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An Efficient Process of Cross-Linking Poly(methylsilane) for SiC Ceramics

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Reflux-treated poly(methylsilane) (PMS) at 420−570 K improves its ceramic yield dramatically. This efficient process was investigated by TG, GC, ^{29}Si, ^{13}C, and ^{1}H NMR, and FT-IR methods. The structural transformation process of the PMS polymer consists of three stages. In the first stage below 500 K, PMS forms $Si-Si_3$ cross-link units predominantly by evolving $MeSiH_3$. This process may proceed mainly via silylene formation. The Si−Si cross-link structure leads to a high ceramic yield up to 89%. In the second stage around 625 K, thermal rearrangement of the $Si-Si_3$ units to $Si-CH_2-Si$ units (Kumada rearrangement) begins to convert the polymers into polycarbosilanes. The third stage occurs above 673 K where almost all polymer units are converted into SiC_4 units. Evolution of H_2 and CH_4 begins in the second stage and becomes the dominant process in the third stage.

Introduction

In the middle of the 70's, the Yajima group successfully fabricated SiC fibers from organosilicon polymers.[1−8] Their work opened a door to preceramic polymer processing for ceramic materials. In particular, studies on Si-based polymers such as polysilanes,[9−30] polycarbosilanes,[9,31−37] and polysilazanes[31,38] were actively performed in this quarter century.

In recent years, poly(methylsilane) (PMS) has been studied extensively as a promising precursor to SiC[13−30] because of its ideal stoichiometry. However, PMS gives relatively low ceramic yields on pyrolysis. Thus, improvement of its ceramic yield is important. Introduction of partially cross-linked structure into PMS is an effective way of enhancing the ceramic yields, and many attempts have been reported.[15,19,20,25]

Metallocene catalysts are, for instance, reported to improve the ceramic yields.[15] However, long reaction times and high pressure are required for the process.

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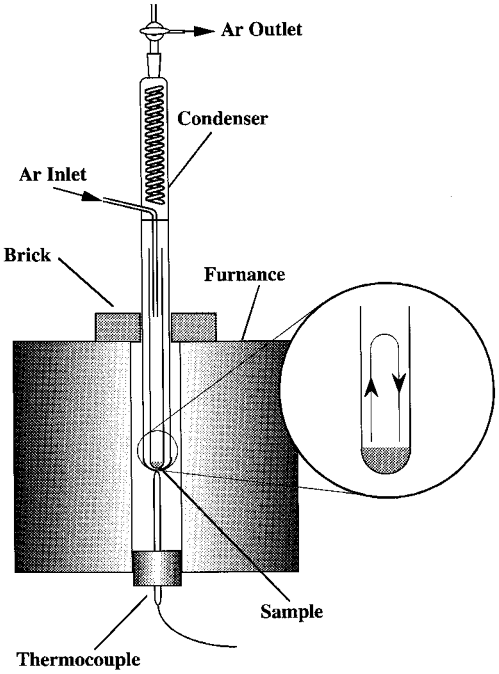
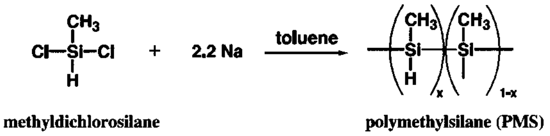


Figure 1. Polymer-refluxing apparatus.

We have recently reported a reflux heat treatment as a simple and effective procedure to enhance the ceramic yields without using catalysts or high pressure.[25] In this paper, we describe the further study on the detail of the transformation processes in the reflux-heat-treated PMS.

Experimental Section

Preparation of PMS. All operations were carried out under argon atmosphere. Toluene and methyldichlorosilane were distilled in the presence of sodium and potassium carbonate, prior to use. PMS was prepared by a Würtz type coupling reaction of methyldichlorosilane with sodium (eq 1). The typical procedure is as follows. In a 500 mL, a four-necked round-bottom flask (equipped with a reflux condenser, an addition funnel, a thermometer, and a mechanical stirrer) were placed 400 mL of toluene and 75.9 g (3.3 mol) of sodium. Heating and stirring made a sodium dispersion. Methyldichlorosilane (172.5 g, 1.5 mol) was then added dropwise to keep a steady reflux. After completion of addition, the mixture was refluxed a further 2 h. The reaction mixture was then cooled, and the obtained suspension was filtered with a Celite layer under argon to remove solid material (excess sodium and sodium chloride). Evaporation of the solvent gave a pale yellow, viscous liquid (39 g, 60% yield). Neat PMS is fairly air sensitive as reported[13−30] and thus was stored as a toluene solution in an Ar-filled desiccator. All handling operations were performed in a glovebox under Ar atmosphere.



