# Ceramization of Reflux-Treated Polymethylsilane Precursors to Silicon Carbide

Masaki Narisawa, Takashi Iseki, Yoshiro Katase, and Kiyohito Okamura<sup>\*</sup>

Department of Metallurgy and Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai 599-8531, Japan

## Kunio Oka and Takaaki Dohmaru

Institute for Advanced Science and Technology, Osaka Prefecture University, Sakai 599-8570, Japan

The pyrolysis of polymethylsilane (PMS) in an argon gas environment with a flow rate of 1 L/min was investigated as a standard pyrolytic process, and the investigation showed Si-Si network formation at 573 K. Subsequently, various condensed PMS resins were prepared by adjusting pre-heattreatment or reflux conditions in the temperature range of 423-723 K. The effect of pre-heat treatment or refluxing on the ceramic yield at 1273 K was quantitatively evaluated. Structural evolution in the PMS resins prepared under various reflux conditions was investigated during pyrolysis up to 1873 K. The X-ray diffraction patterns of the pyrolysis products revealed crystallite growth of β-SiC and silicon at 1273–1473 K.<sup>29</sup>Si solid-state nuclear magnetic resonance with the singlepulse method was also conducted on the pyrolysis products at 1273 K.

### I. Introduction

 $\mathbf{S}_{\text{SYNCE}}$  the work of Schilling *et al.*<sup>1</sup> on polymethylsilane (PMS) synthesis in the mid-1980s, numerous studies have been performed on PMS for use as silicon carbide (SiC) precursors.<sup>2-21</sup> The initial interest in PMS was based on its use for tailoring SiC materials without excess carbon by the polymer precursor method. Toward this purpose, various chemical techniques for PMS manufacture have been reported. In particular, the role of cross-linking agents for PMS pyrolysis has been widely investigated. The use of metallocene catalysts to promote a dehydrogenation reaction on Si-H represented the earliest attempt.<sup>3</sup> In recent years, the use of boron compounds was reported to effectively increase residual ceramic yield<sup>12,17,19</sup> while maintaining the precursor processability.

It has become apparent that SiC materials derived from PMS usually contain a considerable amount of excess silicon, because of the evolution of hydrocarbon gas species during pyrolysis. However, the conversion of the PMS precursors from the amorphous to the crystalline state, including phase segregation,<sup>4,5</sup> has not been characterized in detail. The formation of excess silicon phase at high temperatures is considered to diminish the high-temperature stability of the SiC ceramics derived from the PMS. However, PMS combined with suitable metal sources is a promising precursor system for new functional ceramic hybrids composed of SiC

and a metal silicide,<sup>3,22–24</sup> because the metal additive in the PMS will react with excess silicon during pyrolysis.

On the other hand, we recently found that the overall ceramic yield of PMS was improved simply by heating the polymer at 423-723 K in a long vertical furnace with a reflux condenser attached on the upper side of the sample cell.<sup>16,21</sup> By adjusting the reflux conditions, we obtained various types of condensed resins from the PMS.

In this paper, the structural evolution of these condensed PMS resins is investigated in terms of X-ray diffractometry (XRD) patterns and solid-state <sup>29</sup>Si nuclear magnetic resonance (NMR) spectra obtained by the single-pulse method.<sup>2,4,5</sup> Elemental analyses on the resulting pyrolysis products are also described.

## **II. Experimental Procedure**

#### (1) Preparation of PMS Samples and Pyrolysis Products

The original PMS was prepared by a condensation reaction of methyldichlorosilane with sodium, as described elsewhere.3,20 The PMS obtained was a pale yellow, viscous liquid after evaporation of the solvent  $(M_w) = 1780$ ,  $M_w/M_n = 2.0$ ). The molecular structure of the synthesized PMS was characterized by <sup>1</sup>H NMR analysis to be  $[(CH_3SiH)_{0.60}-(CH_3Si)_{0.40}]_n$ .

The synthesized PMS was placed in a quartz crucible (inner diameter: 15 mm, depth: 100 mm), which was suspended in a furnace equipped with molybdenum silicide (MoSi<sub>2</sub>) heaters. The PMS then was heated from room temperature (RT) to the defined temperatures (523-1273 K) at a rate of 5 K/min in an argon gas flow. The argon flow rate was 1 L/min. The holding time at each temperature was 2 h. For pyrolysis at 1473, 1673, and 1873 K, the sample pyrolyzed at 1273 K was placed in a graphite crucible, and the crucible was rapidly put into the graphite furnace that had been preheated to the appointed temperatures. The argon flow rate again was 1 L/min, and the holding time at each temperature was 15 min.

