquad (5)$$

This results in the formation of more complex, hyper-branched molecules (Fig. 5). The BH$_3$ adduct used is (Me)$_2$S·BH$_3$. (Me)$_2$S·BH$_3$ and TVS are added simultaneously to a solution of Harrod PMS previously heated to 80–90% of its gel point. One BH$_3$ is potentially capable of reacting with three Si–vinyl groups and should increase the MW and polymer viscosity as shown by Riedel *et al.*[27] Indeed, we have reversed engineered B-TVS-PMS (PMS-TVS-B) by first forming TVS-B and then hydrosilylating this material with PMS to form essentially the identical polymer.[15] This more air stable version exhibits the GPC trace shown in Fig. 6 which supports the structure proposed in Fig. 5; note the expected polymodality of a hyper-branched polymer shown in Fig. 6.

The critical issues are whether or not these modifications impart spinnability, curability and sinterability, as discussed below.

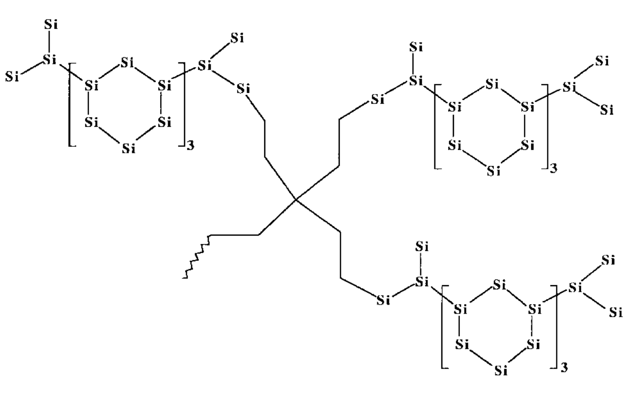


Fig. 4 Proposed molecular structure of TVS-PMS.

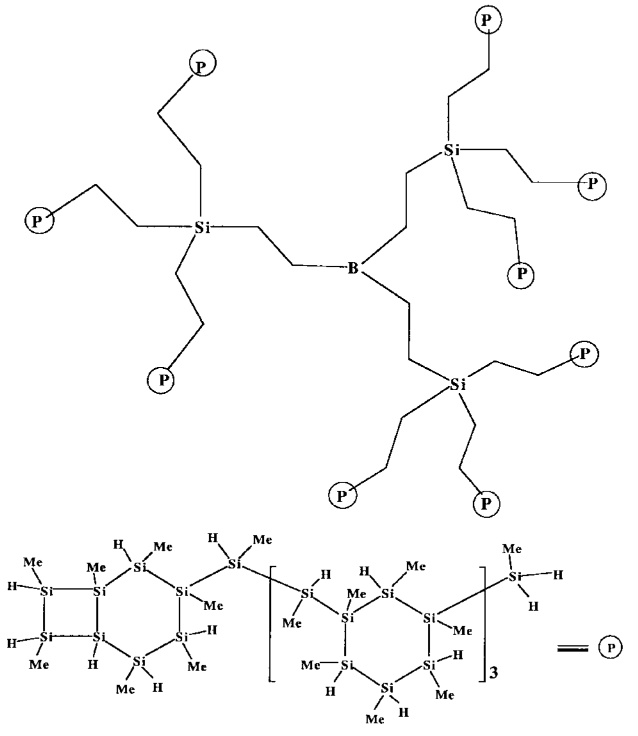


Fig. 5 Proposed B-TVS-PMS molecular structure.

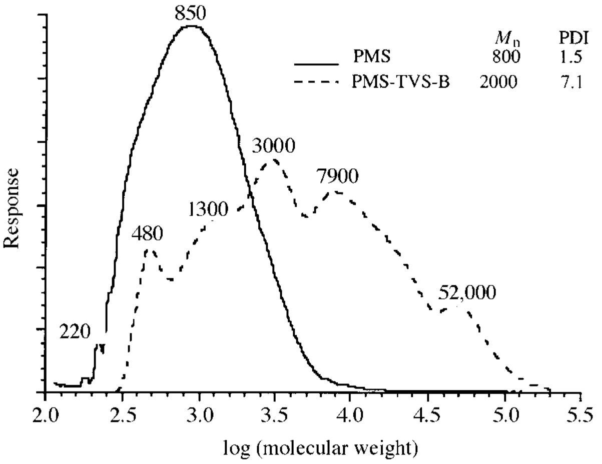


Fig. 6 GPC Trace of reverse engineered PMS and PMS-TVS-B.[15]