$$\mathrm{Cl{-}\underset{H}{\overset{CH_3}{Si}}{-}Cl} + 2.2\ \mathrm{Na} \xrightarrow{\text{toluene}} \left(\underset{H}{\overset{CH_3}{\mathrm{Si}}}\right)_x \left(\overset{CH_3}{\mathrm{Si}}\right)_{1-x} \qquad (1)$$

Preparation of PMS by Würtz type coupling

Reflux Heat Treatment of PMS. The PMS obtained was subjected to reflux heat treatment. Refluxed PMSs were obtained by a following batch process. As shown in Figure 1, a dried Pyrex tube (diameter, 2 cm; length, 50 cm) containing 1.0 g of PMS was placed in a larger Pyrex tube (diameter: 4 cm) with a reflux condenser. The 1.0 g of PMS was put into the smaller tube in the form of toluene solution, and toluene was removed by an evaporator before the smaller tube placement. After the equipment was evacuated to eliminate residual oxygen and moisture by a vacuum pump, purified Ar was constantly flowed at 300 mL/min. The tube was then heated from room temperature (RT) to the defined temperatures (423, 473, 523, 573, 623, 673, and 723 K) at a rate of 10 K/min and held for 2 h. While PMS was kept refluxing at the temperatures, white mists were observed in the smaller tube, indicating that thermal decomposition took place even at the lowest temperature.

Table 1. Peak Assignments at Each Wavenumber in the IR Spectrum of PMS

wavenumbers (cm^{-1})	assignts	wavenumbers (cm^{-1})	assignts
2956, 2894	ν_{CH}	932	γ_{SiH_2}
2102	ν_{SiH}	866	ρ_{CH_3}
1410, 1248	$\delta_{CH,SiCH_3}$	774, 686	ν_{SiC}

Characterization. ^{13}C and ^{1}H NMR spectra for soluble samples were recorded on a Varian Gemini 2000 spectrometer at 50 and 200 MHz, respectively. Benzene-d_6 (C_6D_6) was used as a solvent and an internal standard. The ^{29}Si NMR and ^{13}C NMR measurements for solid samples were carried out using a Varian Unity INOVA-300 spectrometer at 59.6 and 75 MHz, respectively. The cross-polarization magic angle spinning (CP-MAS) method was applied to solid-state NMR experiments. The pulse widths for solution spectra and CP-MAS NMR spectra were 12.2 and 5.5 μs, respectively. Poly(dimethylsilane) was used as a reference sample for ^{13}C and ^{29}Si MAS NMR.

Infrared (IR) spectra were obtained by a Perkin-Elmer 1600 FT-IR spectrometer as neat films on NaCl for liquid samples or as KBr pellets for insoluble solid samples. Molecular weights of polymers were determined by gel permeation chromatography (GPC) referring to polystyrene standards. The GPC apparatus consisted of a RI detector (Yanako M-315), columns (Shodex GPC KF-802, 803), a pump (Jasco PU-980 Intelligent HPLC Pump), and a calculator (SiC Chromatocorder 12). The flow rate (toluene) was 1 mL/min.

TG analysis was performed using Rigaku TAS200. Samples (10 mg) were heated under argon flow from room temperature to 1273 K at a rate of 10 K/min.

Gaseous samples were collected from 0.2 g of PMS heated in a quartz tube, which was connected to a vacuum line system. Pyrolysis was carried out at every 100 K up to 1400 K. Collected gases were subjected to GC/MS (Shimadzu QP5050A) and GC (Hitachi G-5000) analyses on columns of Porapack and Molecular Sieve 5A 60/80, respectively. The GC instrument was equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Integration was performed with a Hitachi D-7500. Argon was used as the carrier gas. The calibration for H_2 and CH_4 was done using a standard mixture. Other gas species were uncalibrated, and the same sensitivity factor with CH_4 was adopted for analyses with the FID.

Results and Discussion

Characterization of PMS. The PMS obtained was an oily liquid polymer. GPC analysis indicated that PMS had a molecular weight (M_w) of 1780 and polydispersity (M_w/M_n) of 2.0. IR spectra of PMS were in accordance with previously reported ones[15,17−19,21,29,30] as shown in Table 1.

