γ-Ray Curing of Poly(methylsilane) and Poly(methylsilane−dimethylsilane) for Improved Ceramic Yields

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Poly(methylsilane) (PMS) and poly(methylsilane−dimethylsilane) copolymers (P(MS−DMS)) were synthesized by Wurtz type polycondensation reactions of methyldichlorosilane or methyldichlorosilane−dimethyldichlorosilane mixtures in toluene. The obtained polymers were sealed in Pyrex tubes under vacuum and cured with γ-rays. Hydrogen, methane, and silane gases formed in the tubes were analyzed by GC-MS spectroscopy. IR, UV, and NMR spectra of the cured precursor suggest the formation of Si−Si cross-links with small amounts of Si−CH_2−Si bridges during irradiation. Ceramic yields of the cured polymers increased as the irradiation dose increased. The pyrolysis of the precursor polymers at 1473 K yielded amorphous products with an almost stoichiometric composition. The precise C/Si ratio in the pyrolysis product depended on the starting polymer composition and the curing conditions.

Introduction

Precursors are useful for the synthesis of non-oxide ceramic materials with unique forms and microstructures that are normally difficult to obtain by conventional powder processing methods. Synthesis of silicon carbide fibers from poly(carbosilane) (PCS) is the earliest and most typical case.[1,2] Various types of silicon carbide fibers are now commercially available.[3−9] Since the original work on PCS thermally derived from poly(dimethylsilane) (PDMS), many efforts have been made to design new SiC precursors. One of the main issues is to control the C/Si ratio while maintaining processability.[10−18] There are now a great number of reviews on the various precursor methods.[19−21] Polymers containing Si−C−Si backbones have long been investigated. On the other hand, most polysilanes are not appropriate SiC precursors, because of their low ceramic yields corresponding to facile chain scission during thermolysis. The one exception is poly(methylsilane) (PMS). The C/Si ratio in the starting PMS is 1, and Si−H bonds in PMS should play an important role in improving the final ceramic yields by promoting cross-linking.[22−31] PMS is, however, not sufficiently oxygen

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stable and is often flammable in air at room temperature.[32] In addition, ceramic products from PMS usually contain considerable amounts of free silicon. Therefore, the PMS-based precursors have been used in the presence of unavoidable additives, such as stabilizers, spinning aides, and cross-linking agents. Recently, boron-containing catalysts has been actively studied as cross-linking agents for adjusting the precursor processability.[33,34] We have investigated the thermal reflux treatment of PMS and obtained highly cross-linked polymers without additives, which show high ceramic yields after pyrolysis.[35] The cross-linking during the reflux treatment, however, proceeds suddenly in a narrow temperature range. Therefore, control of the cross-linking processes is considered to be quite difficult.

In this article, we report on the radiation curing, followed by pyrolysis of PMS itself and poly(methylsilane−dimethylsilane) copolymers (P(MS−DMS)). Radiation curing of PCS fiber is now considered an industrially reliable method to produce high heat resistant SiC fibers with low oxygen contents.[2,5−7] The properties of the P(MS−DMS) system, such as the viscoelastic properties and the resulting ceramic yields, are expected to change gradually with changes in precursor compositions and irradiation conditions. Since the precursors are always free from additives during the irradiation, detailed study of the radiation curing mechanisms is expected to shed light on the role of simple and moderate cross-linking in precursor ceramization.

Experimental Section

Preparation of Poly(methylsilane) and Copolymers. PMS and P(MS−DMS) were synthesized with a typical Wurtz reaction, which has been widely used. Condensation reaction of monomer (methyldichlorosilane or methyldichlorosilane−dimethyldichlorosilane mixture) was carried out at 110 °C in toluene. The reaction mixture was passed through a Celite filter to eliminate solid materials and NaCl. Toluene was removed by evaporation. at 60 °C to yield a polymer as a viscous liquid. Toluene and THF (Wako chemicals) used in the experiments were dried with 3A 1/8 molecular sieves (Wako Chemicals), and toluene was purified by distilling over sodium (Katayama Chemicals) prior to use. Methyldichlorosilane (Cl_2SiMeH) and dimethyldichlorosilane (Cl_2SiMe_2) (Sin-Etsu Chemical Co. Ltd.) were purified by distilling from K_2CO_3.

γ-Ray Curing. Obtained polymer was dissolved in toluene, and a specific amount of the polymer solution was then put into the Pyrex tube with a 10 cm^3 volume. The solvent in the tube was removed from the polymer (total polymer amount in a tube: 1−2 g) by evacuation, and the tube was sealed under vacuum prior to curing. The tube was exposed to γ-rays generated by ^{60}Co with a dose rate of 37.2 kGy/h for a certain period. Total doses adopted for the radiation curing were 1.26, 5.15, and 12.6 MGy.