2 Precursor fiber spinning

Melt-drawing was initially examined using unmodified PMS. While PMS melts and fibers can be drawn from the melt, the melted polymer crosslinks too rapidly to be considered for long term studies. Extensive efforts were made to cure these fibers, using a variety of processes, without success. Efforts then focused on the developing stable, spinnable, and infusible polymers for dry-spinning.

Toreki *et al.* find that Yajima PCS with molecular weights (MWs) of 5–10 kDa decomposes before it melts. Although it no longer melts, toluene solutions can be dry-spun.[5] Furthermore, because it does not melt, air curing is not necessary and low oxygen content fibers result, although excess C remains a problem. Thus, efforts were made to increase the PMS M_n to >5000 Da.

Initially, efforts were made to extend the duration of dehydrocoupling to improve PMS MWs. To increase catalyst efficiency for chain extension, residual $MeSiH_3$ and H_2 were vented, after completion of the Harrod procedure, to ensure that residual monomer ($MeSiH_3$) would not compete with polymer for catalyst. Depolymerization was assumed to play a minor role in the reaction sequence. After venting, the polymer was reheated at 60 °C for 5–10 h under Ar to increase the MW. The solutions were brought to 80–90% of the gel time. The resulting PMS solutions, containing 0.6–0.8 g mL^{-1} upon partial solvent removal, were suitable for dry-spinning, although the resulting fibers were not infusible. Fig. 7 shows an SEM for a typical precursor fiber with a smooth surface and a dense interior without visible microstructure. The irregular cross-section, typical of dry-spun fibers, is due to uneven drying.

Although this procedure provides improved spinnability, the fibers still melt at 100 °C. Further heating led to increased MWs; however, gels formed rapidly with loss of processability. Thus, two different chemical approaches to improving infusibility, without impairing processability, were explored. One was to increase the MW linearly to increase chain entanglement thereby improving spinnability and raising T_m above the curing point (T_c) to provide polymer infusibility. The other was to introduce reactive functional groups into the polymer structure to provide higher latent reactivity.

To achieve these goals, multifunctional vinylsilanes were incorporated into the precursor synthesis. Multifunctional vinylsilanes are capable of linearly linking two or more PMS molecules together, by reaction with terminal $-MeSiH_2$ groups, as discussed above. Linear increases in MW, obtained with divinyldimethylsilane provided better rheological properties as evidenced by a reduction in fiber necking during spinning; however, the fibers still melted. In contrast, the addition of tri- and tetra-vinyl functionalized silanes provided improved spinnability, and remaining unreacted vinyl groups provide sites for further branching with BH_3 and higher latent reactivity to enhance polymer self-curing.

Note that in all cases mentioned here, the increases in MW are assumed to occur as a consequence of the type of chemistry used; however the pyrophoric nature of the polymers produced precluded conducting MW measurements using standard techniques. A future paper will present more details about the development of higher MW PMS using a much less air sensitive derivative.[15]

The utility of adding vinylsilanes to increase MW is strongly dependent on the length of PMS segments linked. If vinylsilane addition occurs too early, many reactive Si–H sites are elimin-