The ^{1}H NMR spectrum showed two broad resonances around 0−1.0 (Si−CH_3) ppm and 3.4−4.3 ppm (Si−H), which are typical for PMS.[15,18,19,21,29,30] Since IR spectra suggest the presence of SiH_2 groups, the resonance at lower field must consist of two resonances of CH_3SiH and CH_3SiH_2 groups.[21] Integration of the signals indicates that the ratio of (Si−H/Si−CH_3) is 0.6, showing the composition of PMS as $[(CH_3SiH)_{0.60}(CH_3Si)_{0.40}]_n$. Thus, our PMS has a highly branched structure. Gener-

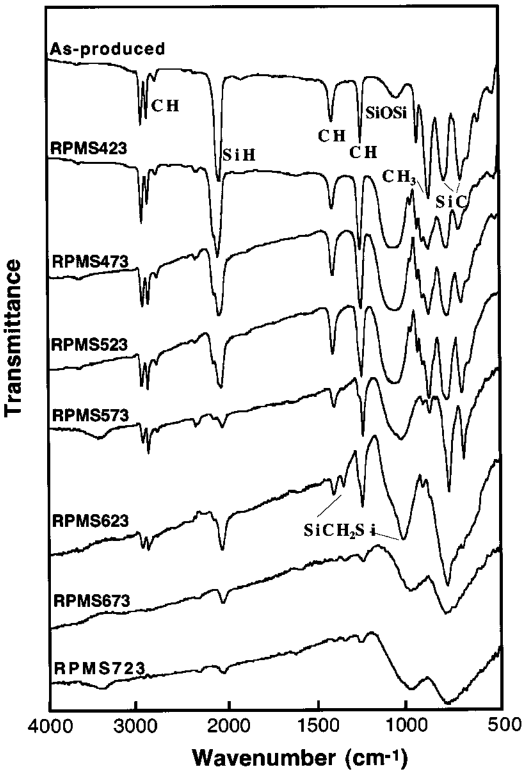


Figure 2. IR spectra of refluxed polymers.

Table 2. Appearance of the Refluxed PMSs

sample	appearance	polym recovery (%)
as-produced	pale-yellow oil	100
423 K	pale-yellow gum	96
473 K	pale-yellow resin	92
523 K	pale-yellow resin	87
573 K	yellow solid	81
623 K	yellow solid	78
673 K	yellow solid	75
723 K	orange solid	74

ally, the ratio of CH_3–Si–H to CH_3–Si groups varies according to the reaction conditions used.

As reported,[21,29,30] ^{29}Si NMR spectra of our PMS showed a broad resonance from −50 to −80 ppm. The resonance is assigned to the superimposed peaks of $(CH_3)H_2\mathit{Si}Si$ (terminal groups) at −63.0 ppm, $(CH_3)H\mathit{Si}Si_2$ at −67.1 ppm (linear unit), and $(CH_3)\mathit{Si}Si_3$ at −74.5 ppm (branching unit).[21,29,30] The branching unit of $(CH_3)\mathit{Si}Si_3$ must be formed by elimination of hydrogen atoms from Si–H groups during reductive coupling. The ^{13}C NMR spectrum shows two signals at −10.2 and 0.8 ppm, corresponding to CH_3 groups.[19,21,29]

Transformation of PMS by Refluxing. Appearance and polymer recoveries of refluxed PMSs were shown in Table 2. Samples refluxed below 423 K were soluble in organic solvents, while those treated above 473 K became insoluble. As reflux temperatures increased, PMS changed from an oily liquid to a rigid solid. The polymer recoveries decrease with an increase of the temperatures because of the liberation of Si-containing gases. However, it is noted that the polymer recoveries is relatively high (>74%) even at the highest temperature (723 K). The details of mass loss reduction during the refluxing will be discussed later.

Figure 2 shows the FT-IR spectra of the PMSs refluxed at 423–723 K. The peaks assigned to Si–O–Si bonds (1040 cm^{-1}) are observed in all polymers. Since this peak intensified with prolonged air exposure, PMSs must be oxidized during the handling and measuring processes for FT-IR.

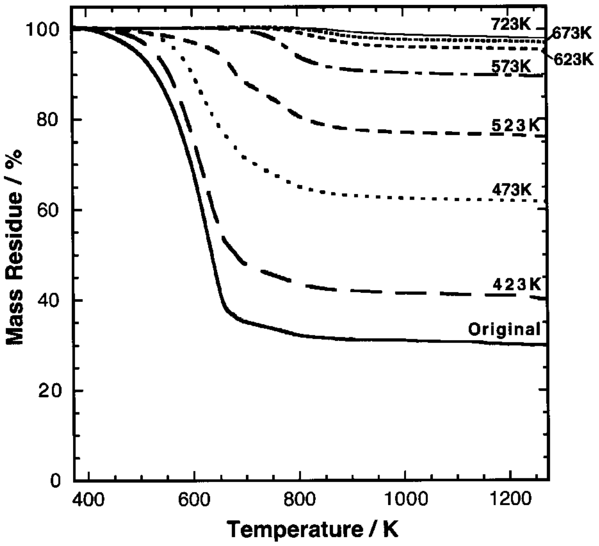


Figure 3. TG curves of refluxed polymers.