Measurements on the Cured Precursors. The gas species accumulated in the tube were analyzed with a D-500 gas chromatograph (HITACHI). A TCD detector, a 5A 60/80 molecular sieve column, and an Ar carrier gas were used for H_2 and CH_4 analyses. A FID detector, PolaPack Q 50/80 column, and a He carrier gas were used for CH_4, $MeSiH_3$, Me_2SiH_2, and Me_3SiH analyses. To determine absolute pressure of an individual gas, reference gas samples (CH_4 and H_2) with an appointed pressure were used for making the calibration curves. For estimation of silane gases, the factor used for methane has been applied for the calibration. GC-MS analysis was performed with a GC-MS QP-5050A (Shimadzu) for the precise identification of the gas species. GPC profiles of the obtained polymer samples were measured on Ultra styragel columns (10^2, 10^3, 10^5, 10^6 Å) (Waters), calibrated with narrow polystyrene standards and using a UV detector. THF was used as the eluent at a flow rate of 1 mL/min. FT-IR spectra were recorded on a FT-210 (Horiba). Infrared spectra of liquid samples were obtained neat on KBr plates, and those of the solid samples were obtained by the KBr pellet method. ^{29}Si NMR spectra were obtained using a Unity INOVA 300 MHz (Varian) with benzene-d_6 as solvent. For the solid samples, the cross polarization−magic angle spinning (CP-MAS) technique was used with a zirconia rotor. $(Me_2Si)_6$ (−41.86 ppm) was used as a standard. TG studies were carried out by a TG-8110D (Rigaku) with a heating rate of 10 K/min under an Ar gas flow. To avoid oxygen contamination, a glovebox with an Ar atmosphere was used for the manipulation of the starting polymers.

Measurements on the Pyrolysis Products. Polymer samples (1−6 g) were pyrolyzed at 1473 K at a heating rate of 1 K/min under an Ar atmosphere. The XRD patterns of the pyrolysis products were measured with a RINT-1100 (Cu Kα, Rigaku). The apparent SiC crystallite sizes were estimated from the half-height line width of (111) line of β-SiC according to the Scherrer equation. Elemental analysis of carbon was performed by a CSA-1 C-S estimation apparatus (Kawatestu Keiryouki). Silicon content was determined by residual weight after the carbon analysis. The third element besides Si and C was assumed to be oxygen, because no other elements were likely to be incorporated into the pyrolysis products.

Results

Curing and Pyrolysis of Poly(methylsilane) (PMS). PMS synthesized with a 50% yield is an oily yellow liquid ($M_w = 1668$, $M_w/M_n = 1.9$). The peaks in an IR spectrum are assigned to C−H (2958, 2896 cm^{-1}), Si−H (2100 cm^{-1}), CH_3 (1407 cm^{-1}), Si−CH_3 (1250 cm^{-1}), Si−O−Si (1050 cm^{-1}), SiH_2 (930 cm^{-1}), CH_3 (867 cm^{-1}), Si−C (771 cm^{-1}), and CH_3 (700 cm^{-1}).[22,27,29,30,32] Oxygen detected as an Si−O−Si absorption band is considered to be incorporated into the sample during the IR spectrum measurement, because the cell in the IR spectrometer is not perfectly free from oxygen.

Figure 1 shows the quantity of gas species accumulated in the tubes during the radiation curing. The quantities of the individual gas species increase as the total irradiation dose increases. At low total dose (1.26 MGy), $MeSiH_3$ evolution is extremely large compared to the other gas species, and Me_2SiH_2 is also evolved as one minor species. On the other hand, the H_2 evolution is remarkable at high doses (12.6 MGy). CH_4 evolution increases linearly with the dose.

The weight average molecular weight (M_w) of the soluble components in PMS cured at 1.26, 5.15, or 12.6 MGy is 1.1×10^4, 4.7×10^3, or 7.4×10^3, while M_w/M_n is 10.1, 14.6, or 19.5, respectively. The sample cured at 1.26 MGy is completely soluble in THF, while the sample cured at 5.15 or 12.6 MGy is partially soluble in THF. In the case of the polymer cured at 5.15 or 12.6 MGy, the soluble component is extracted from the cured

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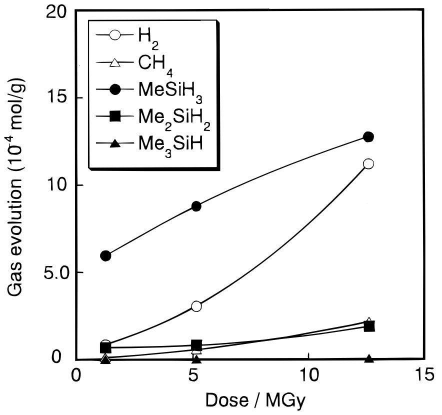


Figure 1. Analysis of the gas species accumulated in the tube during the radiation curing of PMS.