To investigate the effect of PMS condensation on the resulting ceramic yield, the following two types of pre-heat treatment were performed on the PMS.

(1) A quantity (1.0 g) of the synthesized PMS was placed in the aforementioned quartz crucible suspended in the furnace and heat-treated at 523-723 K (heating rate: 5 K/min, holding time: 2 h). The argon flow rate was 1 L/min. All of the volatile compounds that formed from the PMS during the heat treatment were flowed out under this condition.

(2) The PMS (1.0 g) was placed in a Pyrex<sup> $\dagger$ </sup> tube (diameter: 20 mm, length: 500 mm) to be cross-linked under reflux conditions.<sup>16,21</sup> The Pyrex tube was then placed inside a larger Pyrex cell (diameter: 40 mm) equipped with a reflux condenser and a vacuum pump. After evacuation for a sufficient time to remove

G. Grathwohl-contributing editor

Manuscript No. 187445. Received September 24, 2001; approved September 27, 2002

Part of this study in the reflux treatment process for PMS resin condensation was supported by Collaborative Research Project of Materials and Structures Laboratory, Tokyo Institute of Technology. \*Member, American Ceramic Society.

<sup>&</sup>lt;sup>†</sup>Corning, Inc., Corning, NY.



Fig. 1. Residual mass of PMS after simple pyrolysis in an argon gas flow.

oxygen and moisture in the cell, the cell was heated at 423-723 K (heating rate: 5 K/min, holding time: 2 h). During the reflux treatment, formation of mist in the inner Pyrex tube was observed above 473 K.

After the heat treatment (steps (1) and (2) above), the condensed resin had the appearance of a pale-yellow gum at 423–523 K and maintained some elasticity; at 573–723 K, it was an orange, fragile solid. The condensed resins were pyrolyzed at 1073, 1273, 1473,

1673, and 1873 K. Pyrolysis at 1073 and 1273 K was performed using a furnace equipped with  $MoSi_2$  heaters (heating rate: 5 K/min, holding time: 2 h, argon flow rate: 1 L/min). Pyrolysis at 1473, 1673, and 1873 K was performed using the  $MoSi_2$  furnace and the preheated graphite furnace, as described earlier.

## (2) Measurements

Infrared (IR) spectra were obtained using a spectrometer (Model 1600, Perkin–Elmer, Inc., Norwalk, CT). NMR spectra for the soluble samples also were recorded on a spectrometer (Model Gemini 2000, Varian, Inc., Palo Alto, CA). Solid-state NMR for <sup>29</sup>Si and <sup>13</sup>C was conducted (Model Unity INOVA-300, Varian) at 75 and 59.6 MHz. A cross-polarization magic-angle-spinning (CP-MAS) method was applied up to the pyrolysis temperature of 1073 K. In addition, the single-pulse method, with a delay time of 30 s, was used for the pyrolysis products at 1073, 1273, or 1473 K, to obtain the <sup>29</sup>Si NMR spectra.

Thermogravimetric (TG) analyses were conducted (Model TAS 200, Rigaku Co., Ltd., Tokyo, Japan) on 10 mg of the PMS samples in an argon gas flow, at a heating rate of 10 K/min, up to 1273 K. Decomposition gas analyses during the step-by-step pyrolysis were conducted using gas chromatography/mass spectrometry (Model QP5050A, Shimadzu Corp., Kyoto, Japan) and gas chromatography (Model G-5000, Hitachi Co., Ltd., Tokyo, Japan) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). A quantitative estimation of the individual gas species was performed in terms of standard methane and hydrogen gas samples with defined partial pressures.

The XRD patterns were investigated (Model RINT 1100, Rigaku) using CuK $\alpha$  radiation. Elemental analyses of the pyrolyzed products at 1673 K were conducted by electron probe



Fig. 2. NMR spectra of PMS after simple pyrolysis in an argon gas flow: (a) <sup>29</sup>Si NMR and (b) <sup>13</sup>C NMR.



Fig. 3. Gas-evolution profile of PMS during step-by-step pyrolysis.

microanalysis (EPMA; Model JXA-870, JEOL, Tokyo, Japan), with the averaged values of five points. A polished cross section of Nicalon<sup>‡</sup> fiber (NL-200: SiC<sub>1.34</sub>O<sub>0.36</sub>) was used as the standard for elemental silicon, carbon, and oxygen.