TG curves of the PMS and the refluxed PMSs are shown in Figure 3. The mass loss of untreated PMS begins at 400 K, and the onset temperature of mass loss correlates to the refluxed temperature; the higher the reflux temperature becomes, the higher the onset temperature. The mass loss is due to elimination of volatile species from PMS. The low onset temperature of PMS implies that some volatile, low molecular weight oligomers are contained in the samples. The high onset temperature and the high polymer recovery after reflux treatment suggest that these oligomers are efficiently incorporated into the cross-linked PMS during the reflux-treatment process. The TG curves also show that both the onset temperature of mass loss and the final mass residue of pyrolysates increase as the reflux temperature increases.

Thermally produced gaseous products were collected and analyzed. Methylsilanes ($MeSiH_3$, Me_2SiH_2, Me_3SiH, and $Me_2Si_2H_4O$), methane, and hydrogen were identified by GC and GC-MS analyses. Gas evolution below 500 K was relatively low. Methylsilane, $MeSiH_3$, was the major product as seen in pyrolysis of Nd-catalyzed PMS,[16] while methane and hydrogen were produced in almost negligible amounts. Methane and hydrogen were the dominant products in the temperature ranges of 500–700 K.

As shown in Figure 3, mass loss of original PMS begins around 400 K, becomes steep around 500 K and levels off around 625 K. Thus, we discuss each stage of the PMS pyrolysis below.

First Stage (Up to 500 K). In accordance with the small TGA mass loss (Figure 3), polymer recovery of the PMS refluxed below 500 K exceeds 90% (Table 2) and the amount of gas evolution is low (Figure 4). The oily PMS became a resinlike solid at this stage and gave higher ceramic yields on pyrolysis. This is attributed to substantial cross-linking in PMS.

Information on cross-link formation was provided by ^{1}H and ^{29}Si NMR and IR spectra. As shown in Figure 5, the Si–H/Si–CH_3 ratio of RPMS423 becomes smaller

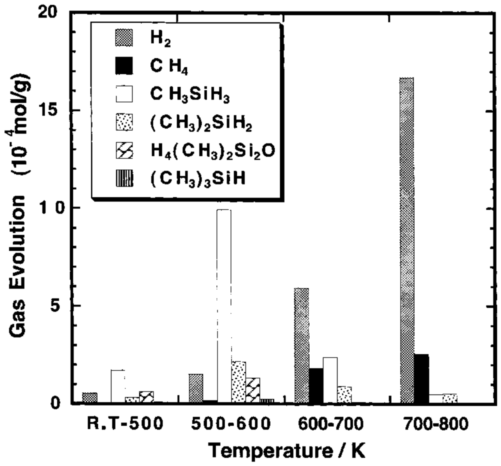


Figure 4. Gas evolution profile of PMS.

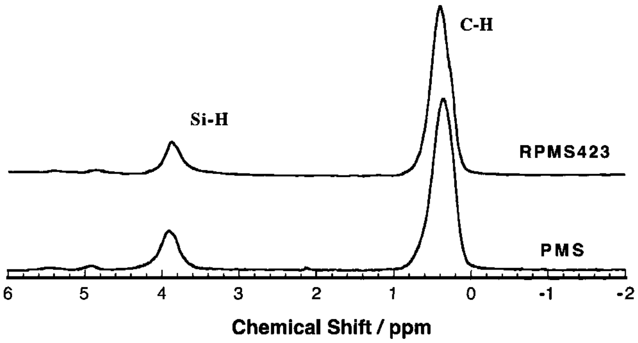


Figure 5. ^1H NMR spectra of PMS and RPMS423.

