

# Structure and Properties of Polycarbosilane Synthesized from Polydimethylsilane under High Pressure

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**ABSTRACT:** The polycarbosilane (PCS), which is the precursor of SiC fiber, was synthesized under high pressure by thermal decomposition of polydimethylsilane. The composition, structure, and properties of the PCS were characterized by the measurements of softening point, elemental analysis, IR, GPC, NMR, TG-DTG-DTA, XRD, and oxidative reaction activity, respectively. Structure model of the PCS was therefore inferred. The results showed that the PCS was the polymer with a Si—C backbone with  $M_n$  about 1587. IR and NMR showed the presence of SiC<sub>4</sub> and SiC<sub>3</sub>H structure units containing Si—CH<sub>3</sub>, Si—CH<sub>2</sub>—Si, and Si—H groups. The ratio between H in C—H bond and H in Si—H bond was about 8.84 with SiC<sub>3</sub>H/SiC<sub>4</sub> and about 0.51 from <sup>1</sup>H NMR and <sup>29</sup>Si NMR, respectively. Elemental analysis gave

an empirical formula of SiC<sub>1.87</sub>H<sub>7.13</sub>O<sub>0.03</sub>. TG analysis showed that the ceramic yield of the PCS at 1200°C in a N<sub>2</sub> flow was about 78.9%. β-SiC microcrystal could be obtained when PCS was pyrolyzed at 1250°C with the crystal size about 37.5 Å. Compared with the PCS with similar softening point synthesized under normal pressure, the PCS synthesized under high pressure had approximate elemental composition, higher Si—H bond content and reaction activity, higher molecular weight, and higher ceramic yield, but lower ratio of SiC<sub>3</sub>H and SiC<sub>4</sub>. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1188–1194, 2006

**Key words:** polydimethylsilane; polycarbosilane; high pressure; composition and structure; property

## INTRODUCTION

The silicon carbide (SiC) fibers, which were well known for their excellent abilities, such as high tensile strength, high stiffness, excellent heat, oxidation and corrosion resistance, and intermiscibilities with resins, metal, and ceramics, had been applied widely in the fields of aviation and high temperature applications. Usually SiC fibers were used as a kind of fiber reinforcement and structural radar-wave absorbing materials.<sup>1,2</sup>

In recent years, preparation of organic polymer precursor derived SiC fiber had attracted considerable attention. In this way, the SiC fiber was obtained through melt-spinning from polycarbosilane (PCS), curing, and pyrolysis. It was thought that the composition, structure, and main physical chemistry characteristics of preceramic precursor had a significant effect on the properties of SiC fiber. Recent researches on precursor therefore mainly focus on the synthesis of new precursor and PCS modification.

The technology of the PCS synthesized by thermal decomposition of (polydimethylsilane). PDMS under normal pressure (PCS-NP) has been developed in China since 1980s. However, the molecular weight, softening point, and Si—H bond content of the PCS obtained were lower than those reported by Yajima,<sup>3,4</sup> which meant that the composition and structure of the PCS-NP should be improved. In the paper, PCS was synthesized by thermal decomposition of PDMS at high temperature under high pressure (PCS-HP). The composition, structure, and properties of the PCS-HP were studied. For comparison, those of PCS-NP with an approximate softening point were also studied.

## EXPERIMENTAL

### Synthesis and refining of PCS

In an autoclave was put a mount of PDMS, with filling by N<sub>2</sub> at 1 atm. It was then heated up to 450°C for 6 h. The final pressure was about 10 MPa. The unrefined PCS, an admixture of yellow–brown viscous and solid substance, was then obtained.

The unrefined PCS was dissolved in xylene and the solution was filtered. By vacuum distillation at certain temperature, the solvent and the fraction were removed. The final product was yellowish-brown glassy PCS-HP.