#### III. Results and Discussion

## (1) Thermal Decomposition Process of PMS in an Argon Gas Flow

The residual mass of the PMS after heat treatments in flowing argon gas is shown in Fig. 1. The plotted residual masses at individual temperatures are consistent with the reported TG curves of PMS polymers with low ceramic yields ( $\sim$ 30 mass% at 1273 K).<sup>3,8</sup> A large mass loss,  $\sim$  40%, occurred at 523–623 K, and the mass loss up to 523 K was  $\sim$ 15%. Above 623 K, a small, continuous mass loss was observed up to 723 K.

The <sup>29</sup>Si and <sup>13</sup>C NMR spectra of the pyrolysis products are shown in Figs. 2(a) and (b), respectively. After pyrolysis at 573 K, the signal assigned to <u>Si</u>C(H)Si<sub>2</sub> (-67 ppm) disappears, and the sharp signal assigned to <u>Si</u>CSi<sub>3</sub> (-75 ppm) appears in the <sup>29</sup>Si NMR spectra.<sup>8,13</sup> On the other hand, the signal assigned to <u>C</u>(H<sub>3</sub>)Si (methyl groups: -10 ppm) in the <sup>13</sup>C NMR spectra shows a small down-field shift but is a dominant peak at 573 K.<sup>8,12,13</sup> In the measured IR spectra, decreases in the Si—H stretching band

<sup>‡</sup>Nippon Carbon Co., Tokyo, Japan.

 $(2102 \text{ cm}^{-1})$  and the SiH<sub>2</sub>-deformation band (terminal groups: 932 cm<sup>-1</sup>) are shown at 573 K. These results indicate the formation of a Si—Si cross-link at 573 K, whereas the methyl groups have not decomposed.

Above 573 K, the signals assigned to  $\underline{SiC}_2(H)Si (-38 \text{ ppm})$ ,  $\underline{SiC}_3Si$ , or  $\underline{SiC}_3H (-15 \text{ ppm})$ , and  $\underline{SiC}_4 (0 \text{ ppm})$  appear in the <sup>29</sup>Si NMR spectra,<sup>25–27</sup> and the signal assigned to  $\underline{C}(H_2)Si_2 (0 \text{ ppm})$ appears in the <sup>13</sup>C NMR spectra.<sup>25</sup> At 723 K, these signals assigned to  $\underline{SiC}_2(H)Si$ ,  $\underline{SiC}_3Si$  (or  $\underline{SiC}_3H$ ), and  $\underline{SiC}_4$  in the <sup>29</sup>Si NMR spectra show a marked increase, while the signals assigned to  $\underline{SiCSi}_3$  disappear. At the same temperature, the signal assigned to  $\underline{C}(H_2)Si_2$  in the <sup>13</sup>C NMR spectra becomes dominant, while the signal assigned to  $\underline{C}(H_3)Si$  disappears. This temperature range is consistent with the large increase of the Si—CH<sub>2</sub>—Si band (1100 cm<sup>-1</sup>)<sup>2,28</sup> in the IR spectra. These results indicate cleavage of the Si—Si bonds at 573–723 K and the incorporation of methyl groups into Si—Si to form Si—CH<sub>2</sub>—Si bridges (Kumada rearrangement process).<sup>27–30</sup>

Above 723 K, several overlapping signals near -40 ppm to  $\sim 40$  ppm are convoluted to one broad signal (0 ppm) in the <sup>29</sup>Si NMR spectra. The shift of the <u>CSi<sub>4</sub></u> signal, from 0 ppm to 20 ppm is also observed in the <sup>13</sup>C NMR spectra. These changes in the NMR spectra probably correspond to hydrogen loss during heat treatment.

Figure 3 shows gas evolution from the PMS during the step-by-step pyrolysis. The large mass loss and the evolution of gaseous silicon compounds at 523–623 K suggest fragmentation

oligomer)



Fig. 4. Mechanism of redistribution reaction via silyl radicals.



Fig. 5. Residual mass of PMS with reflux heat treatment.

of PMS chains, whereas the <sup>29</sup>Si NMR and <sup>13</sup>C NMR spectra suggest Si—Si cross-linking. The evolution of methane is substantial at 623–823 K. Most of the methyl groups in the PMS have been incorporated into Si—Si bonds to form Si—CH<sub>2</sub>—Si bridges in the same temperature region, which were observed in the change of the IR and NMR spectra. However, some of the methyl groups have been eliminated in the form of methane. The evolution of hydrogen occurs over a wide temperature range. In particular, the hydrogenevolution peak at 823–923 K is consistent with the conversion process of the Si—CH<sub>2</sub>—Si bridges into a SiC network.