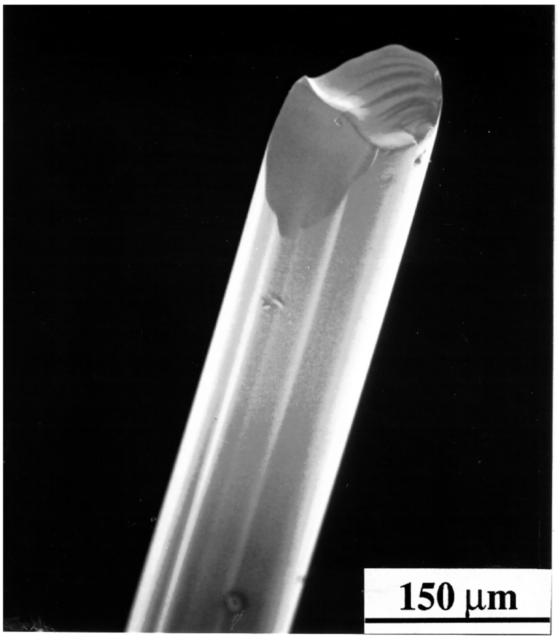


Fig. 7 SEM of an as-spun PMS precursor fiber.

ated at an early stage and only short chain segments are linked together. This limits the MW increases possible and impairs the processability/infusibility. For example, the addition of TVS to PMS heated to <50% of the gel time did not give spinnable materials even after all the solvent was removed. The PMS chains, before vinyl modification, were too short. This led us to add vinylsilane only at 80–90% of the gel time.

After a thorough evaluation of di- and tri-functional vinyl compounds (see Experimental section), TVS was selected for further extensive studies. TVS contains the excess carbon needed to offset the excess silicon produced during pyrolysis and no nitrogen. In principle, TVS offers the opportunity to improve spinnability by increasing the MW (therefore chain entanglements), and because it offers latent reactivity which enhances self-curing. Furthermore, because it appears to cap reactive –MeSiH$_2$ endgroups, it stabilizes the spinning solution. Finally, B-TVS-PMS displays even better spinnability (evidenced by the absence of necking during spinning) than TVS-PMS, likely because the higher degree of branching and higher MW provide better chain entanglement leading to better viscoelastic properties.

The only drawback that remains is the high degree of air sensitivity as illustrated by Fig. 8 which shows the TGA of B-TVS-PMS precursor fibers held at 30 °C for 24 h in dry air. The fibers exhibit a mass gain of *ca.* 30 wt.%, indicating extensive oxidation. This oxidation sensitivity impairs the opportunity to obtain phase pure SiC fibers unless the fibers are processed in an inert atmosphere.

3 Curing unmodified PMS fibers

Before precursor fibers are subjected to high temperature pyrolytic processing, they must be made infusible (cured/crosslinked) so they will not melt on heating. Prior to our discovery of the utility of vinyl-modified PMS, several curing studies were run on unmodified PMS fibers, including the use of low temperature long term pyrolyses, curing with traces of ammonia,[29–31] γ-irradiation[32–34] and by using an excess of catalyst.[10,35] None of these methods proved particularly useful, and efforts turned to enhancing chemical reactivity using vinyl compounds.

4 Curing of vinyl-modified PMS fibers

Schmidt *et al.*[36] showed that on thermolysis, vinylic polysilanes heated at low temperatures generate $R_3Si\cdot$ free radicals solely by scission of Si–Si bonds. These free radicals promote Si–H addition across C=C double bonds (hydrosilylation) which leads to crosslinking. In related work, Seyferth *et al.* showed that radical initiated hydrosilylative crosslinking gave improved PMS ceramic yields.[10,11] These results, coupled with our inability to cure unmodified PMS, led to PMS synthetic strategies that incorporated multifunctional vinyl silanes. In principle, vinyl groups that survive the incorporation process [see Fig. 2(b)] provide the requisite latent reactivity such that fiber melting no longer occurs (see below).

Fig. 2(b) shows that addition of *ca.* 20 wt.% TVS (*ca.* 26 mol% vinyl groups) to PMS solutions provides access to vinyl-modified PMS. Fibers spun from this modified precursor, TVS-PMS, were infusible. However, PMS modified with 20 wt.% $Me_2Si(CH{=}CH_2)_2$ (*ca.* 17 mol% vinyl groups) still melts. One explanation is that precursor infusibility comes not only from amounts of added vinyl groups, but also from macromolecular architecture. Each TVS is potentially capable of linking four PMS chains to form a star branched polymer whereas $Me_2Si(CH{=}CH_2)_2$ can only increase the PMS MW by extending the chain in one dimension to form a new, linear molecular structure. The linear molecular structure may provide insufficient chain entanglement to achieve infusibility.

