

Hydropolysilanes as Precursors to Silicon Carbide

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SYNOPSIS

A systematic study of the roles of three different types of monomers and their compositions in hydropolysilane homo-, co-, and terpolymers on their pyrolytic yields to silicon carbides was performed. The diorganodichlorosilane monomer, serving to increase molecular weights of the polymers, is not a significant factor in pyrolytic yields. The organotrichlorosilane monomer, leading to branched structures of the polymers, is helpful in obtaining high pyrolytic yields. The monoorganodichlorosilane monomer, providing crosslinking sites for the polymers, is useful in retarding decomposition during pyrolysis. The precursor-to-ceramic conversion chemistry was studied using thermogravimetry, infrared spectroscopy, X-ray powder diffraction, and Rutherford backscattering spectrometry. The pyrolytic yields were not pyrolysis-time-dependent but decreased as the pyrolysis temperature increased. The apparent crystalline size increased as both the pyrolysis time and temperature increased. For a 30 min pyrolysis, the pyrolysis temperature must be over 1000–1200°C to provide a crystalline pyrolytic residue. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Silicon carbide (SiC) is a ceramic material with high thermal and chemical stability, high mechanical strength and hardness, and high thermal conductivity. SiC is also a high-temperature semiconductor. Silicon carbide is traditionally made from silicon oxide and graphite by a high-temperature process.¹ This process is not applicable for the preparation of fibers or films. The need for soluble or fusible precursors whose pyrolysis will give the desired ceramic material has led to a new area of research in polymer science. In the search for polymeric precursors, polysilanes have become the primary candidates.

The first preparation of silicon carbide fiber from a polysilane was demonstrated by Yajima and co-workers,² who converted the intractable polydimethylsilane to a tractable polycarbosilane by heating in argon in an autoclave to 400°C. This polycarbosilane was then melt-spun into fibers, crosslinked in air at 350°C, and converted to pre-

dominantly SiC and mixed with excess carbon and SiO₂ on heating in N₂ to 1300°C. The second successful preparation was reported by West et al.,³ where poly(phenylmethyl-*co*-dimethyl silane) was converted into silicon carbide after photoinduced crosslinking and pyrolysis at temperature of at least 800°C in an inert atmosphere. The West process produces SiC without converting a precursor to an intermediate polycarbosilane and it avoids the introduction of oxygen. Oxygen incorporation leads to undesired properties for the SiC. However, incomplete crosslinking because of the limited depth of UV light results in hollow SiC fibers and some degradation always takes place along with photoinduced crosslinking.^{4–6} It would therefore be desirable to develop a precursor with the ability to effectively crosslink in an inert gas under heat before pyrolysis.

Hydropolysilanes,⁷ a new class of the polymonoorganosilylene polymers, contain a reactive unsubstituted hydrogen which can provide crosslinking sites. Recently, a wide range of hydropolysilanes were synthesized⁸ and studied as silicon carbide precursors in our laboratories. In this article, we present data from a systematic study of pyrolysis of a series of hydropolysilanes including homopoly-

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mers, copolymers, and terpolymers with a variety of substituents and compositions. Factors affecting properties of the pyrolytic products are examined in detail, as are the possible mechanisms of the pyrolysis process with the aid of thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and Rutherford backscattering spectrometry (RBS). An understanding of the conversion chemistry from these polymer precursors to SiC ceramics is vital to successfully control their applications as fiber and matrix materials in ceramic composites.

EXPERIMENTAL

Hydropolysilane copolymers and terpolymers were prepared by the Wurtz-type condensation from mixtures of dichlorosilane monomers in refluxing toluene with molten sodium as described in the literature.⁴ The compositions and molecular weights of these polymers were determined by proton nuclear magnetic resonance spectroscopy (¹H-NMR), FTIR, and gel permeation chromatography (GPC).

The pyrolysis of hydropolysilanes, in amounts ranging from 5 to 15 mg, was performed in a TGA (DuPont TGA 2950) for temperatures lower than 1000°C under a highly purified argon atmosphere with oxygen content less than 1 ppm at a heating rate of 20°C/min. For pyrolysis temperatures higher than 1000°C, polymer samples, ranging from 0.2 to 1 g, were heated in a radio-frequency induction furnace in a molybdenum crucible. The radio-frequency induction furnace was heated at a rate of about 100°C/min under an atmosphere of titanium gettered argon with an oxygen content much less than 1 ppm. The temperatures in the radio-frequency induction furnace were measured using optical pyrometry. The pyrolytic yield from each polymer was measured by gravimetry.

Combustion analyses were performed using TGA at 800°C isothermally for 30 min in air to examine the free carbon contents in the pyrolytic residues. Under these conditions, graphite foil shows an almost 100% weight loss, whereas pure commercial SiC shows an ~ 1% weight change.

Elemental analysis for Si, C, and O were performed by RBS spectrometry measurements. Samples were placed with their surfaces normal to the incident proton beam with an energy of 1.5 MeV collimated to an area of 1.5 mm². A silicon surface barrier detector with an energy resolution of about 13 keV for protons was placed at an angle of 165° to the proton beam to detect scattered protons.

High-purity quartz (SiO₂) and commercial silicon carbide (SiC) were used as standards to calibrate the RBS spectra. It was assumed in composition calculations of pyrolytic residues that no elemental Si atoms existed and all oxygen atoms existed as SiO₂.

¹H-NMR analysis was performed on a polymer solution of 10 wt/vol % in deuterated chloroform. The spectra was recorded on a Bruker WP-270SY spectrometer using tetramethylsilane as a reference.

GPC traces were carried out for soluble samples in chloroform by a Waters pump, Model 610, and a series of ultrastryragel columns with pore sizes of 10⁴, 10³, 500, and 100 Å. A Hitachi multichannel photodiode array, Model L-3000, was used as the detector. A software system, Lab Calc, available from Galactic Industries Corp., was used to do the necessary calculations on all GPC traces.

FTIR analyses were performed by a MATTSON Galaxy Series Model 2020 FTIR spectrophotometer using the conventional KBr pellet technique for insoluble samples and cast thin films from toluene solution on KBr crystal for soluble samples. The wide-angle X-ray diffraction patterns for the pyrolytic residues were obtained on a Rigaku X-ray diffractometer operating at 45 kV and 20 mA using nickel-filtered CuK α radiation with a wave length of 1.54 Å as an X-ray source.