It may seem strange that Si—Si cross-linking is accompanied by Si—Si cleavage at ~573 K. Numerous schemes have been proposed for Si—Si cross-link formation in PMS, which should depend on the chemical nature of the adopted cross-linking processes. In this simple heat-treatment process, the redistribution reaction mechanism proposed by Boury would be applicable,<sup>12</sup> because the redistribution reaction always yields low-molecularweight components in addition to the Si—Si network.

The silyl radicals formed during cleavage of the PMS main chains probably play a role in the redistribution reaction. Figure 4 shows the mechanism of the redistribution reaction in terms of the radical behavior. In Fig. 4, Si—H groups in the PMS trap the silyl



**Fig. 6.** Overall ceramic yield of PMS after heat treatment at 423-723 K and pyrolysis at 1273 K ((- - -) direct pyrolysis in an argon gas flow with a heating rate of 5 K/min from RT to 1273 K and a holding time of 2 h at 1273 K).



Fig. 7. XRD patterns of the PMS pyrolysis products in a simple argon gas flow.

radicals formed by the cleavage of the PMS main chains. Thus, hydrogen radicals form. Some of these radicals can attack Si—H or Si—Si in the PMS again, while the remaining radicals form stable species (hydrogen gas, methylsilane gases, and terminal groups in silane oligomers). On the other hand, silylene intermediates are known to be stable when compared thermodynamically with the silyl radicals.<sup>27,31,32</sup> The insertion of the silylene into the Si—H bonds is another promising chemical reaction to explain the sudden formation of <u>Si</u>CSi<sub>3</sub> at ~573 K. Silylene would form easily, particularly at the terminal groups (—Si(CH<sub>3</sub>)H<sub>2</sub>) of the PMS.

#### (2) Effect of Reflux Treatment on PMS

Figure 5 shows the residual masses of the PMS samples after reflux treatment. Up to 523 K, the residual masses after reflux treatment are almost the same as those of PMS simply heat-treated in an argon gas flow. Above 523 K, the residual masses are still high under reflux treatment, whereas the values suddenly decrease under simple heat treatment (Fig. 1). IR and NMR spectroscopic analyses revealed that structural evolution in PMS accelerates with reflux treatment, as compared with simple heat treatment at exactly the same temperature. However, the observed difference in the spectra was smaller than that caused by a 50 K difference in the heat-treatment temperature.

Thus, it is natural to suppose that the main chemical reactions under reflux conditions are almost the same as those under simple heat treatment in flowing argon gas. Because the formed lowmolecular-weight components (silane oligomers) are cooled at the upper side of the cell, they revert to a condensed resin to be cross-linked again. This effective incorporation of the oligomers should increase the residual mass.

When PMS is heat-treated once at >623 K, either under reflux conditions or in a simple argon gas flow, the obtained resins do not show large mass loss at higher temperatures. The residual masses at 1273 K are usually >95%, based on the condensed resin masses. Figure 6 summarizes the overall ceramic yields after the two-step heat treatment (first step: 423-723 K, second step: 1273 K). The overall ceramic yield becomes a stable value,  $\sim$ 75%, above 623 K in the case of reflux treatment. Even under simple heat treatment in flowing argon gas, the overall ceramic yield is improved by holding at 523 or 573 K. However, the overall ceramic yield does not exceed 50%. Holding at higher temperature, >573 K, in flowing argon gas is not as effective as holding at 523 or 573 K for improving ceramic yield. The overall ceramic yield tends to decrease to  $\sim 40\%$  under those conditions, although the value is still higher than after direct pyrolysis (heating rate: 5 K/min from RT to 1273 K, holding time: 2 h).



Fig. 8. XRD patterns of the products derived from the refluxed PMS resins after pyrolysis at (a) 1273 K and (b) 1473 K.

## (3) Conversion Process from Amorphous to Crystalline State The XRD patterns of the PMS pyrolyzed in an argon gas flow

are shown in Fig. 7. SiC crystallites and excess silicon are shown at 1073 K. Up to 1273 K, the SiC crystallites are small (1-3 nm). At 1473 K, the SiC crystallites show substantial growth. In the



Fig. 9. Apparent crystallite sizes estimated from the XRD (111) line width in the pyrolysis products at 1273–1873 K (crystallite sizes ( $\sim$ 3 nm) estimated for pyrolysis at 1273 K are not completely precise, because the measured lines are highly broadened).

observed temperature region, all of the peaks in the XRD patterns have been assigned to  $\beta$ -SiC and silicon.