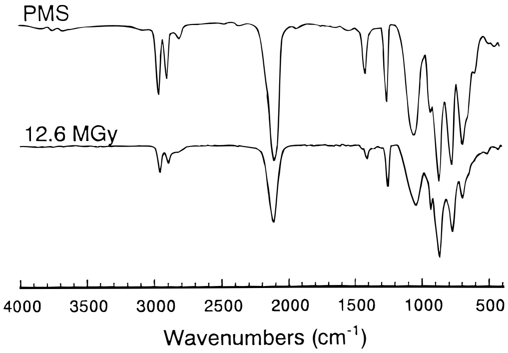


Figure 2. IR spectra of the radiation-cured PMS.

polymers by THF to measure the GPC profiles. After the radiation curing, the M_w of the extractable polymer increases above 10 000 Da. As the dose increases, PMS changes gradually to viscous yellow liquid (1.26 MGy), hardened yellow gel (5.15 MGy), and yellow solid powder (12.6 MGy).

As the irradiation dose for PMS increases, the peaks originating from Si−H bonds (2100, 930 cm^{-1}) in the IR spectra decrease slightly, while the peaks at 900−600 cm^{-1} broadened (Figure 2). Such minor changes in IR spectra suggest that the original PMS chain structure is mostly maintained during the curing process. The UV absorption spectra of the soluble components, however, indicate that the absorption edge shifts to the longer wavelength after the radiation curing, which means the Si−Si cross-links.

Figure 3 shows the ^{29}Si NMR spectra (C_6D_6: 59.6 MHz; δ, ppm) of the uncured PMS and PMS cured at 12.6 MGy. The primary signal at −45 to −75 ppm in the original spectrum is assigned to the overlapping of Si−(Me***Si***H)−Si (−45 to −55 ppm) and Si−(Me***Si***)=Si$_2$ (−60 to −75 ppm) in polysilane chains. After the curing, the observed signals are broadened. The shoulder at −75.0 ppm likely originates from increases in the number of Si−(Me***Si***)=Si$_2$ units.[29,30,32] The small and broadened signal at 0 to −20 ppm (***Si***C3, ***Si***C4) indicates the small amount of Si−CH$_2$−Si bridges in the cured sample.[5,29,30,32,35] The increase of the signal at −31.0 ppm would correspond to the formation of terminal groups, such as −Me***Si***H$_2$ groups. On the other hand, the formation of Si−H bonds close to methylene bridge, such as Si−(Me***Si***H)−(CH$_2$), must be taken into consideration to explain the signal at −31.0 ppm.[29,30,32] The precise assignment of the signal at −30 to −40 ppm is, however, difficult, because second-neighbor effects due to changes in the substitution of the silicon atoms often lead to variations in chemical shifts.

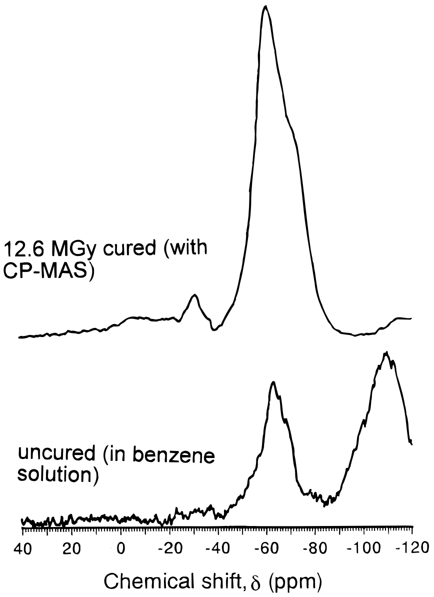


Figure 3. ^{29}Si NMR spectra of the original and the radiation-cured PMS (−110 ppm peak in the starting PMS spectrum originates from quartz of a sample cell).