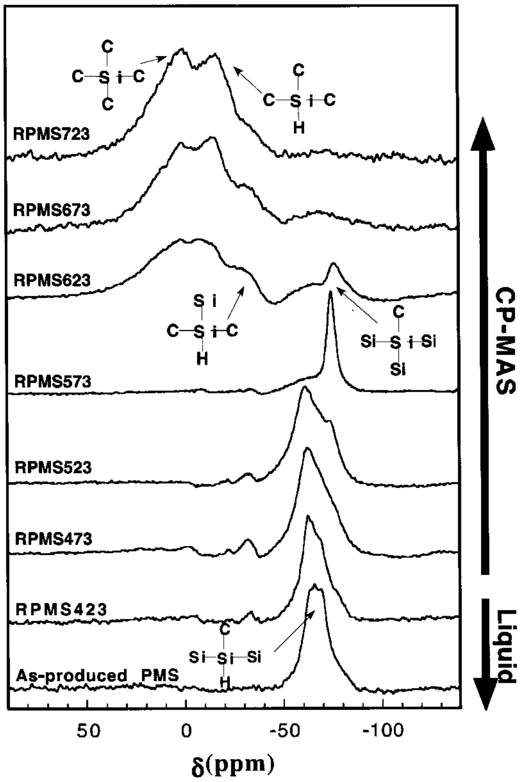


Figure 6. ^{29}Si NMR spectra of the refluxed polymers.

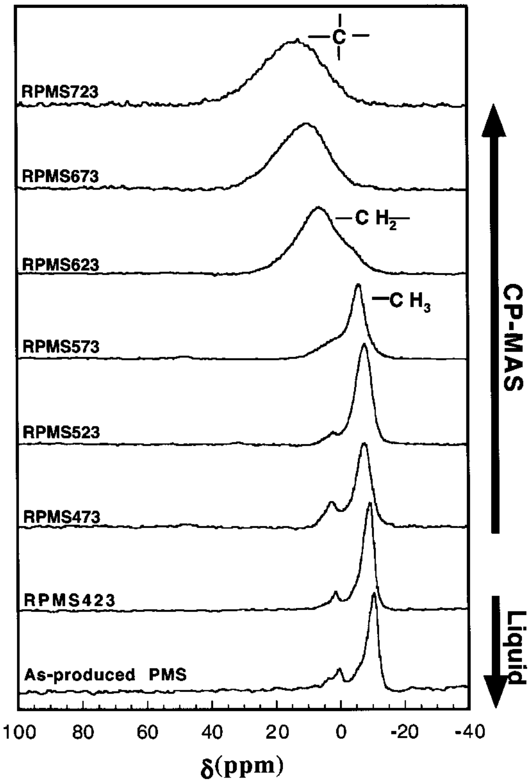


Figure 7. ^{13}C NMR spectra of the refluxed polymers.

(0.41) than that of PMS (0.60), indicating the consumption of the Si−H bonds during refluxing. IR spectra of RPMS423−573 (Figure 2) also indicate the gradual decrease of Si−H groups (2100 cm^{-1}) with increasing reflux temperatures. Analysis of the evolved gas species from RT to 500 K (Figure 4) indicates that this decrease in Si−H moieties is mostly responsible for the evolution of CH_3SiH_3 and that the hydrogen evolution is small compared to CH_3SiH_3. Boury et al. reported oligosilane evolution in the pyrolysis of catalyzed PMS.[19] However, PMS oligomers were not detected by GC/MS in the present experiment probably because oligosilanes were adsorbed in the columns. Instead, white mists were observed probably due to oligomers in the range of 500−600 K during pyrolysis with the conclusion that some amounts of oligomers are also evolved in addition to methylsilanes.

^{29}Si NMR spectra of the refluxed polymers show the shift of the peak maximum to −63 ppm ($(CH_3)\mathit{Si}H_2$−) and the growth of the shoulder at −74 ppm ($(CH_3)\mathit{Si}Si_3$) while intensity at −68 ppm ($(CH_3)\mathit{Si}H$) decreases with increasing reflux temperatures (Figure 6). The decrease of the linear part and the increase of the cross-linking parts and the terminal groups imply that PMS becomes a highly branched, globular structure with the terminal groups ($(CH_3)\mathit{Si}H_2$−). ^{13}C NMR spectra exhibit continuous downfield shifts of the major peak around −10 ppm while the minor peak around 0 ppm intensifies on reflux in the first stage (Figure 7). The downfield shift may correspond to a more congested PMS structure and the intensification of lower field resonance may imply increases in terminal moieties. Although no Kumada rearrangement is observed in the first stage, significant increase of ceramic yield is achieved by refluxing PMS below 500 K. Therefore, we may conclude that highly branched or cross-linked structures assist in improving ceramic yields.