The importance of molecular architecture on curability is further supported by the fact that addition of 20 wt.% $[SiMe(CH{=}CH_2)NH]_3$ (*ca.* 11 mol% vinyl groups) also provides infusible precursor fibers. This result may arise because $[SiMe(CH{=}CH_2)NH]_3$, with one more vinyl group than $SiMe_2(CH{=}CH_2)_2$, can potentially link three PMS chains to form a star-branched polymer thereby providing sufficient entanglement to aid in spinning and curing. For the reasons mentioned above, TVS was found to be the best choice for further processing studies.

As discussed below, pyrolysis of unmodified PMS gives a mixture of SiC and excess Si. Using TVS to modify PMS compensates for the carbon loss by introducing additional carbon content. However, the correct balance between carbon loss and introduction must be identified to produce phase pure SiC fibers. Fortunately, 5 wt.% TVS provides infusible PMS precursor fibers as effectively as 20 wt.%. This result permits selection of an optimal quantity of TVS to produce stoichiometric SiC.

5 Pyrolysis

After curing, the subsequent step is pyrolytic conversion of the precursor fibers to SiC fibers. In the following section, studies on bulk pyrolytic processing of precursors using thermogravimetric analyses (TGA), differential thermal analyses (DTA) and powder X-ray diffraction (XRD) are discussed. Scanning electronic microscopy and chemical analysis data on SiC fibers will also be described.

Thermogravimetric analyses (TGA) of unmodified PMS and TVS-PMS

Fig. 9 shows the TGA curves for PMS with selected amounts of added TVS. Both unmodified PMS and TVS-PMS precursors have higher ceramic yields (79 and 83 wt.% respectively) than typical Yajima PCS (55 wt.%).[1–4]

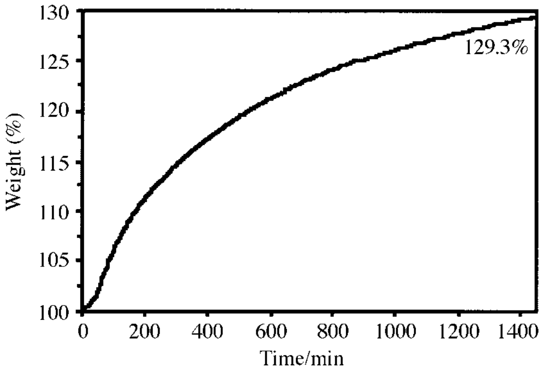


Fig. 8 TGA of TVS-PMS precursor fibers (10 wt.% TVS added) isothermed at 30 °C in dry air for 24 h.

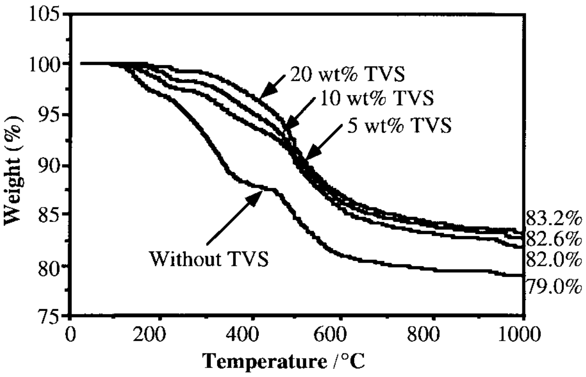


Fig. 9 TGAs of batches of PMS with selected amounts of TVS added. Samples were heated at 10 °C min^{-1} to 1000 °C in Ar.