Table 1. Elemental Analysis Results of Pyrolysis Products at 1473 K Derived from PMS (Accuracy: ±0.3 mass %)

	C/mass %	Si/mass %	(O/mass %)	SiC$_x$(O$_y$)
noncured	22.6	71.2	6.2	SiC$_{0.75}$(O$_{0.15}$)
cured at 12.6 MGy	28.4	69.3	2.3	SiC$_{0.96}$(O$_{0.06}$)

TG analysis in an Ar atmosphere is performed on the radiation-cured PMS. The mass losses of the samples begin at 500 K and finish at 800 K.[22,24,30,32] Onset temperatures for mass loss do not depend on the irradiation dose. As the total dose increases, the residual mass after pyrolysis increases monotonically. The residual mass at 1273 K is 28, 46, 56, or 70 mass % for uncured, 1.26 MGy-cured, 5.15 MGy-cured, or 12.6 MGy-cured PMS, respectively.

XRD patterns of the pyrolysis products at 1473 K derived from noncured PMS and 12.6 MGy-cured PMS were measured. Broad peaks in XRD patterns are assigned in the ascending order to (111), (220), (311) lines of β-SiC.[25,28−30] The apparent crystallite size calculated from (111) line is 5.8 or 4.4 nm for uncured or 12.6 MGy-cured PMS, respectively. The results of the elemental analysis of the pyrolyzed samples are summarized in Table 1. The product derived from the uncured PMS contains a small amount of free silicon, which is shown by small peaks at 26 and 48° in 2θ in the XRD pattern.[25,28−30] On the other hand, the product derived from the uncured PMS manifests an almost stoichiometric composition. The oxygen content in the products decreases from 6.2 to 2.3 mass % on curing.

Curing and Pyrolysis of Poly(methylsilane−dimethylsilane) Copolymers (P(MS−DMS)). Three types of copolymers, P(MS−DMS)-7, -5, and -3, were synthesized. The molar ratios of methyldichlorosilane/(methyldichlorosilane + dimethyldichlorosilane) in the

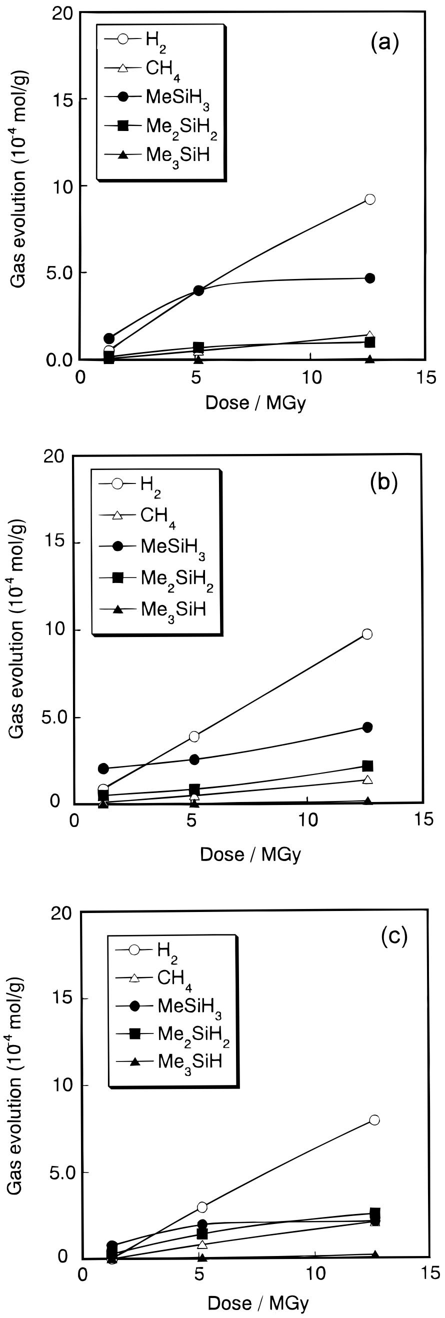


Figure 4. Analysis of the gas species accumulated in the tube during the radiation curing: (a) P(MS−DMS)-7; (b) P(MS−DMS)-5; (c) P(MS−DMS)-3.

starting monomer mixtures were adopted as 0.7, 0.5, or 0.3 for P(MS−DMS)-7, -5, or -3. The synthesized copolymers were white turbid liquids at room temperature. M_w of the P(MS−DMS)-7, -5, or -3 was 1600, 1600, or 1800, while M_w/M_n was 1.9, 1.7, or 2.0, respectively. New peaks assigned to CH_3 (830 cm^{-1}) and Si−C (800 cm^{-1}) were observed in IR spectra besides the peaks observed in PMS. These peaks originate from dimethysilane units incorporated into the copolymers.