Splitting of the Si−H absorption is also characteristic of PMS refluxed below 523 K. According to Schilling[30] the splitting is caused by the formation of (O−)Si−H moieties, which is supported by the increase in the Si−O stretching absorption around 1050 cm^{-1}. Oxygen content in the pyrolysis products at 1273 K, however, remains almost constant (3−4 mass%), which is independent of the refluxing temperature. The influence of terminal SiH_2 groups on Si−H absorption band splitting may be considered as well as the influence of possible oxygen contamination.

The process of the first stage is summarized as follows. PMS becomes agglomerated shape with highly cross-linked moieties inside it with $-SiH_2CH_3$ groups converting its surface.

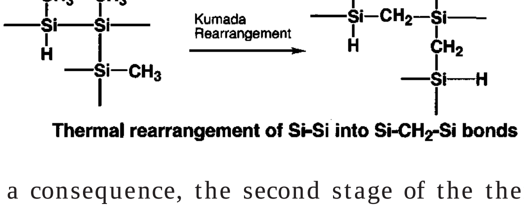
Second Stage (500−625 K). PMS changes from a resin to a nearly insoluble yellow rigid solid by refluxing. Polymer recovery of the PMS refluxed in the temperature range of the second stage is 78 to 87%. Methylsilane is still the major gaseous product, which is responsible for the steep mass loss. The evolution of dimethylsilane is also prominent in the second stage, while negligible amounts of methane are formed.

The shift of the absorption peak around 1000−1050 cm^{-1} toward lower frequency and decreases in the Si−H stretching vibration are characteristic of the PMS refluxed at the temperature of the second stage (Figure 2).

In the middle of the second stage, a drastic change in ^{29}Si NMR is observed (Figure 6). The signal assigned to $(CH_3)\mathit{Si}Si_3$ units becomes a dominant one in exchange for the consumption of the lower field ($(CH_3)\mathit{SiH}$ and $(CH_3)\mathit{Si}H_2$ units). Therefore, transformation from $(CH_3)\mathit{Si}H$ and $(CH_3)\mathit{Si}H_2$ units to $(CH_3)\mathit{Si}Si_3$ units is completed before 573 K. Downfield shifts in ^{13}C NMR resonance around −6 ppm ($Si-CH_3$ units) are completed. At the same time, the minor peak around 0 ppm is replaced with a broad shoulder, which suggests that terminal CH_3SiH_2- groups have almost disappeared.

Another significant chemical reaction takes place between 573 and 623 K. IR absorption peaks at <1000 cm^{-1} become a broad, superimposed peak. New absorptions at 1412 and 1012 cm^{-1} in RPMS623 prove the existence of $Si-CH_2-Si$ moieties.[15,19]

^{29}Si and ^{13}C NMR also show drastic structural changes between 573 and 623 K. The resonance at −74 ppm ($(CH_3)\mathit{Si}Si_3$ units) in the ^{29}Si NMR markedly diminishes in intensity and breadth; diffuse signals appeared around −60 ppm and −40 to 50 ppm. The latter seems composed of at least three peaks at −38 ppm ($C_2(H)\mathit{Si}Si$),[35,37,39] −15 ppm($\mathit{Si}C_3H$), and 0 ppm ($\mathit{Si}C_4$).[32] ^{13}C NMR also shows a broad signal at −15 to 30 ppm (6.0 ppm for $Si-CH_2-Si$).[32] All NMR data are in accord with the formation of $Si-CH_2-Si$ groups by the Kumada rearrangement (eq 2). Therefore, RPMS623 contains partial carbosilane structures in the highly cross-linked PMS structure.



(2)

Thermal rearrangement of Si-Si into Si-CH$_2$-Si bonds

As a consequence, the second stage of the thermal transformation of PMS is described as the two processes. The Si−Si cross-linking reactions occur rapidly and are completed at 573 K, and then the Kumada rearrangement takes place to form $Si-CH_2-Si$ units. Thermally labile moieties are mostly incorporated into polymer frameworks or converted to gaseous products. Thus, RPMS573 possesses a highly cross-linked structure and RPMS623 has a poly(carbosilane) structure as well as unconverted Si−Si bonds and $Si-CH_3$ groups. Both structures give higher ceramic yields than RPMS473.

Third Stage (<625 K). PMS refluxed above 625 K becomes a deep yellow to orange solid and contains almost no soluble fraction. Polymer recovery of PMS of the third stage is 74−75%. IR spectra of RPMS673 and RPMS723 show almost no absorption peaks ascribable to organic groups such as a CH_3 group but show only inorganic characteristics around 500−1200 cm^{-1} (Figure 2). Similarly, the Si−H stretching absorption diminishes in intensity. Both suggest that hydrogen is evolved as the main gaseous product in this temperature range. Hydrogen is actually detected as the major product, and the yield is proportional to the heating temperature (Figure 3). Thus, the Kumada rearrangement is completed in an early part of the third stage and hydrogen loss is the main process in this stage. It is, however, noteworthy that methane is also detected in this stage. This indicates that some of the $-CH_3$ groups are consumed as gaseous products without contributing to the Kumada rearrangement.