RESULTS AND DISCUSSION

Comparison of Pyrolysis of Polysilanes with Other Polymers

Figure 1 shows a TGA graph in which pyrolytic results for five different kinds of polymers are compared. As expected, silicone grease (curve a), having the composition [(CH₃)₂SiO]_n, has the highest degradation temperature at about 600°C based on its first derivative TGA curve. Polystyrene (curve b), an organic polymer with only carbon in the backbone, has a relatively high degradation temperature compared to polysilanes (curves c–e) having only silicon in the polymer backbone.

The homolytic bond dissociation energy^{9,10} of the Si—Si bond (51 kcal/mol) is much lower than that of the Si—O bond (160 kcal/mol) and the C—C bond (83 kcal/mol). Thus, the principal thermal degradation of polymers originates mainly by cleavage of the polymer chain. Among the three kinds of silane polymers, aromatic-substituted polysilanes (curves c and d) have relatively high degradation temperatures. This can be explained by the fact that

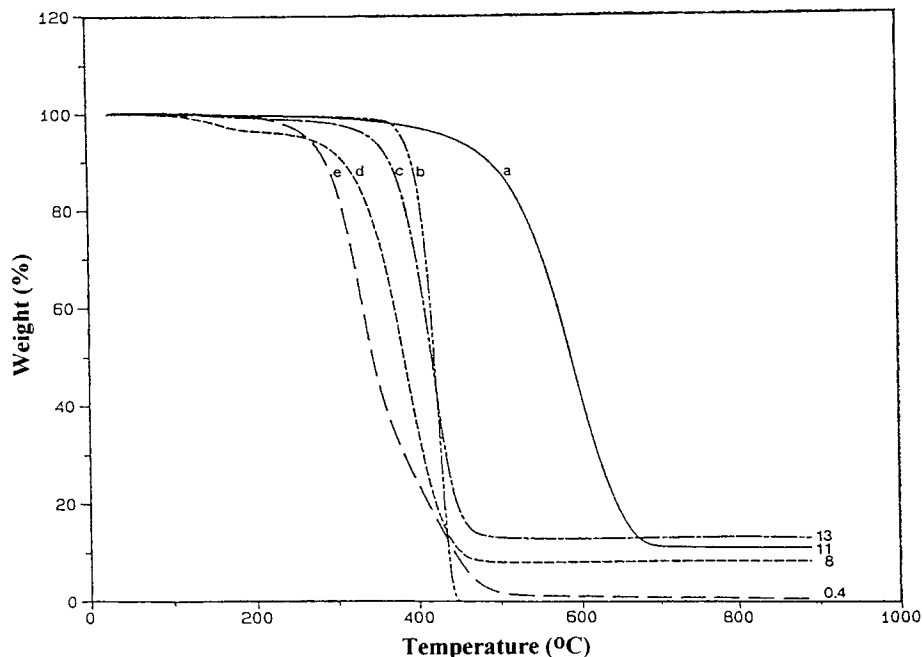


Figure 1 TGA traces obtained at a heating rate of 20°C/min in N₂ for (a) silicone grease, (b) polystyrene, (c) polyphenylmethylsilane, (d) [(CH₃SiH)₃₀(CH₃SiC₆H₅)₇₀]_n, and (e) poly(*n*-propylmethylsilane).

the resonance effect of the phenyl substituent on the Si atom strengthens the Si—Si bond in the polysilane backbone. Evidence of a minor degradation that has been found for the hydropolysilane (curve d) below 200°C is perhaps due to the volatilization of cyclics that remain in the precipitated polymer after purification.

The effect of the phenyl content on the thermal degradation temperatures is shown in Figure 2 where the degradation temperatures increase as the phenyl content in the polymer increases. The pyrolytic yields of the polymers also increase with increasing contents of the phenyl substituents (Figs. 1 and 2).

In addition to the resonance effect, another role played by the phenyl substituents, namely, retardation of the reversion reactions (depolymerizations) during pyrolysis, may also contribute to the explanations for the experimental observations. The retardation of reversion reactions during pyrolysis of the polysilanes facilitates the transformation from a silane structure to a carbosilane structure. These structural rearrangements then facilitate the formation of the SiC network which has high thermal stability in an inert environment.¹¹ For the pyrolysis of polysiloxane (silicone grease, Fig. 1, curve a), on the other hand, SiO₂ is the major component of the pyrolytic residue (from FTIR data, not shown). Thus, the facilitation of the formation of thermally stable residues such as SiC and SiO₂ may account

for the increases of the pyrolytic yields. The need of forming a thermally stable structure in the pyrolytic residue to obtain a high pyrolytic yield becomes apparent in the pyrolysis of polystyrene that produces a negligible residue (Fig. 1, curve b). There are many ways to promote the carbosilane rearrangements, and thus the formation of SiC, such as precursors having carbosilane structures, having small values of the C/Si ratio, and having the abilities to crosslink, to name a few. These factors will be demonstrated and discussed below in more detail.

Pyrolysis of Hydropolysilanes

A series of hydropolysilane copolymers and terpolymers have been synthesized and pyrolyzed in our laboratories. Table I shows various monomers and their abbreviations. High-purity argon gas was employed for pyrolysis experiments to avoid the complications introduced by a nitrogen atmosphere (nitride formation) or an oxygen atmosphere (silica formation). Table II shows pyrolytic yields of various hydropolysilanes after pyrolysis at 1400°C for 30 min under argon.

The nonvolatile pyrolytic residues were all black, indicating that excess carbon (including some free carbon) was present. This was later confirmed by elemental analysis for Si and C and by combustion