Figures 8(a) and (b) show the XRD patterns of the pyrolysis products derived from the refluxed PMS resins at 1273 and 1473 K, respectively. At 1273 K, all of the XRD patterns are broad, showing a SiC amorphous structure with traces of silicon. The difference in the pre-heat-treatment conditions has no influence on



Fig. 10. Results of deconvolution of the <sup>29</sup>Si NMR spectrum of the pyrolysis product at 1273 K in a simple argon gas flow.



Fig. 11.  $^{29}$ Si NMR spectra of the pyrolysis products at 1273 K derived from the refluxed PMS resins.

the observed XRD patterns. At 1473 K, all of the products show substantial growth of  $\beta$ -SiC and silicon. However, the XRD patterns of the products derived from the PMS resin refluxed at 523 K maintain a broad appearance, compared with those of the other three samples.

Figure 9 shows the apparent SiC crystallite sizes in the pyrolysis products derived from the refluxed PMS resins, estimated from the half-height line width of the (111) line at 1273–1873 K. The crystallites in the pyrolysis products derived from the resin refluxed at 523 K always show the smallest sizes among the four samples. On the other hand, the crystallites in the products derived from the untreated PMS or the resin refluxed at 723 K are usually larger. Crystallite growth of silicon decreases under reflux treatment at 523 K.

In the <sup>29</sup>Si solid-state NMR spectra for the products of pyrolysis in flowing argon gas under the single-pulse method, the product at 1073 K shows a broad signal with a maximum at -10 ppm. This result is consistent with the amorphous structure indicated in the XRD patterns. However, at 1273 and 1473 K, the observed signals are composed of several sharp signals that overlap each other.

Figure 10 shows the result of deconvolution for the observed spectra under pyrolysis at 1273 K (R<sub>1</sub>: -13.1 ppm, R<sub>2</sub>: -15.2 ppm, R<sub>3</sub>: -20.1 ppm, R<sub>4</sub>: -24.0 ppm). The signal at -15.2 ppm (R<sub>2</sub>) can be assigned to type A (second neighbors: 12Si, cuboctahedron) silicon atoms in  $\beta$ -SiC (3C). On the other hand, the signals at -13.1, -20.1, and -24.0 ppm (R<sub>1</sub>, R<sub>3</sub>, R<sub>4</sub>) have been assigned to type A, type B (second neighbors: 12Si, twinned cuboctahedron), and type C (second neighbors: 12Si and 1C, capped cuboctahedron) silicon atoms in  $\alpha$ -SiC (6H, 15R,...), respective-ly.<sup>5,33,34</sup> The difference in the peak positions of R<sub>1</sub> (type A in  $\alpha$ ) and R<sub>2</sub> (type A in  $\beta$ ) probably reflects the change in long-range ordering in the pyrolysis products.

Surprisingly, some of the silicon atoms in such amorphous or nanocrystalline SiC possess the same coordination as those in

Table I. Elemental Analyses of Pyrolysis Products<sup>†</sup>

		Content (at.%	)		
Sample condition	Silicon	Carbon	Oxygen	$SiC_xO_y$ formula <sup>‡</sup>	
Original 523 K 623 K 723 K	54.16 51.05 51.69 52.36	42.10 44.52 44.10 43.97	3.74 4.43 4.21 3.67	$\begin{array}{c} {\rm SiC}_{0.78}{\rm O}_{0.07} \\ {\rm SiC}_{0.87}{\rm O}_{0.09} \\ {\rm SiC}_{0.85}{\rm C}_{0.08} \\ {\rm SiC}_{0.84}{\rm O}_{0.07} \end{array}$	

<sup>†</sup>All samples were pyrolyzed at 1673 K under argon gas. <sup>‡</sup>Five points averaged.

 $\alpha$ -SiC, although the evidence of  $\alpha$ -SiC or stacking faults (peak or shoulder at 33.6°) is absent in the XRD patterns.<sup>35</sup> However, quantitative estimation of the individual polytypes in the SiC synthesized by solid-state NMR may give ambiguous results, because of the long relaxation time of the silicon atom.<sup>36</sup>

Figure 11 shows the <sup>29</sup>Si NMR spectra of the pyrolysis products (1273 K) derived from the refluxed PMS resins. All of the spectra consist of the previously explained four signals ( $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ). However, the spectrum of the product derived from the resin refluxed at 523 K shows the most-broadened signals.