Figure 4a−c shows the quantities of gas species accumulated in the tubes during the curing process. Total gas evolution is drastically reduced by the incorporated dimethylsilane units. In particular, the evolution of $MeSiH_3$ is reduced remarkably. The $MeSiH_3$ evolves at relatively low dose, and the evolution rate is slower at high doses. On the other hand, H_2 and CH_4 are evolved linearly with dose.

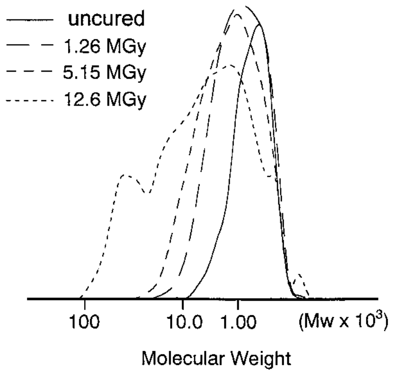


Figure 5. GPC profiles of the radiation-cured P(MS−DMS)-5.

Table 2. Molecular Weight of the Soluble Components Extracted from the Radiation-Cured Copolymers

samples	M_w	M_w/M_n	appearance	mass residue at 1273 K
	P(MS−DMS)-7			
noncured	1.6×10^3	1.9	white liquid	0.18
cured at 1.26 MGy	2.4×10^3	2.4	yellow liquid	0.49
cured at 5.15 MGy	6.5×10^3	4.7	yellow gel	0.49
cured at 12.6 MGy	3.7×10^3	5.0	yellow solid	0.57
	P(MS−DMS)-5			
noncured	1.6×10^3	1.9	white liquid	0.22
cured at 1.26 MGy	2.6×10^3	2.4	yellow liquid	0.42
cured at 5.15 MGy	4.1×10^3	2.9	yellow gel	0.44
cured at 12.6 MGy	23.0×10^3	11.5	yellow solid	0.47
	P(MS−DMS)-3			
noncured	1.8×10^3	2.0	white liquid	0.23
cured at 1.26 MGy	2.0×10^3	1.8	yellow liquid	0.29
cured at 5.15 MGy	4.3×10^3	3.1	yellow liquid	0.32
cured at 12.6 MGy	37.0×10^3	14.2	yellow caramel	0.35

As the dose increases, P(MS−DMS)-7 and -5 gradually change from viscous liquids to yellow gels. After being cured at 12.6 MGy, the samples are partially soluble in THF. On the other hand, P(MS−DMS)-3 changes from fluid liquid to highly viscous yellow liquid after the curing at 12.6 MGy. The appearance of the yellow liquid is similar to caramel and can be drawn as fibers with a spatula. Figure 5 shows the GPC profiles of the soluble components in the cured P(MS−DMS)-5 as a representative sample. The distribution of the molecular weight also increases, and several peaks and shoulders are seen in the GPC profiles. Molecular weight and M_w/M_n of the cured copolymers are presented in Table 2.

Figures 6 and 7 show the ^{29}Si NMR spectra of the uncured and the radiation cured copolymers. Besides the signals observed in PMS, a new sharp signal is observed at −40 ppm in the uncured copolymers, which can be assigned to Si−($\boldsymbol{Si}Me_2$)−Si units. After curing at 12.6 MGy, the spectra of the copolymers show common characteristic changes. The signals at −55 to −75 ppm broaden, the broad signal around −35 ppm increases, and a broad signal at 0 to −20 ppm assigned to $\boldsymbol{Si}C_3$ or $\boldsymbol{Si}C_4$ appears.[29,30,32] IR spectra of the cured copolymers show decreases in Si−H bonds and broadening of the peaks at 900−600 cm^{-1} in the same way as the spectra of the cured PMS.

TG curves of the cured copolymers indicate that the radiation curing improves the ceramic yield effectively.

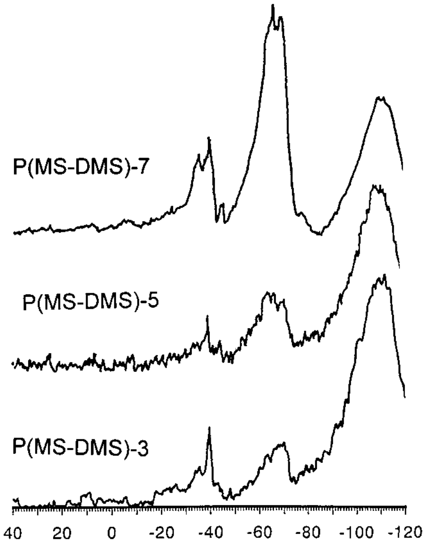


Figure 6. ^{29}Si NMR spectra of the uncured precursors in benzene solution (−110 ppm peaks originate from quartz of a sample cell).