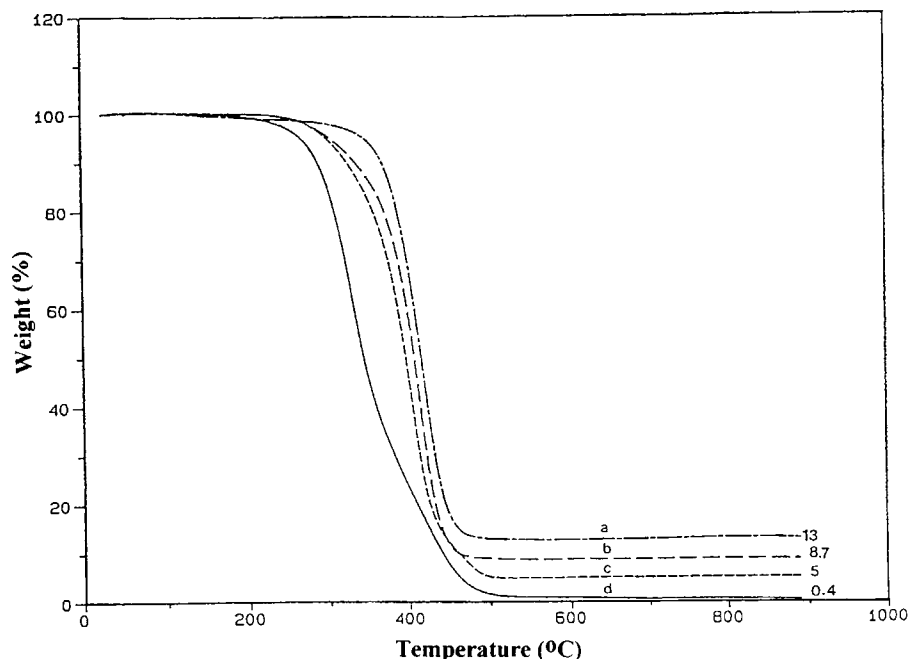


Figure 2 TGA traces obtained at a heating rate of 20°C/min in N₂ for (a) [(CH₃SiC₆H₅)₁₀₀]_n, (b) [(CH₃SiC₆H₅)₇₅(*n*-propylSiCH₃)₂₅]_n, (c) [(CH₃SiC₆H₅)₅₀(*n*-propyl-SiCH₃)₅₀]_n, and (d) [(*n*-propylSiCH₃)₁₀₀]_n.

analysis for free carbon. A small peak at roughly 1100 cm⁻¹ in the FTIR spectra, assigned to either silica (SiO₂)¹² or silicon oxycarbide,¹³ for the residue of polymer 9 pyrolyzed in argon (Fig. 3, spectrum a) indicated that oxygen had become incorporated into the polymers before pyrolysis. SiO₂ is the major product, however, if pyrolysis of polymers are performed in air as seen in Figure 3, spectrum *d*.

The effect of molecular weights of polysilanes on their pyrolytic yields is insignificant. This was evidenced by the pyrolysis of polyphenylmethylsilane homopolymers with varied molecular weights in TGA under nitrogen at a heating rate of 20°C/min to 900°C. The pyrolytic yields were 13.9, 13.8, 16.5, and 14.1%, corresponding to the molecular weights of 1000, 10,000, 100,000, and 1 million, respectively. Although the molecular weight is not a significant factor in pyrolysis, the molecular weight is an important consideration when either film or fiber formation is desired.

Combustion analyses were performed using TGA in air to examine the free carbon contents in the pyrolytic residues. It was found (Fig. 4) that the free carbon content increases with increase of the C/Si ratio. In addition, the threshold value of the C/Si ratio to give free carbon in the residues is about 4.5.

The monomer TM provides branching structures that are helpful in obtaining high yields of residues as seen in Table II. The effect of TM content in the terpolymer system on the yields of residues after pyrolysis is shown in Figure 5. The monomer functionality values *f* could be used to calculate average molar functionality values *f*_{av} for any hydrosilane prepared from a given mixture of monomers, according to the equation¹⁴

$$f_{av} = \frac{xf_1 + yf_2 + zf_3}{x + y + z}$$

Table I Abbreviations of Various Monomers

Monomers	Formula	Abbreviations
Methyldichlorosilane	(CH ₃)HSiCl ₂	MH
Phenyldichlorosilane	(C ₆ H ₅)HSiCl ₂	PH
Phenylmethyldichlorosilane	(C ₆ H ₅)(CH ₃)SiCl ₂	PM
Dimethyldichlorosilane	(CH ₃) ₂ SiCl ₂	DM
Diphenyldichlorosilane	(C ₆ H ₅) ₂ SiCl ₂	DP
Trichloromethylsilane	(CH ₃)SiCl ₃	TM

Table II Pyrolytic Yields of Hydropolysilanes as a Function of Composition, Average Molar Halogen Functionality, and C/Si Ratio

Polymers	Polymer Compositions	f_{av} ^a	C/Si Ratios	Pyrolytic Yields ^b	Free Carbon Contents ^c
1	MH/PM = 0/100	2	7.0	18.9%	26.0%
2	MH/PM = 25/75	2	5.5	20.5%	6.8%
3	MH/PM = 40/60	2	4.6	—	4.3%
4	MH/PM = 45/55	2	4.3	23.6%	Indiscernible
5	PH/DM = 30/70	2	3.2	42.0%	11.0%
6 ^d	PH/PM = 30/50	2	7.9	31.2%	22.0%
7 ^d	PH/DP = 15/65	2	11.3	31.0%	39.8%
8	MH/PM/TM = 35/50/15	2.15	4.0	24.5%	Indiscernible
9	MH/PM/TM = 45/50/5	2.05	4.0	21.2%	Indiscernible
10	MH/PM/TM = 45/45/10	2.1	3.7	23.7%	< 1%
11	MH/PM/TM = 45/40/15	2.15	3.4	34.5%	Indiscernible
12	MH/PM/TM = 25/40/35	2.35	4.4	41.3%	Indiscernible
13	MH/DM/TM = 30/30/40	2.4	1.3	28.5%	Indiscernible
14 ^e	PH/DM/TM = 50/25/15	2.15	5.0	52.6%	5.7%
15 ^e	PH/PM/TM = 30/40/20	2.2	6.1	38.2%	9.0%

^a f_{av} are average molar halogen functionality values.

^b RF furnace was carried out at a ramping rate of about 100°C/min to 1400°C and holding 30 min under argon.

^c Free carbon contents of the pyrolytic residues were performed by combustion analyses on TGA.

^d Polymers contain 20 mol % of $-\text{C}_6\text{H}_5\text{SiC}_6\text{H}_4\text{CH}_3-$ component.

^e Polymers contain 10 mol % of $-\text{C}_6\text{H}_5\text{SiC}_6\text{H}_4\text{CH}_3-$ component.⁸

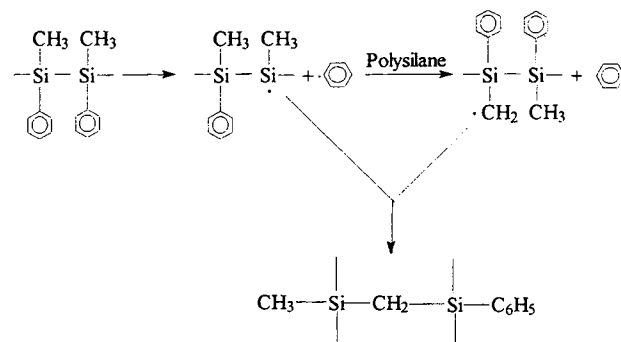
where f_1 , f_2 , and f_3 are the respective molar halogen functionality values for monomers reacted in the molar ratio $x : y : z$. Hydropolysilane terpolymers, which have an average molar functionality (f_{av}) value over 2 (Table II), lead to higher pyrolytic yields.