Apparently, the ceramic materials derived from the precursor under reflux treatment at 523 K possess the most disordered (amorphous-like) structure after pyrolysis. One of the important factors for determining the crystallite sizes is the chemical composition of the pyrolysis product itself. Table I shows the EPMA results for the elemental compositions of the pyrolysis products at 1673 K. The products at 1673 K exhibit the highest C/Si value, 0.87, with reflux treatment at 523 K and the lowest value, 0.78, with no reflux treatment. The large amount of free silicon in the product derived from the PMS without reflux treatment may induce crystallite growth at 1273-1473 K. However, the C/Si values are 0.85 or 0.84 in the materials with reflux treatment at 623 or 723 K, respectively. These values are close to that for reflux treatment at 523 K. Therefore, crystallite growth probably is not directly controlled by the amount of free silicon out of the Si-C network.

The temperature at which the efficient cross-link starts is 523 K. The observed phenomenon regarding the SiC crystallite sizes just represents the same issue as the thermal history of organosilicon precursors in the resulting ceramic crystallization. This is a very difficult theme that encompasses various factors. In the case of polycarbosilane or polysilazane pyrolysis, a sudden increase and decrease in radical concentration, accompanied by hydrogen evolution, have been observed just before crystallite growth.<sup>37</sup> A precise estimation of the hydrogen content in the pyrolysis products derived from the PMS resins at 1073–1273 K and an evaluation of the remaining radical concentration during pyrolysis probably are required to characterize the effect of pre-cross-linking on the resultant crystallite growth at high temperatures.

#### IV. Conclusions

Study of the thermal decomposition process of PMS in flowing argon gas reveals the formation of a Si—Si cross-link at 573 K, accompanied by cleavage of the PMS chains (redistribution reaction). The formed Si—Si cross-link is converted to Si—CH<sub>2</sub>—Si bridges at 723 K, by the Kumada rearrangement process. The resulting network is gradually converted into a Si—C network by losing hydrogen at high temperatures. Reflux treatment above 523 K effectively increases overall ceramic yield, based on the original PMS mass. In the environment of reflux treatment, fragments formed by chain cleavage probably cool to cross-link with residual resin at the bottom. The maximum ceramic yield under reflux treatment is ~75% at a reflux temperature of 623 K. Simple holding at 523 or 573 K, without the reflux condenser, also effectively increases ceramic yield; however, the ceramic yield under simple heat treatment is ~50%.

The growth of SiC and silicon crystallites in the pyrolysis products derived from refluxed PMS resins is remarkable at 1273–1473 K. However, pyrolysis products derived from the resin

refluxed at 523 K possess the most disordered structure, as shown by the XRD patterns of the pyrolysis products at 1473–1873 K and the  $^{29}$ Si NMR spectra of the product at 1273 K.

#### References

<sup>1</sup>C. L. Schilling, J. P. Wesson, and T. C. Williams, "Polycarbosilane Precursors for Silicon Carbide," *Am. Ceram. Soc. Bull.*, **62** [8] 912–15 (1983).

<sup>2</sup>Z. Zhang, F. Babonneau, R. M. Laine, Y. Mu, J. F. Harrod, and J. A. Rahn, "Poly(methylsilane)—A High Ceramic Yield Precursor to Silicon Carbide," *J. Am. Ceram. Soc.*, **74** [3] 670–73 (1991).

<sup>3</sup>D. Seyferth, T. G. Wood, H. J. Tracy, and J. L. Robisoe, "Near-Stoichiometric Silicon Carbide from Economical Polysilane Precursor," *J. Am. Ceram. Soc.*, **75** [5] 1300–302 (1991).

<sup>4</sup>T. Kobayashi, T. Sakakura, T. Hayashi, M. Yumura, and M. Tanaka, "Neodymium-Catalyzed Dehydrogenative Condensation of Methylsilane and Ceramization of the Resulting Polymer," *Chem. Lett.*, 1157–60 (1992).

<sup>5</sup>R. M. Laine and F. Babonneau, "Preceramic Polymer Routes to Silicon Carbide," *Chem. Mater.*, **5** [3] 260–79 (1993).

<sup>6</sup>Y. Mu, R. M. Laine, and J. F. Harrod, "Some Further Observations on Polymethylsilane as a Precursor for Silicon Carbide," *Appl. Organomet. Chem.*, **8**, 95–100 (1994).

<sup>7</sup>Z.-F. Zhang, C. S. Scotto, and R. M. Laine, "Pure Silicon Carbide Fibers from Polymethylsilane," *Ceram. Eng. Sci. Proc.*, **15** [4] 152–61 (1994).