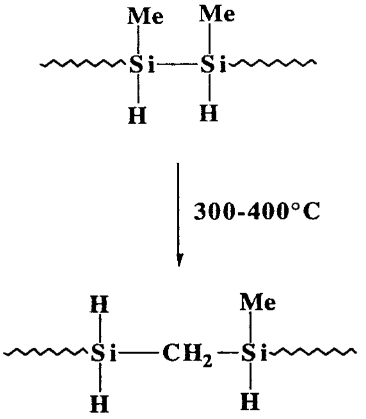
Unmodified PMS has a 1 : 1 Si : C ratio. Ideally, H_2 will be the only gaseous species released during pyrolysis and the 1 : 1 Si : C stoichiometry will be retained after pyrolysis. The theoretical ceramic yield for linear, unmodified $-[MeSiH]_x-$ is 90.9 wt.%. Branched structures, *e.g.*, $-[MeSiH]_x[MeSi]_y-$, will have slightly higher ceramic yields. However, TGAs of different batches of unmodified PMS gave ceramic yields ranging from 61 to 79 wt.% (Fig. 9) indicating some loss of C and/or Si occurs concurrent with release of H_2. The TGA profiles of PMS and TVS-PMS (Fig. 9) reveal several stages of mass loss.

Stage 1: below 200 °C, the mass loss is insignificant (<3 wt.%), indicating good stability to this temperature. The observed mass loss is likely due to volatile low MW species.

Stage 2: in the 200–400 °C range unmodified PMS undergoes mass losses in the range 13–30 wt.%, indicating that primary decomposition processes take place in this range and/or low molecular weight cyclics volatilize. Kobayashi *et al.* observe release of $MeSiH_3$ in this range.[13] They suggest that $MeSiH_3$ forms by cleavage of terminal $-MeSiH_2$ groups. Low MW, short chain and/or branched polymers will have more terminal groups than high MW, long chain, linear polymers or species containing cyclic structures. The mass loss ranges for Harrod PMS batches vary considerably depending on the reaction conditions, storage time after synthesis and solution concentration because reaction continues under ambient conditions.

TVS-PMS has smaller, quite consistent mass losses (7–10 wt.%), implying that TVS modification provides a more stabile PMS with a well defined MW and architecture. By heating TBS-PMS to 50–150 °C, retained vinyl groups will react with remaining $-MeSiH_2$ groups, and internal Si–H sites to crosslink the polymer. This process, seen in the DTA (below), ties up terminal $-MeSiH_2$ groups increasing ceramic yield and coincidentally reducing gas evolution related defects in the resulting ceramic fibers. TVA-PMS also appears to undergo Kumada rearrangement [reaction (6)] as discussed below.

Stage 3: in the 400–600 °C range, unmodified PMS undergoes Kumada rearrangement (as seen by FTIR and NMR studies)[14,15] and loses 7–8 wt.%. The mass loss in this temperature range is ascribed to release of CH_4 and H_2 per Kobayashi *et al.*[13]



$$\sim\!\mathrm{Si(Me)(H)}-\mathrm{Si(Me)(H)}\!\sim \xrightarrow{300\text{-}400^\circ C} \sim\!\mathrm{SiH_2}-\mathrm{CH_2}-\mathrm{Si(Me)(H)}\!\sim \quad (6)$$

Stage 4: in the 600–1000 °C range, only minor mass loss (<2 wt.%) is observed, likely due to H_2 evolution (see DRIFTS below).

The TGA profile of 10 wt.% TVS-PMS precursor fibers is very similar to that of the bulk material.

DTAs of unmodified PMS and TVS-PMS

DTAs (Ar) or PMS precursors with selected amounts of added TVS are shown in Fig. 10. As can be seen, the DTA profiles indicate a multitude of events that are discussed as for the TGA studies.

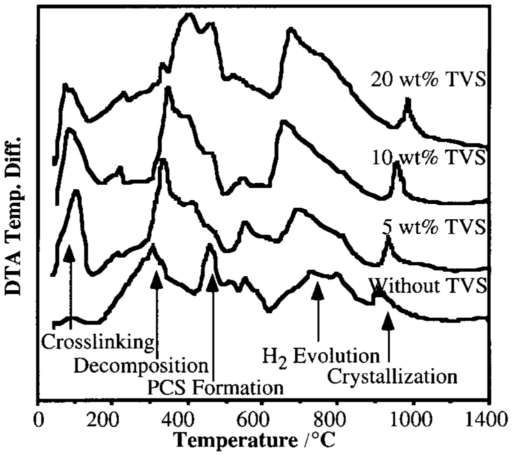


Fig. 10 DTAs of PMS with selected amounts of TVS added. Samples were heated at 10 °C min^{-1} to 1000 °C in Ar.