MH or PH comonomers provide sites which form crosslinks in the course of pyrolysis to retard decomposition as seen in Figure 5, where the pyrolytic yields increase as the contents of MH increase. PH, compared with MH, is unexpectedly good for obtaining high pyrolytic yields as shown in Table II. The phenyl group in PM is not as effective as that in PH in terms of obtaining high pyrolytic yields. The reasons for this are still under investigation. However, evidence that the phenyl group in PH introduces more free carbon into the pyrolytic residue than that in PM supports the suggestion that the phenyl group in the PH monomer behaves in a unique manner during pyrolysis.

PM, DM, or DP is used to increase molecular weight in the synthesis of hydropolysilane copolymers or terpolymers. These comonomers lead to linear structures that undergo chain entanglements which are required for good polymer fiber or film properties. Examination of Table II reveals that none of the PM, DM, or DP contents correlate with the pyrolytic yields. In general, linear polymers without the ability of useful crosslinking give negligible pyrolytic yields because of decomposition as

demonstrated by the direct pyrolysis of polydimethylsilane in the Yajima process.² This result is supported by Worsfold et al.,¹⁵ who heated polydimethylsilane up to 1000°C under argon and found a yield of only 1% residue. Nevertheless, as shown in Table II, polymer 1 gave a relatively high residue yield (18.9%) for the pyrolysis of polyphenylmethylsilane, which is also consistent with previous work (24.6%) by Worsfold et al.¹⁵

Two possible factors may account for the difference in the pyrolytic yields between homopolymers of PM and DM. First, for the pyrolysis of poly(PM), the bulky phenyl group may retard the reversion reactions (depolymerizations). Second, the pyrolysis of poly(PM) may lead to the ready loss of phenyl radicals followed by hydrogen abstraction and radical coupling reactions to form polycarbosilane, as shown below:



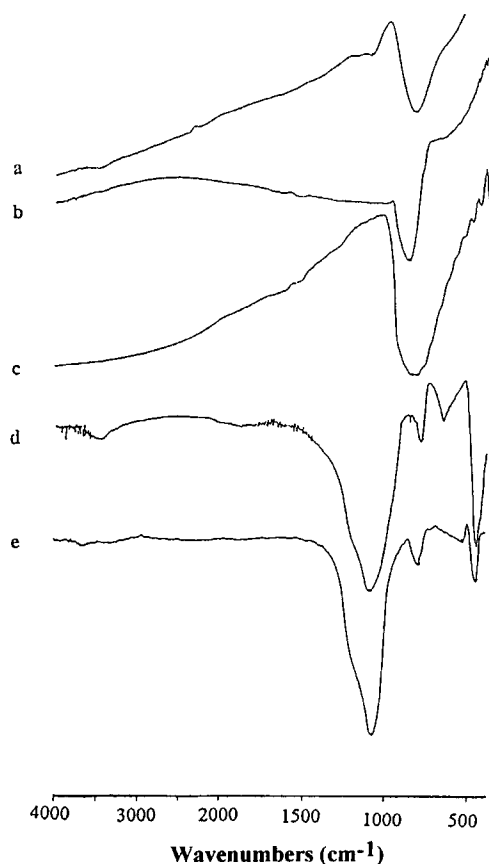


Figure 3 FTIR spectra of (a) the residue of polymer 9 pyrolyzed at 1400°C for 30 min in argon, (b) β -SiC, (c) α -SiC, (d) the residue of polymer 9 pyrolyzed at 1000°C for 30 min in air, and (e) fumed silica.

The latter hypothesis is supported by the observation that benzene has been detected from the pyrolysis of phenyl-substituted, silicon-backbone polymers.¹⁶ The first hypothesis also supports the formation of polycarbosilane facilitated by the retardation of reversion reactions during pyrolysis. Therefore, effective carbosilane rearrangement is found to be an important factor to obtain high pyrolytic yields.

Elemental analyses for Si, C, and O were performed by RBS spectrometry. Table III shows the residue compositions obtained by RBS analysis on each pyrolytic residue. Excess carbon is defined as the excess amount of carbon over the stoichiometric carbon content in SiC in the pyrolytic residue. As indicated in column 5 in Table III showing the residue composition in wt %, excess carbon exists in the pyrolytic residue for all analyzed samples except for polymer 13. The excess carbon ranges from 56.3 wt % for polymer 7, which has the highest polymer C/Si ratio (11.3), to 0 wt % for polymer 13, which

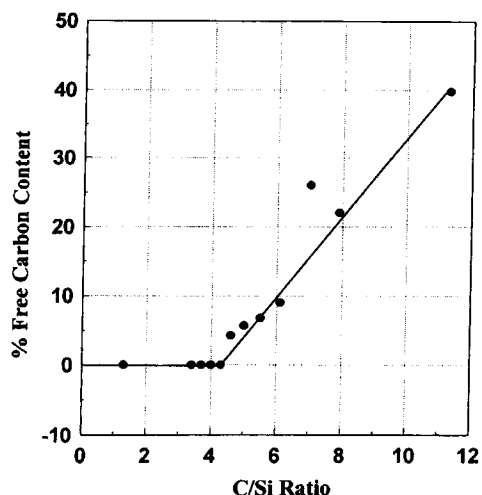


Figure 4 Percent of free carbon in pyrolytic residues of hydropolysilanes as a function of the polymers' C/Si ratios. The polymers were pyrolyzed at 1400°C for 30 min under argon. Free carbon was determined by TGA analyses in air.

has the lowest polymer C/Si ratio (1.3). Free carbon is defined as the carbon which has no chemical bondings to any other atoms than carbon atom. Thus, the evidence that the amount of excess carbon is much greater than the amount of free carbon for all analyzed residues except for polymer 1 (Table III, column 5) indicates that there is an unidentified carbon-containing phase in the pyrolytic residue in