In ^{29}Si NMR spectra of RPMS673 and RPMS723, signals attributed to $\mathit{Si}C_4$ (−15 ppm) and $-\mathit{Si}C_3$ units (0 ppm) intensify in compensation for $C\mathit{Si}Si_3$ (−74 ppm) and $-C_2\mathit{Si}Si$ (−38 ppm) units. In accordance with this, ^{13}C NMR spectra of RPMS673 and RPMS723 show the disappearance of almost all CH_3 groups. The broad resonance of RPMS623 shows downfield shifts to +13 ppm for RPMS723 and becomes symmetrical in peak shape. Broadening of the resonance is related to an increase in the disordered nature around carbon atoms or to a variety of environments such as $\mathit{C}Si_4$, $-\mathit{C}Si_3$, and $=\mathit{C}Si_2$.

Thus, the third stage is the processes of converting all Si−Si bonds to Si−C bonds by the Kumada rearrangement and dehydrogenation takes place to form inorganic structures. It is natural that RPMS673 and RPMS723 show only slight mass loss on heating and gives high ceramic yields (>95%).

Mechanistic Consideration of the Thermal Decomposition. As described above, Si-containing gases such as methylsilanes and oligosilanes are the main products below 650 K and are closely related to the Si−Si cross-link formation. Thermolysis of silicon compounds proceeds via both silylene and radical mechanisms. These mechanisms would account for the cross-linking of PMS. Two kinds of mechanisms may be considered. One is via free radicals. Kobayahi et al. pyrolyzed PMS and found $MeSiH_3$ evolution at 473−673 K.[16] They propose a hydrogen abstraction from Si−H bonds by methylsilyl radicals to form Si−Si cross-links as shown in Scheme 1 a. Schematic illustration of the other mechanism via a silylene is shown in Scheme 1b. Silylenes may be formed accompanying the formation of $MeSiH_3$. The resultant silylene intermediate reacts with Si−H bonds to form Si−Si cross-links.

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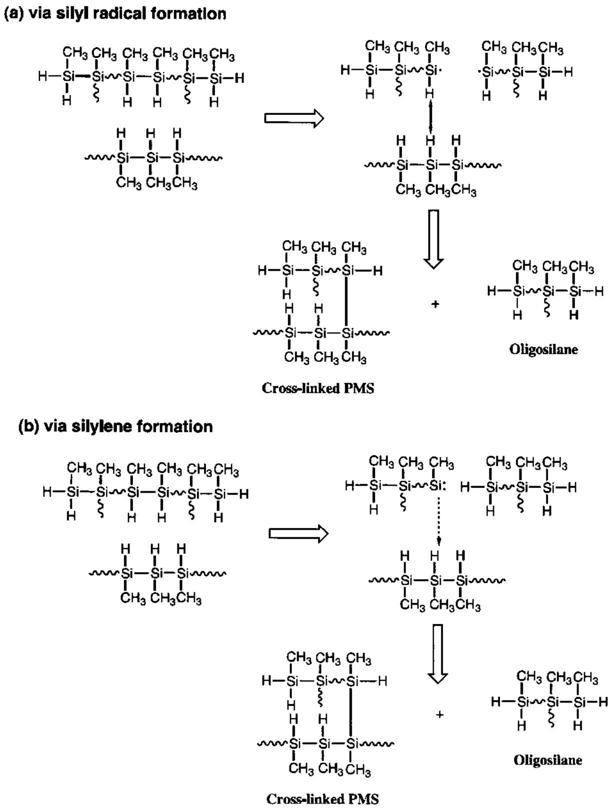
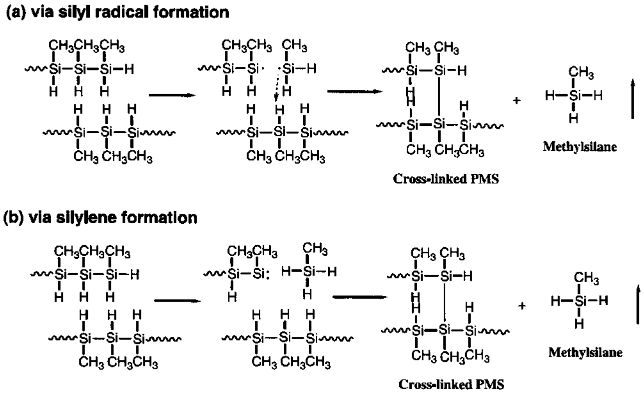
Scheme 1. Proposed Mechanism for Cross-Linking of PMS at an Internal Position