Stage 1: below 200 °C, unmodified PMS exhibits a slight endotherm, likely due to volatilization of low MW species, or residual solvent. The TVS-PMS precursors exhibit an exotherm at low temperatures (50–150 °C) not seen for unmodified PMS. This exotherm is ascribed to thermally promoted hydrosilylative crosslinking of remaining vinyl groups. Schmidt *et al.*[36] and Schilling[37] observed similar exotherms at 150–300 °C for such processes. The lower temperature range observed here is probably due to the presence of active catalyst.

Stage 2: between 200 and 400 °C, a broad exotherm appears in the DTA of the unmodified PMS. This transition could result from a decomposition reaction that involves cleavage of terminal $-MeSiH_2$ groups, with simultaneous coupling of the resulting fragments, and evolution of $MeSiH_3$, as proposed by Kobayashi *et al.*[13] who report the release of H_2 at this stage indicating that dehydrocoupling continues with heating. A similar exotherm is not observed in the DTAs of TVS-PMS precursors. The probable reason is that loss of $-MeSiH_2$ groups is minimized by crosslinking as discussed above and as supported by TGA results which show only minor mass losses for TVS-PMS in the 200–300 °C range compared to unmodified PMS.

An exotherm for the TVS-PMS precursors is seen in the 300–450 °C region. Similar exotherms are also observed by Schmidt *et al.*[36] and Schilling[37] in DTAs of vinyl-substituted polysilane decomposition. The exact source of this exotherm is not clear at this point, but may be associated with the Kumada rearrangement, see below.

Stage 3: between 400 and 500 °C, a strong exotherm appears in the DTA for unmodified PMS. IR and ^{29}Si solid state NMR indicate that the Kumada rearrangement occurs in this temperature range.[14,15] The Kumada rearrangement also occurs in TVS-PMS, as shown by DRIFTS studies.[38] However, the TVS-PMS DTA does not show the same strong, sharp exotherm. It seems that the PMS to PCS transition exotherm shifts to lower temperature, and is partially hidden by an exotherm ascribed to loss of CH_4 and H_2. If this is in fact the case, then it is possible that the two events occur simultaneously. Another possibility is that free radicals generated during thermally promoted hydrosilylative crosslinking promote the PMS to PCS transition. More detailed studies are required to understand the exact source of these transitions and exotherms.

Stage 4: the DTAs for unmodified PMS and TVS-PMS precursors show broad exotherms between 600 and 900 °C. These exotherms most likely result from H_2 evolution, according to the studies of Kobayashi *et al.*[13] and hydrogenated SiC results. The relatively sharp peaks at $\geqslant 900\,^{\circ}C$ result from crystallization of SiC, as supported by solid state NMR, DRIFTS and XRD studies.[14,18,38]

Powder X-ray diffraction (XRD) of unmodified PMS and TVS–PMS

In stages 1–4 (pyrolysis $\leqslant 800\,^{\circ}C$), the XRD patterns of unmodified PMS and TVS-PMS exhibit amorphous features. No defined diffraction peaks can be observed in XRDs of samples heated to $< 800\,^{\circ}C$. Samples heated to 1000 °C (not shown) show three broad peaks at $2\theta \approx 35$, 60 and 72° corresponding to the (111), (220) and (311) peaks of β-SiC, and indicating crystallization occurs at $\leqslant 1000\,^{\circ}C$.

Chemical analyses of TVS-PMS derived SiC

Chemical analyses show that pyrolysis of unmodified PMS to 1000 °C (1 h, Ar) produces a material containing *ca.* 72.4 wt.% Si, 25.4 wt.% C and trace amounts of H, indicating the presence of excess Si (Si : C = 1.22 : 1). Adding TVS permits balancing the carbon loss, thus chemical analysis of 10 wt.% TVS-PMS produces a material with 68.9 wt.% Si and 31.4 wt.% C (Si : C = 1 : 1.06), after pyrolysis to 1000 °C (1 h, Ar). Chemical analysis of 1000 °C pyrolyzed fibers derived from this TVS-PMS gives 69.7 wt.% Si and 29.0 wt.% C (Si : C = 1.03 : 1). Therefore, careful control of the amount of added TVS leads to near-stoichiometric SiC fibers.