<sup>8</sup>M. F. Gozzi and I. V. P. Yoshida, "Thermal and Photochemical Conversion of Poly(methylsilane) to Polycarbosilane," *Macromolecules*, **28** [21] 7235–40 (1995).

 <sup>9</sup>F. I. Hurwitz, T. A. Kacik, X.-Y. Bu, J. Masnovi, P. J. Heimann, and K. Beyene, "Pyrolytic Conversion of Methyl- and Vinylsilane Polymers to Si-C Ceramics," *J. Mater. Sci.*, **30** [12] 3130–36 (1995).
<sup>10</sup>M. F. Gozzi and I. V. P. Yoshida, "Structural Evolution of a

<sup>10</sup>M. F. Gozzi and I. V. P. Yoshida, "Structural Evolution of a Poly(methylsilylene)/Tetra-Allylsilane Mixture," *Eur. Polym. J.*, **33** [8] 1301–306 (1997).

<sup>11</sup>P. Czubarow and D. Seyferth, "Application of Poly(methylsilane) and Nicalon<sup>®</sup> Polycarbosilane Precursors as Binders for Metal/Ceramic Powders in Preparation of Functionally Graded Materials," *J. Mater. Sci.*, **32** [8] 2121–30 (1997).

<sup>12</sup>B. Boury, N. Bryson, and G. Soula, "Borate-Catalyzed Thermolysis of Polymethylsilane," *Chem. Mater.*, **10** [1] 297–303 (1998).

<sup>13</sup>P. Czubarow, T. Sugimoto, and D. Seyferth, "Sonochemical Synthesis of a Poly(methylsilane), a Precursor for Near-Stoichiometric SiC," *Macromolecules*, **31** [2] 229–38 (1998).

[2] 229–38 (1998).
<sup>14</sup>M. F. Gozzi, M. D. Goncalves, and I. V. P. Yoshida, "Near-Stoichiometric Silicon Carbide from a Poly(methylsilylene)/Tetra-Allylsilane Mixture," *J. Mater. Sci.*, **34** [1] 155–59 (1999).

*Sci.*, **34** [1] 155–59 (1999). <sup>15</sup>K. W. Chew, A. Sellinger, and R. M. Laine, "Processing Aluminum Nitride Silicon Carbide Composites via Polymer Infiltration and Pyrolysis of Polymethylsilane, a Precursor to Stoichiometric Silicon Carbide," *J. Am. Ceram. Soc.*, **82** [4] 857–66 (1999).

<sup>16</sup>T. Iseki, M. Narisawa, K. Okamura, K. Oka, and T. Dohmaru, "Reflux Heat-Treated Polymethylsilane as a Precursor to Silicon Carbide," *J. Mater. Sci. Lett.*, **18** [3] 185–87 (1999).

<sup>17</sup>B. Boury, N. Bryson, and G. Soula, "Stoichiometric Silicon Carbide from Borate-Catalyzed Polymethylsilane–Polyvinylsilane Formulations," *Appl. Organomet. Chem.*, **13**, 419–30 (1999).

 $^{18}M.$  A. Nechanicky, K. W. Chew, A. Sellinger, and R. M. Laine, " $\alpha$ -Silicon Carbide/β-Silicon Carbide Particulate Composites via Polymer Infiltration and

Pyrolysis (PIP) Processing Using Polymethylsilane," J. Eur. Ceram. Soc., 20 [4] 441-51 (2000).

<sup>19</sup>J.-G. Kho, D.-S. Min, and D.-P. Kim, "Polymethylsilane Post-treated with a Polyborazine Promoter as a Precursor to SiC with High Ceramic Yield," *J. Mater. Sci. Lett.*, **19** [4] 303–305 (2000).

<sup>20</sup>M. Narisawa, T. Yoshida, T. Iseki, Y. Katase, K. Okamura, K. Oka, and T. Dohmaru, "γ-Ray Curing of Poly(methylsilane) and Poly(methylsilanedimethylsilane) for Improved Ceramic Yields," *Chem. Mater.*, **12** [9] 2686–92 (2000).

<sup>21</sup>T. Iseki, M. Narisawa, Y. Katase, K. Okamura, K. Oka, and T. Dohmaru, "An Efficient Cross-Linking Process of Polymethylsilane for SiC Ceramics," *Chem. Mater.*, **13** [11] 4163–69 (2001).

<sup>22</sup>D. Seyferth and P. Czubarow, "Application of Preceramic Polymers in Powder Metallurgy: Their Use as Low-Loss Binders and for the *in Situ* Formation of Dispersed Ceramic Phases in the Metal Matrix," *Chem. Mater.*, **6** [1] 10–12 (1994).