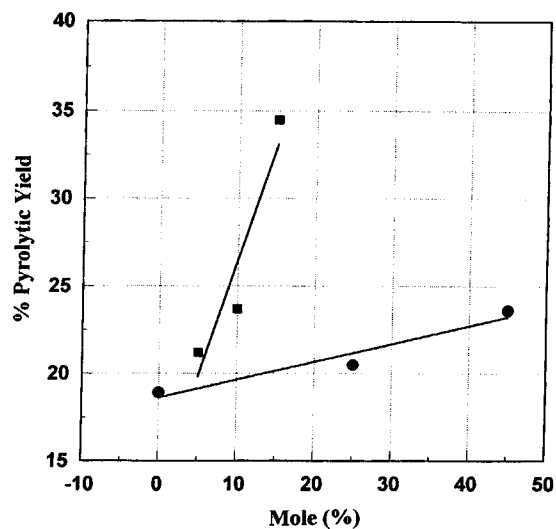


Figure 5 Percent of pyrolytic yields as a function of the mol % of MH (filled circle) in poly(MH/PM)s and the mol % of TM (filled square) in poly(MH/PM/TM)s. These polymers were pyrolyzed at 1400°C for 30 min under argon. The composition of MH in the terpolymer is 45 mol %.

addition to the carbon contained in stoichiometric SiC and free carbon. From columns 3 and 4 in Table III, a least-square linear fit shows that the yields of the pyrolytic residues for the variety of hydropolysilanes evaluated have nearly no dependence on C/Si ratios of the polymer precursors. However, C/Si ratios of polymers do significantly affect the SiC yields in the residues. Figure 6 shows that the SiC yields in the residues increase as the C/Si ratios of polymers decrease toward 1.0. The excess carbon in the pyrolytic residues increases as the C/Si ratios of the polymers increase (not shown). Column 6 in Table III shows mol ratios of C : Si : O calculated from residue compositions in column 5. Silicon-rich residue was found from polymer 13. C/Si ratios of the pyrolytic residues were found to be proportional to the C/Si ratios of the polymers with a slope of about 1/2 (Fig. 7).

Figure 8 and Table IV show that the yields of pyrolytic residues are pyrolysis-temperature-dependent. However, the effect of the pyrolysis time on the pyrolytic yields is insignificant. For example, polymer 9 was pyrolyzed at 1400°C for 30 min and 3 h under argon. It was found (Table IV) that the yields of residues (21.2 and 21% for 30 min and 3 h, respectively) are not dependent on the pyrolysis

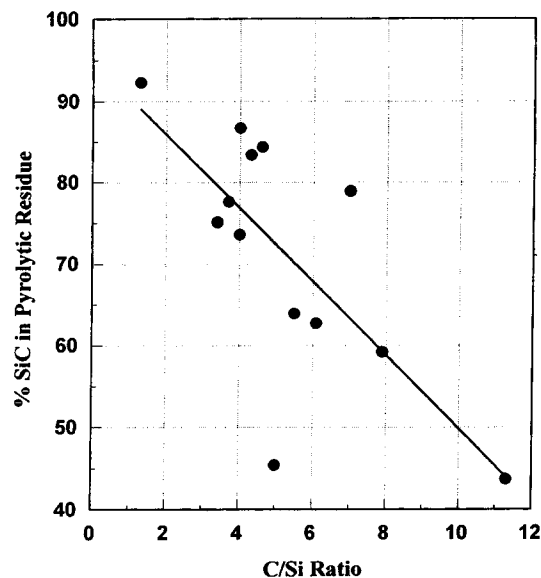


Figure 6 Percent of SiC in the pyrolytic residues as a function of C/Si ratios of hydropolysilanes that were pyrolyzed at 1400°C for 30 min under argon.

time, even though the pyrolysis time has an effect on the morphology of the residues, as will be discussed below.

Table III The Yields, Free Carbon Contents, Compositions, C/Si Ratios, and Apparent Crystalline Sizes of Pyrolytic Residues as a Function of Compositions and C/Si Ratios of Hydropolysilanes That Were Pyrolyzed at 1400°C for 30 Min in an RF Furnace Under Argon

Polymers	Polymer Compositions (Mol %)	Polymers' C/Si Ratios	Residue Yields	Residue Compositions (wt %)			C : Si : O (Mol Ratio)	Residues' C/Si Ratios	Apparent Crystalline Sizes L_{111} (nm)
				SiC	SiO ₂	C (Free C)			
1	MH/PM = 0/100	7.0	18.9%	78.9	0	21.1 (26)	1.89 : 1 : 0	1.89	4.64
2	MH/PM = 25/75	5.5	20.5%	63.9	2.9	33.2 (6.8)	2.65 : 1 : 0.06	2.65	4.42
3	MH/PM = 40/60	4.6	—	84.4	0	15.6 (4.3)	1.62 : 1 : 0	1.62	4.50
4	MH/PM = 45/55	4.3	23.6%	83.4	5.3	11.3 (0)	1.50 : 1 : 0.08	1.50	4.42
5	PH/DM = 30/70	3.2	42.0%	—	—	—	—	—	3.65
6 ^a	PH/PM = 30/50	7.9	31.2%	59.2	0	40.8 (22)	3.30 : 1 : 0	3.30	5.46
7 ^a	PH/DP = 15/65	11.3	31.0%	43.7	0	56.3 (39.8)	5.29 : 1 : 0	5.29	4.88
8	MH/PM/TM = 35/50/15	4.0	24.5%	86.7	0	13.3 (0)	1.50 : 1 : 0	1.50	6.19
9	MH/PM/TM = 45/50/5	4.0	21.2%	73.6	7.9	18.5 (0)	1.72 : 1 : 0.13	1.72	3.87
10	MH/PM/TM = 45/45/10	3.7	23.7%	77.6	6.5	15.9 (0)	1.59 : 1 : 0.11	1.59	3.31
11	MH/PM/TM = 45/40/15	3.4	34.5%	75.1	9.5	15.4 (0)	1.55 : 1 : 0.16	1.55	3.93
12	MH/PM/TM = 25/40/35	4.4	41.3%	—	—	—	—	—	—
13	MH/DM/TM = 30/30/40	1.3	28.5%	92.3	7.7	0 (0)	0.95 : 1 : 0.11	0.95	6.19
14 ^b	PH/DM/TM = 50/25/15	5.0	52.6%	45.4	14	40.6 (5.7)	3.30 : 1 : 0.34	3.30	3.09
15 ^b	PH/PM/TM = 30/40/20	6.1	38.2%	62.7	2.8	34.5 (9)	2.75 : 1 : 0.06	2.75	3.44

^a Polymers contain 20 mol % of the —C₆H₅SiC₆H₄CH₃— component.