Scheme 2. Proposed Mechanism for Cross-Linking of PMS at a Terminal Position



On the other hand, oligosilane evolution may also lead to the formation of Si−Si cross-links. Boury et al. proposed a redistribution reaction between Si−Si and Si−H bonds in the internal chains to provide Si−Si cross-links (Scheme 2 a).[19] The reaction simultaneously yields low molecular weight species as byproducts. A silylene mechanism (Scheme 2b) can also be adapted to the internal chain scission. This reaction can also provide low molecular weight species in addition to the silylene intermediates.

Table 3 shows the activation energy for primary reactions via free radicals or silylenes in the pyrolysis of methyldisilane.[39−41] In the case of $Me_3SiSiMe_3$, the activation energies show that homolysis of Si−Si bonds is hard to occur compared with the silylene formation. Furthermore, the activation energy for silylene formation in $Me_3SiSiMe_2H$ is smaller than that in $Me_3SiSiMe_3$. This could suggest that H-substituted methyldisilane is preferable for the formation of silylenes. Since PMS also possesses Si−H groups, the silylene formation is more favorable in the pyrolysis of PMS. The insertion of silylenes into Si−H bonds takes place with no barrier (−7.8 kcal/mol).[42] Therefore, such reactions would lead to the formation of interchain Si−Si cross-links as shown in Scheme 1b and Scheme 2b. In addition, silylene intermediates can react with any Si−H site to form cross-link points while silyl radicals can afford ones only when they recombine. The Si−Si cross-link formation between two Si−H bonds is hard to occur below 600 K because the activation energy for homolytic Si−H cleavage (370 kcal/mol[43]) is high and the amounts of evolved H_2 gases are low. Thus, we favor the silylene mechanism for the Si−Si cross-link formation below 600 K.

Table 3. Activation Energy for Primary Reactions in the Pyrolysis of Methyldisilane

reacns	*E* (kJ/mol)	ref
$Me_3SiSiMe_2H \rightarrow Me_2Si: + Me_3SiH$	198 × 3.9	41
$Me_3SiSiMe_3 \rightarrow Me_2Si: + Me_4Si$	282 × 12	40
$Me_3SiSiMe_3H \rightarrow Me_3Si: + Me_3Si\cdot$	337 × 4	40

As mentioned above, Boury et al. reported oligosilane formation during pyrolysis of PMS.[19] Volatilization of these oligomers volatile gives low mass residue of PMS (<30%) at 1273 K. In the case of a reflux (closed) system, these oligomers stay in the reaction system to contribute to cross-link formation. Hence, refluxing below 573 K is critically important to afford ceramic products in high yields through efficiently introducing the $CSiSi_3$ cross-linking structure in PMS polymer. This is the most significant advantage in the reflux process.

Between 600 and 700 K, PMS undergoes the thermal conversion of $Si(CH_3)$−Si into Si−CH_2−Si. The rearrangement also forms Si−H bonds. On the other hand, some of the methyl groups are eliminated in the form of methane without contributing Si−CH_2−Si bridges.

Amounts of H_2 mainly increase above 600 K. The dehydrogenation reaction promotes transformation from organic materials to inorganic ones. H_2 may be generated due to recombination of H atoms in residual Si−H or C−H bonds.

Conclusion

The thermal transformation of poly(methylsilane) by refluxing consists mainly of three stages as follows: (1) $CSiSi_3$ unit formation via evolution of methylsilane and hydrogen (RT−500 K); (2) completion of cross-linking and the onset of thermal conversion of Si−Si to Si−C−Si bonds (625 K); (3) completion of the Kumada rearrangement followed by the process to form an inorganic structure (625−723 K).

The reflux processing is an effective way to promote cross-linking of PMS without any catalysts or auto-

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claves. Conversion of linear Si−Si units into C*Si*Si_3 units prior to the Kumada rearrangement is critically important in preparing SiC ceramics from PMS. Highly cross-linked PMS gives a high ceramic yield. The Si−Si cross-linking of PMS probably proceeds via a silylene mechanism, but it still involves unknown reaction processes. By virtue of its high ceramic yields, PMS could be applied to SiC matrixes for SiC-based composites.

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