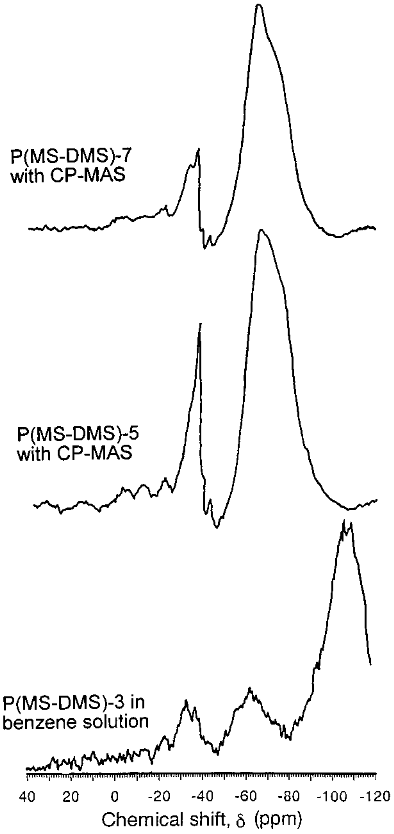


Figure 7. ^{29}Si NMR spectra of the 12.6 MGy cured precursors (−110 ppm peaks in the solution sample originate from quartz of a sample cell).

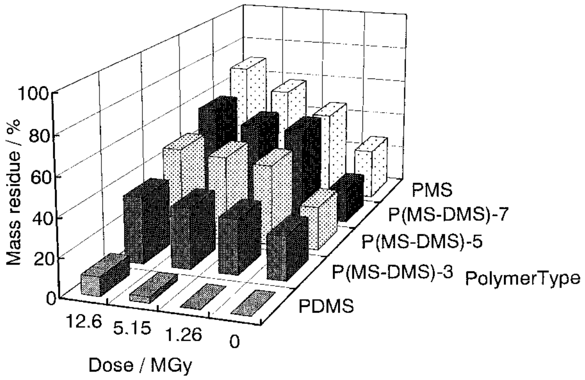


Figure 8. Ceramic yields at 1273 K of the radiation-cured precursors.

Table 3. SiC Crystallite Size (d_{111} Line) of Pyrolysis Products at 1473 K Derived from Noncured or Radiation-Cured Copolymers (Accuracy: ±0.1 nm)

samples	noncured/nm	cured at 12.6 MGy/nm
P(MS−DMS)-7	5.2	4.8
P(MS−DMS)-5	6.5	5.2
P(MS−DMS)-3	5.3	4.4

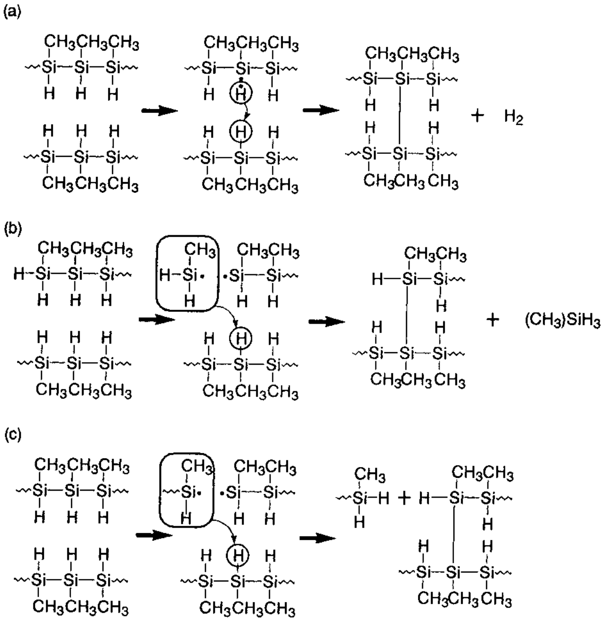
Table 4. Elemental Analysis Results of Pyrolysis Products at 1473 K Derived from Copolymers (Accuracy: ±0.3 mass %)