^b Polymers contain 10 mol % of the —C₆H₅SiC₆H₄CH₃— component.⁸

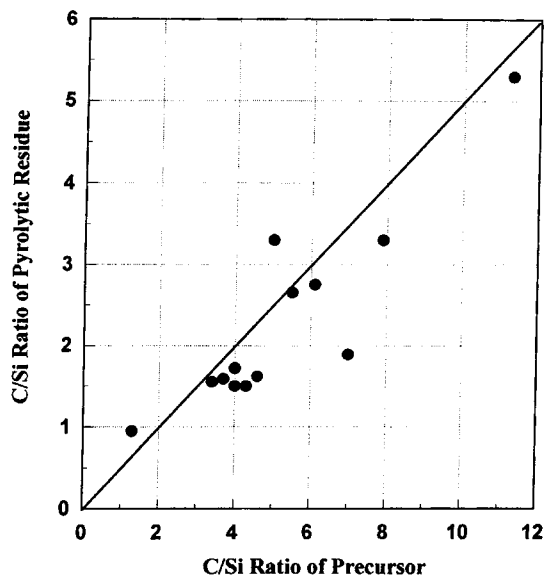


Figure 7 C/Si ratios of pyrolytic residues as a function of C/Si ratios of hydropolysilanes.

Silicon carbide (SiC) has over 130 polytypes,¹⁷⁻¹⁹ such as 3C, 6H, and 15R. The cubic structure of SiC exists only as the 3C polytype, also known as β -SiC. Other polytypes of hexagonal or rhombohedral structures are termed α -SiC. β -SiC is formed at a relatively low temperature. The X-ray patterns of commercial α -SiC and β -SiC are shown in Figure 9. The peaks in the X-ray patterns of β -SiC at approximately $2\theta = 36^\circ, 42^\circ, 60^\circ, 71^\circ,$ and 75° can be assigned to (111), (200), (220), (311), and (222), respectively, indicating that β -SiC has a face-centered cubic structure.

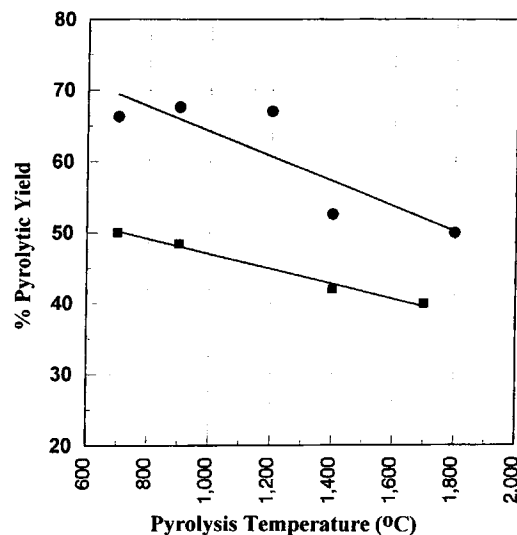


Figure 8 Percent of pyrolytic yields as a function of pyrolysis temperature for polymers 5 (filled square) and 14 (filled circle).

The residues from the pyrolysis of polymers reported in Table III at 1400°C for 30 min under argon in the RF furnace all show X-ray patterns of β -SiC. All have the two weakest peaks at $2\theta = 42^\circ$ and 75° missing because of the small crystalline size. These two peaks appear for the samples with larger crystalline size when the pyrolysis temperature is 1700°C or higher for 30 min (Figs. 10 and 11) or when the pyrolysis time is 3 h at 1400°C (Fig. 12). The peak at $2\theta = 28^\circ$ was characterized as a (101) diffraction line of α -quartz.²⁰ Peaks with angles other than $2\theta = 28^\circ, 36^\circ, 42^\circ, 60^\circ, 71^\circ,$ and 75° have not been

Table IV The Yields, Free Carbon Contents, and Apparent Crystalline Sizes of Pyrolytic Residues as a Function of Pyrolysis Conditions

Polymers	Compositions	C/Si Ratios	Pyrolysis Conditions	Pyrolytic Yields	Free Carbon Contents (Wt %)	Apparent Crystalline Sizes L_{111} (nm)
9	MH/PM/TM = 45/50/5	4.0	$1400^\circ\text{C} \times \text{Ar} \times 30 \text{ min}$	21.2%	0	3.87
9	MH/PM/TM = 45/50/5	4.0	$1400^\circ\text{C} \times \text{Ar} \times 1 \text{ hrs}$	—	0	5.15
9	MH/PM/TM = 45/50/5	4.0	$1400^\circ\text{C} \times \text{Ar} \times 3 \text{ hrs}$	21.0%	0	7.14
5	PH/DM = 30/70	3.2	$700^\circ\text{C} \times \text{N}_2 \times 30 \text{ min}$	50.1%	18.5	—
5	PH/DM = 30/70	3.2	$900^\circ\text{C} \times \text{N}_2 \times 30 \text{ min}$	48.5%	2.8	—
5	PH/DM = 30/70	3.2	$1400^\circ\text{C} \times \text{Ar} \times 30 \text{ min}$	42.0%	11	3.65
5	PH/DM = 30/70	3.2	$1700^\circ\text{C} \times \text{Ar} \times 30 \text{ min}$	40.0%	20.6	15.5
14 ^a	PH/DM/TM = 50/25/15	5.0	$700^\circ\text{C} \times \text{N}_2 \times 30 \text{ min}$	66.3%	21.9	—
14 ^a	PH/DM/TM = 50/25/15	5.0	$900^\circ\text{C} \times \text{N}_2 \times 30 \text{ min}$	67.6%	15.5	—
14 ^a	PH/DM/TM = 50/25/15	5.0	$1200^\circ\text{C} \times \text{Ar} \times 30 \text{ min}$	67.0%	0	2.11
14 ^a	PH/DM/TM = 50/25/15	5.0	$1400^\circ\text{C} \times \text{Ar} \times 30 \text{ min}$	52.6%	5.7	3.09
14 ^a	PH/DM/TM = 50/25/15	5.0	$1800^\circ\text{C} \times \text{Ar} \times 30 \text{ min}$	50.0%	21.2	13.25

^a This polymer contains 10 mol % of the $-\text{C}_6\text{H}_5\text{SiC}_6\text{H}_4\text{CH}_3-$ component.⁸