<sup>23</sup>P. Greil, "Active-Filler-Controlled Pyrolysis of Preceramic Polymers," J. Am. Ceram. Soc., **78** [4] 835–48 (1995).

<sup>24</sup>D.-P. Kim, "Preparation of Electrically Conducting SiC/MoSi<sub>2</sub> Composites from Metal Mixtures of Preceramic Polymer," *Mater. Res. Bull.*, **36**, 2497–505 (2001).

<sup>25</sup>G. D. Soraru, F. Babonneau, and J. D. Mackenzie, "Structural Evolutions from Polycarbosilane to SiC Ceramics," *J. Mater. Sci.*, **25** [9] 3886–93 (1990).

<sup>26</sup>A. T. Hemida, M. Birot, J. P. Pillot, J. Dunogues, and R. Pailler, "Synthesis and Characterization of New Precursors to Nearly Stoichiometric SiC Ceramics," *J. Mater. Sci.*, **32** [13] 3475–83 (1997).

<sup>27</sup>Q. Liu, H.-J. Wu, R. Lewis, G. E. Maciel, and L. V. Interrnate, "Investigation of the Pyrolytic Conversion of Poly(silylenemethylene) to Silicon Carbide," *Chem. Mater.*, **11** [8] 2038–48 (1999).

<sup>28</sup>K. Shiina and K. Kumada, "Thermal Rearrangement of Hexamethyldisilane to Trimethyl(dimethylsilylmethyl)silane," *J. Org. Chem.*, **23**, 139 (1958).

<sup>29</sup>S. Yajima, Y. Hasegawa, J. Hayashi, and M. Iimura, "Synthesis of Continuous Silicon Carbide Fiber with High Tensile Strength and High Young's Modulus. Part 1.

Synthesis of Polycarbosilane as Precursor," *J. Mater. Sci.*, **13** [12] 2569–79 (1978). <sup>30</sup>M. Birot, J.-P. Pillot, and J. Dunoguès, "Comprehensive Chemistry of Polycarbosilanes, and Polycarbosilazanes as Precursors of Ceramics," *Chem. Rev.*, **95** [5] 1443–77 (1995).

<sup>31</sup>A. Tachibana, Y. Kurosaki, K. Yamaguchi, and T. Yamabe, "Quantum Chemical Study of Silicon Carbide Formation," *J. Phys. Chem.*, **95** [18] 6849–54 (1991).

<sup>32</sup>P. J. P. Corriu, D. Leclercq, P. H. Mutin, J.-M. Planeix, and A. Vioux, "Mechanism of Pyrolysis of Polycarbosilanes: Poly(silylenethylene) and Poly(dimethylsilyl ethylene)," *Organometallics*, **12** [2] 454–62 (1993).

<sup>33</sup>J. S. Hartman, M. F. Richardson, B. L. Sheriff, and B. G. Winsborrow, "Magic Angle Spinning NMR Studies of Silicon Carbide: Polytypes, Impurities, and Highly Inefficient Spin-Lattice Relaxation," J. Am. Chem. Soc., **109** [20] 6059–67 (1987).

<sup>34</sup>K. R. Carduner, S. S. Shinozaki, M. J. Rokosz, C. R. Peters, and T. J. Whalen, "Characterization of β-Silicon Carbide by Silicon-29 Solid-State NMR, Transmission Electron Microscopy, and Powder X-ray Diffraction," *J. Am. Ceram. Soc.*, **73** [8] 2281–86 (1990).

<sup>35</sup>H. Tanaka and N. Iyi, "Polytype, Grain Growth, and Fracture Toughness of Metal Boride Particulate SiC Composites," *J. Am. Ceram. Soc.*, **78** [5] 1223–29 (1995).

<sup>36</sup>H. Fujimori, N. Sato, K. Ioku, S. Goto, and T. Yamada, "<sup>29</sup>Si MAS NMR Spin-Lattice Relaxation Study of α-, β-, and Amorphous Silicon Nitride," *J. Am. Ceram. Soc.*, **83** [9] 2251–54 (2000).

<sup>37</sup>M. Narisawa, M. Shimoda, K. Okamura, M. Sugimoto, and T. Seguchi, "Reaction Mechanism of the Pyrolysis of Polycarbosilane and Polysilazane as Ceramic Precursors," *Bull. Chem. Soc. Jpn.*, **68** [4] 1098–1104 (1995).