	C/mass %	Si/mass %	(O/mass %)	$SiC_x(O_y)$
	P(MS−DMS)-7			
noncured	25.2	69.6	5.2	$SiC_{0.85}(O_{0.13})$
cured with 12.6 MGy	26.4	68.0	5.6	$SiC_{0.91}(O_{0.15})$
	P(MS−DMS)-5			
noncured	27.5	69.2	3.3	$SiC_{0.93}(O_{0.09})$
cured with 12.6 MGy	26.7	67.1	6.2	$SiC_{0.93}(O_{0.16})$
	P(MS−DMS)-3			
noncured	30.2	67.3	2.5	$SiC_{1.05}(O_{0.07})$
cured with 12.6 MGy	27.3	64.3	8.4	$SiC_{0.99}(O_{0.23})$

The residual masses of the cured copolymers after pyrolysis are also given in Table 2. The mass losses for the cured copolymer begin at 400 K and end at 700 K. The onset temperature of mass loss, which does not depend on the dose, is considerably lower than that for the cured PMS. Figure 8 graphically summarizes the effect of the radiation curing on the residual mass at 1273 K. The ceramic yields of the radiation cured poly(dimethylsilane) (PDMS) estimated by the same TG apparatus are also included in Figure 8 for reference. The effect of radiation curing on the ceramic yield is remarkable in the precursor containing a large amount of methylsilane units. The ceramic yields of P(MS−DMS)-7 shows sudden increase even at 1.26 MGy, while the ceramic yield of P(MS−DMS)-3 increases gradually with the irradiation dose.

XRD patterns of the pyrolysis products at 1473 K derived from uncured and cured copolymers show broad peaks of β-SiC. The peaks assigned to free silicon are not observed. The apparent crystallite sizes in the obtained products calculated from the (111) line are summarized in Table 3. The radiation curing at 12.6 MGy slightly reduces the crystallite sizes in the pyrolysis products derived from the copolymers. The results of the elemental analyses of the pyrolysis products are summarized in Table 4. In the case of the uncured copolymers, the C/Si ratio in the pyrolysis products increases with increasing dimethylsilane units incorporated in the starting copolymers. These copolymer precursors yield SiC ceramics with the slight excesses of silicon or carbon. After radiation curing at 12.6 MGy, the differences in C/Si ratio from the stoichiometric composition are reduced. Despite the use of a glovebox, the small amount of oxygen is incorporated into the precursors after the radiation curing. In particular, the pyrolysis product from P(MS−DMS)-3 contains a large

Scheme 1. Proposed Mechanism of Si−Si Bond Formation in the Polymers during the Radiation Curing



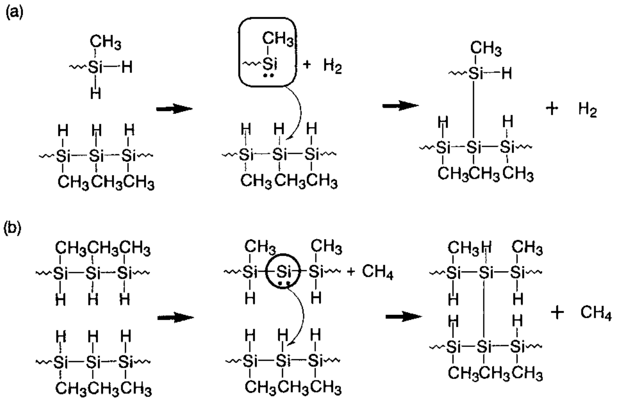
amount of oxygen. The reaction of the residual radicals in the copolymers with oxygen is suggested.

Discussion

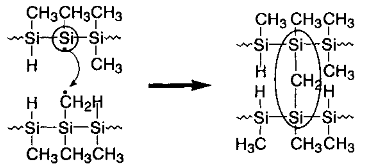
Our research has been oriented toward the characterization of the role of radiation curing on the preceramic polymers with methylsilane units incorporated in main chains. Radiation curing of such polymers in a vacuum was found to yield large amounts of hydrogen and methylsilane gases with a small amount of methane gas. The hydrogen evolution probably corresponds to cross-linking where Si−H groups form Si−Si bonds (Scheme 1a).[26] The evolution of methylsilane and dimethylsilane at an early stage of irradiation below 1.26 MGy is, however, characteristic to the studied precursors, while commercially available PCS mainly evolves CH_4 and H_2 gas species under irradiation.[2,13] The ceramic yield of P(MS−DMS)-7 is remarkably improved with curing at 1.26 MGy. Kobayashi et al. heat-treated PMS and found methylsilane evolution at 473−673 K under a nitrogen gas flow. Their scheme proposes a hydrogen abstraction reaction from Si−H bonds by methylsilyl radicals to form silicon−silicon cross-links (Scheme 1b).[28] The sources of the methylsilyl radicals are terminal groups in the starting polymer chains. On the other hand, Boury et al. proposed a rather complicated scheme for PMS cross-linking at 513 K using a boron-containing catalyst. The scheme is based on the redistribution reaction between Si−Si bonds and Si−H bonds in the separate chains (Scheme 1c).[32] The redistribution reaction always yields the low molecular weight components besides the silicon−silicon network. There are large numbers of $-MeSiH_2$ terminal groups in the low molecular weight components, and methylsilane gas is formed from these terminal groups as a final product.