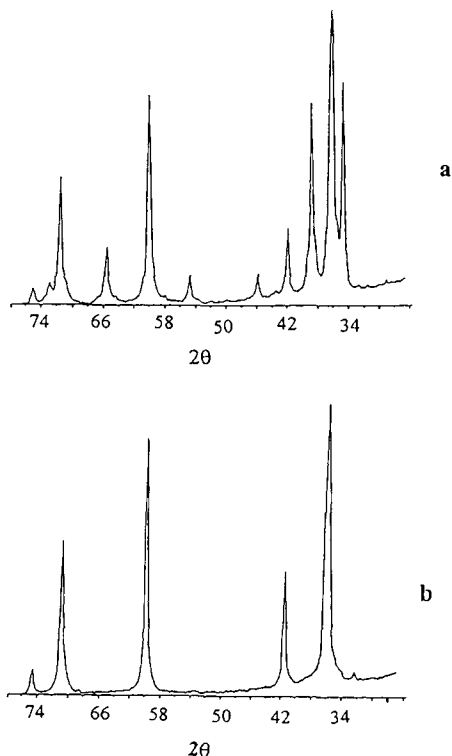


Figure 9 X-ray diffraction patterns for commercial (a) α -SiC and (b) β -SiC.

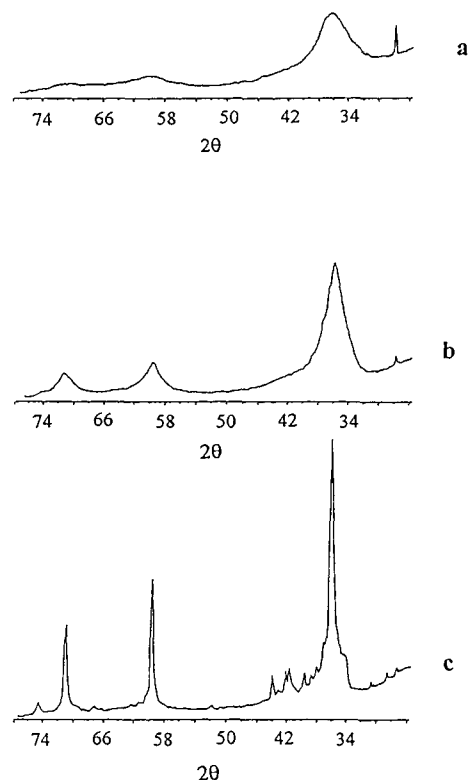


Figure 11 X-ray diffraction patterns of the pyrolytic residue of polymer 14 that was pyrolyzed for 30 min under argon at (a) 1200°C, (b) 1400°C, and (c) 1800°C.

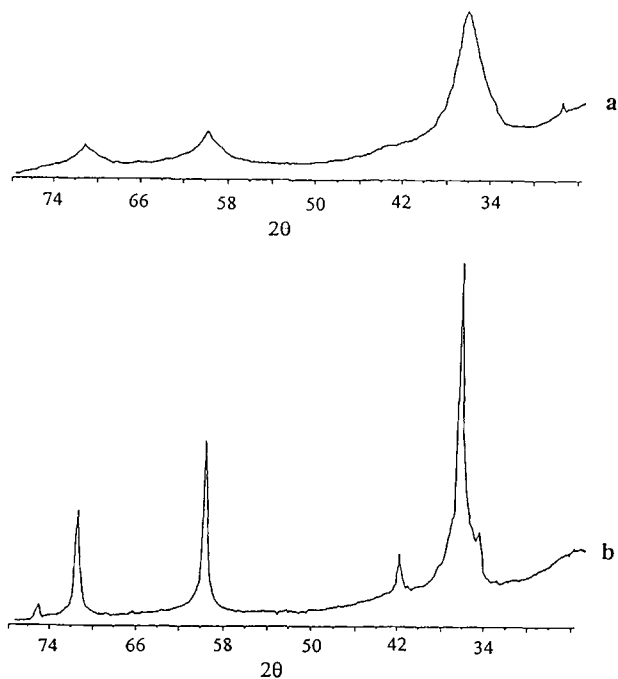


Figure 10 X-ray diffraction patterns of the pyrolytic residue of polymer 5 that was pyrolyzed for 30 min under argon at (a) 1400°C and (b) 1700°C.

assigned, but must correspond to certain types of crystal other than β -SiC and α -quartz.

The half-width of the strongest β -SiC peak, i.e., the (111) diffraction line at $2\theta = 36^\circ$, was used to investigate the apparent crystalline size. Peak half-width is inversely proportional to crystalline size. The apparent crystalline size L_{111} was calculated from the half-width β of the (111) line of the β -SiC using Scherrer's equation:¹²

$$L_{111} = 1.0\lambda/(\beta \cos \theta)$$

where λ is the wavelength of X-rays, and θ , the diffraction angle.

It is shown in Figure 13 and column 8 in Table III that apparent crystalline sizes, in the range of 3.09–6.19 nm, of residues are weakly proportional to contents of SiC in residues based on the same pyrolysis conditions for all polymers at 1400°C for 30 min under argon in the RF furnace. For different pyrolysis conditions, apparent crystalline sizes seem to increase with either increasing pyrolysis temperature or pyrolysis time as seen in Figures 10–12 and column 7 in Table IV. Apparent crystalline sizes are

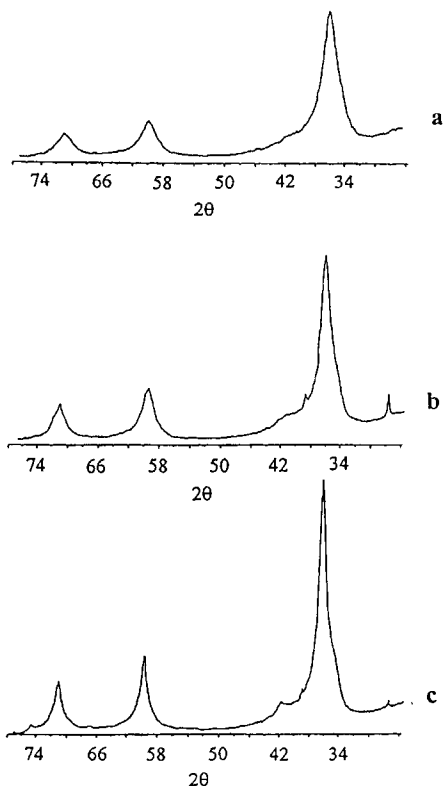


Figure 12 X-ray diffraction patterns of the pyrolytic residue of polymer 9 that was pyrolyzed at 1400°C under argon for (a) 30 min, (b) 1 h, and (c) 3 h.