Scanning electron microscopy (SEM) of TVS-PMS/B-TVS-PMS derived SiC fibers

Fig. 11 shows a SEM micrograph of a 10 wt.% TVS-PMS precursor fiber heated to 1000 °C. The fibers exhibit dense interiors and surfaces; however, at this point the fibers are nanocrystalline (2–4 nm size crystallites) and have densities (2.3 g cm^{-3}) that are much lower than theory (3.2 g cm^{-3}). Heating to temperatures of up to 1800 °C leads to densification to *ca.* 3.1 g cm^{-3}.[28]

SiC produced from B-TVS-PMS (0.04 wt.% B after pyrolysis) behaves identically to TVS-PMS derived SiC up to 1000 °C. No changes are observed by any of the analytical techniques used above. Likewise fibers produced using B-TVS-PMS are essentially identical to those produced without B; however, densities increase slightly to 2.5 g cm^{-3}. It is only on processing these fibers to higher temperatures that significant changes occur. These changes and fiber mechanical properties are the subject of the next paper in this series. In future papers, we will describe the synthesis of a more air stable precursor,[39] the use of PMS for joining applications[40] and for the manufacture of particle and fiber reinforced composites.[41,42]

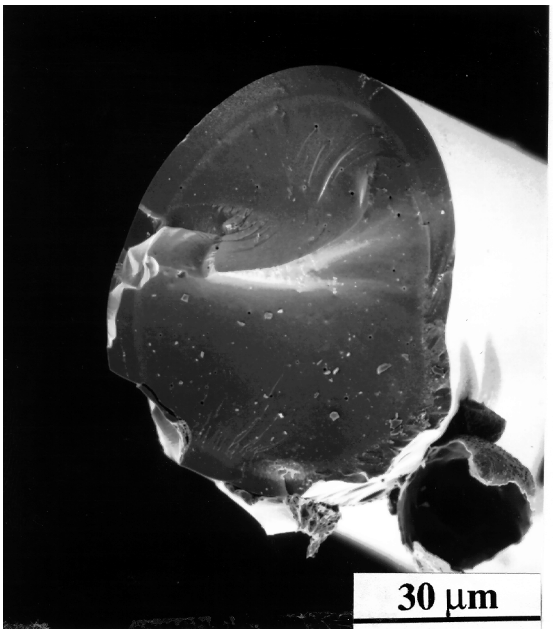


Fig. 11 SEM micrograph of a TVS-PMS fiber (10 wt.% of TVS added) heated to 1000 °C for 1 h in Ar.

Conclusions

Extensive efforts were made to learn to modify polymethylsilane (PMS) produced directly by dehydrocoupling of $MeSiH_3$ to obtain spinnable polymers. It was determined that careful control of the polymerization reaction conditions provided access to a branched version of PMS that exhibits viscoelastic properties that just permit it to be spun. Unfortunately, the spun fibers do not survive pyrolysis to give SiC ceramic fibers. Furthermore, the as-synthesized PMS is highly flammable.

The addition of chain extending/branching molecular additives containing tri- and preferably tetra-vinyl functionality, prior to the PMS gel point, provides access to higher molecular weight, highly branched materials with improved viscoelastic properties such that improvements in spinning are attained with increased resistance to oxidation. The latter appears to result from capping of residual Si–H groups that are more susceptible to oxidation. Furthermore, the added vinyl compounds provide reactive sites that promote thermal crosslinking and decomposition of the spun fibers before they melt. Finally, by controlling the amounts of additives, it is possible to adjust the stoichiometry of the resulting ceramic fiber from silicon rich, to exactly stoichiometric SiC, to carbon rich fibers. The results of these studies have suggested a new way to prepare related spinnable precursors that are even less air sensitive and permit processing in air.[41,42]

Acknowledgements

The authors would like to thank the Army Research Laboratories for generous support of this work through contract No. DOD-C-DAAL04-91-C-0068.

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Paper 8/05288C