In our study, NMR and UV spectra of the cured PMS and copolymers verified the formation of a silicon−silicon network. It is certain that cross-linking processes with the radiation curing should proceed by a combination of the stated mechanisms, but the mechanisms shown in Scheme 1a,b are the probably main reactions, because cross-linking in the precursors proceeds gradually with irradiation with evolution of methylsilane and hydrogen.

Scheme 2. Proposed Mechanism of Si−Si Bond Formation with Silylene Intermediates



Scheme 3. Proposed Mechanism of Si−CH_2−Si Bridging Formation in the Polymers during the Radiation Curing



To correlate Si−Si cross-linking with the hydrogen evolution, 1,1-elimination of hydrogen from SiH_2 or SiH_3 at terminal groups followed by the insertion of the silylene in the polymer chains may be promising (Scheme 2a). Formation of silylene is also appropriate to explain methane evolution during the radiation curing accompanied with Si−C scission (Scheme 2b). Such a mechanism is proposed in the case of pyrolytic conversion of poly(silylmethylene) or poly(silylethylene) to silicon carbide.[11,36,37] The conversion of free radicals formed on silicon atoms by γ-ray irradiation to silylene intermediates is, however, ambiguous at room temperature.[38,39] The role of silylene in the curing should strongly depend on molecular structure, cross-linking density, and the curing temperature.

Besides the silicon−silicon network, hydrogen abstraction from Si−H bonds and C−H bonds may eventually lead to the formation of Si−CH_2−Si bridging groups (Scheme 3). After radiation curing, the PMS and copolymers show broad signals around 0 to −35 ppm in the NMR spectra. One candidate for the signal assignment is silicon atoms located in the vicinity of Si−CH_2−Si bridging groups. The signals are, however, observed in wide range of chemical shift.

As the methyl group content on the polymer chain increases, the Si−CH_2−Si bridging groups should in-

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crease, reducing silicon network formation. Therefore, the P(MS−DMS)-3 remains as liquid state after irradiation. In addition, the ceramic yield of P(MS−DMS)-3 improves moderately as the irradiation dose increases, while that of P(MS−DMS)-7 improves remarkably even at low doses.

The composition of the pyrolysis products derived from PMS and copolymers depends on the starting precursor composition. By adjustment of the amount of dimethylsilane units in the copolymers, the C/Si ratio of the pyrolysis product can be controlled over a wide range. From a viewpoint of heat resistance, near stoichiometric composition with a slight amount of excess carbon is desirable. On the other hand, SiC materials with complete stoichiometric composition are attractive for electrical use. Not only the macroscopic chemical composition but also the control of the microscopic fluctuation in cross-linked precursors should become important to tailor available materials for such applications.

The difference in C/Si ratio of the pyrolysis products is reduced by the radiation curing. The pyrolysis products from the cured precursors show almost stoichiometric composition. This appears to be curious, because the precursors with high methylsilane unit content form Si−Si networks by the radiation curing, and is expected to yield silicon-rich products. The Kumada rearrangement process in such a cross-linked precursor to form a Si−C−Si backbone during pyrolysis should influence the resulting ceramics composition, which have not been quantitatively investigated for such cross-linked polysilanes.

Conclusion

γ-Ray radiation curing for poly(methylsilane−dimethylsilane) copolymer precursors is effective to improve the ceramic yields after pyrolysis. The change in appearance of the polymer precursors in the sample tubes, liquid to solid, suggest the occurrence of the intermolecular cross-linkings together with the gas evolutions of methylsilane and hydrogen. When the precursor contains high percentages of the methylsilane units, the radiation curing increases the ceramic yields effectively. Radiation curing cause silicon−silicon bonds with small amounts of $Si-CH_2-Si$ bridges. The formation of $Si-CH_2-Si$ bridges is detectable in the precursors containing a high percentage of dimethylsilane units. The noncured polymer precursors containing a high percentage of methylsilane units usually yields silicon-rich product after pyrolysis. Ceramic yield, the appeared viscoelastic property, and resultant ceramic chemical composition can be controlled by adjusting the copolymer composition and the dose for the radiation curing.

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