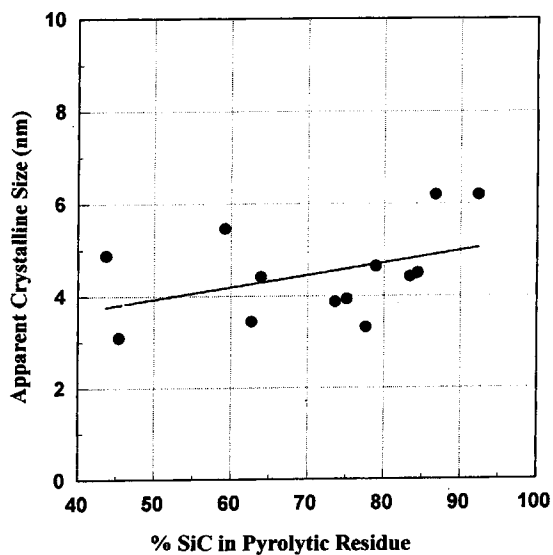


Figure 13 Apparent crystalline sizes of the pyrolytic residues of hydropolysilanes as a function of the SiC contents in the residues. These polymers were pyrolyzed at 1400°C for 30 min under argon.

15.5 and 13.3 nm for polymers 5 and 14 pyrolyzed at 1700 and 1800°C, respectively, as compared to 13.3 nm, calculated from Figure 9, for the commercial β -SiC product.

As seen in Figure 8 and Table IV for polymers 5 and 14, the yields of the residues decrease as the pyrolysis temperature increases, indicating that the evolution of carbon (evolved as CO or CO₂) from the residue and rearrangements in the residue continue to occur even at temperatures over 1400°C. These results are supported by the plot (Fig. 14) of free carbon content vs. the pyrolysis temperature for polymers 5 and 14. Free carbon content decreases as the pyrolysis temperature increases in the lower-temperature region but increases as pyrolysis temperature increases in the higher-temperature region.

A minimum content of free carbon is found in the course of heating. It can be explained as follows: The residue is totally amorphous and its density is low when the pyrolysis temperature is low, e.g., 700°C. The density of the residue increases and therefore less free carbon is detected in the densified inorganic residue when the pyrolysis temperature increases in the lower pyrolysis temperature region. However, the density of the inorganic residue reaches an almost constant value when pyrolysis temperature is higher than a certain value, after which the morphological changes determine the free carbon content as a function of the pyrolysis temperature. More excess carbon continues to evolve from the densified inorganic residue as indicated by the increases of free carbon and degree of crystal-

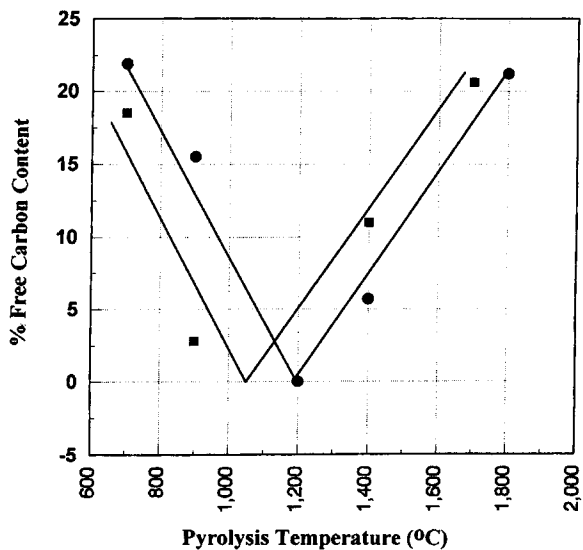


Figure 14 Percent of free carbon contents in the pyrolytic residues as a function of pyrolysis temperatures for polymers 5 (filled square) and 14 (filled circle).

linity of the residue when the pyrolysis temperature increases in the higher pyrolysis temperature region. Therefore, the minimum point of the curve of the plot of free carbon contents vs. the pyrolysis temperatures can roughly indicate the transition where the morphology of the inorganic residue changes from an amorphous phase to a crystalline phase. This is supported by the evidence of X-ray diffraction patterns. As seen in Figure 14, the minimum point is about 1200°C for the residue (from polymer 14) which shows a very weak X-ray diffraction pattern (Fig. 11). However, a strong X-ray pattern was found for the residue of polymer 14 pyrolyzed at 1400°C or higher (Fig. 11). Therefore, as found previously, the pyrolysis temperature should be over about 1000–1200°C to give crystalline SiC.

CONCLUSIONS

A series of hydropolysilane copolymers and terpolymers have been pyrolyzed and appear to have potential for use as precursors to β -silicon carbide. Properties of the pyrolytic residues are dependent on the type of monomer used and compositions of hydropolysilanes. The diorganodichlorosilane monomer, serving to increase molecular weights of the polymers, has been found not to be a significant factor in pyrolytic yields. The organotrichlorosilane monomer, leading to branched structures of the polymers, has been found to be helpful in obtaining high pyrolytic yields. The monoorganodichlorosilane monomer, providing crosslinking sites for the polymers, has been found useful in retarding decomposition during pyrolysis.

The nonvolatile pyrolytic residues were all black, indicating that excess carbon (including some free carbon) was present. This has been confirmed by elemental analysis for Si and C and by combustion analysis for free carbon. It has been found that the pyrolytic yields are not related to C/Si ratios of polymers, while SiC yields in the pyrolytic residues increase as C/Si ratios of polymers decrease. C/Si ratios of residues have been found to be proportional to C/Si ratios of polymers.

The pyrolytic residues from the pyrolysis of hydropolysilanes show a face-centered structure based on X-ray analyses. The yields and the morphologies of pyrolytic residues are pyrolysis-temperature-dependent. The yield of the pyrolytic residue becomes small and the apparent crystalline size becomes large as the pyrolysis temperature increases. The effects of the pyrolysis time on the pyrolytic yields are insignificant, even though the pyrolysis time has a

significant effect on the morphology of the pyrolytic residues. With increasing pyrolysis time, apparent crystalline sizes of the pyrolytic residues have been found to increase. In terms of apparent crystalline size, the pyrolysis temperature of about 1700°C is observed to produce a ceramic residue similar to a commercial SiC powder product. The pyrolysis temperature must be over 1000–1200°C to provide a crystalline residue based on the analysis of free carbon content and X-ray diffraction.

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