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TABLE I  
The Elemental Composition of PDMS and PCS

Sample	Si (wt %)	C (wt %)	H (wt %)	O (wt %)	Experimental formula
PDMS	44.82	38.66	14.96	1.56	SiC <sub>2.01</sub> H <sub>9.34</sub> O <sub>0.06</sub>
PCS-HP	48.33	38.65	12.31	0.71	SiC <sub>1.87</sub> H <sub>7.13</sub> O <sub>0.03</sub>
PCS-NP	48.22	38.14	13.11	0.53	SiC <sub>1.85</sub> H <sub>7.61</sub> O <sub>0.02</sub>

### Preparation of the PCS-HP green fiber

The PCS-HP green fiber was obtained by melt-spinning at about 310°C.

### Characterization

Softening points were measured with a HMK melting point testing instrument. The temperature corresponding to the first bright spot was regarded as the softening point of the PCS.

Elemental analysis was made for three elements: Si (by gravimetric method), C (by combustion volumetric method), and O (by gas analysis). The content of H was obtained by the difference.

IR spectra were obtained over the range of 4000–400 cm<sup>-1</sup> using a Nexus670 Fourier Transform Infrared Spectrometer by the KBr pellet method. Si—H bond content of PCS fiber was calculated from the absorbency ratio of characteristic absorption peaks at 2100 and 1250 cm<sup>-1</sup> ( $A_{\text{Si-H}}/A_{\text{Si-CH}_3}$ ). Reaction degree *P* of Si—H bond was defined as the following:

$$P = \frac{(A_{\text{Si-H}}/A_{\text{Si-CH}_3})_{\text{greenfiber}} - (A_{\text{Si-H}}/A_{\text{Si-CH}_3})_{\text{curedfiber}}}{(A_{\text{Si-H}}/A_{\text{Si-CH}_3})_{\text{greenfiber}}} \times 100\%$$

Molecular weight distribution was measured with a Waters-1515 by Gel Permeation Chromatography (GPC) with tetrahydrofuran eluant at a flow rate 1.0 mL/min. Polystyrene standards were used for calibration.

<sup>1</sup>H NMR spectra were measured with a varian inova-300 NMR spectrometer with C<sub>6</sub>D<sub>6</sub> as solvent. <sup>29</sup>Si NMR spectra were measured with a CDCl<sub>3</sub> solvent. TG-DTG-DTA curves of PCS were obtained by a NETZSCH STA 449C up to 1200°C with a heating rate of 10°C/min in a N<sub>2</sub> flow. X-ray diffraction pattern was obtained with an ADVANCED X-ray diffractometer using Cu K $\alpha$  radiation. Gel content was measured with suo-distillation instrument. Cured PCS fiber was distilled for 24 h with xylene as solvent.

## RESULTS AND DISCUSSION

### Composition and structure of PCS

#### Elemental analysis

The softening point of the obtained PCS-HP was 220°C. The composition, structure, and properties of

the PCS-HP were compared with PCS-NP with a softening point 215°C.<sup>3,4</sup> The elemental composition of PDMS and PCS were shown in Table I.

Table I indicates that, PCS-HP and PCS-NP had close Si, C, H, and O content. The experimental formulas were therefore similar. Compared with PDMS, PCS had lower C, H, and O content. Because PDMS with Si—Si backbone converted to PCS with Si—C backbone in the process of thermal decomposition and rearrangement to the byproduct of low molecular weight hydrocarbon, hydrogen, and cyclosiloxane,<sup>5</sup> high pressure during the synthesis process had little influence on the elemental composition of PCS.

#### Infrared spectra

The IR spectra of PDMS, PCS-NP, and PCS-HP were shown in Figure 1. In Figure 1, the peaks at 2950 and 2900 cm<sup>-1</sup> contributed to C—H stretching in Si—CH<sub>3</sub>, the peaks at 1410 cm<sup>-1</sup> to C—H stretching or CH<sub>2</sub> deformation in Si—CH<sub>3</sub>, 1250 cm<sup>-1</sup> to Si—CH<sub>3</sub> deformation, 690–860 cm<sup>-1</sup> to Si—CH<sub>3</sub> rocking, and Si—C stretching. The peak at 1000–1100 cm<sup>-1</sup> in PDMS spectra was Si—O stretching. Besides these peaks, in the PCS-HP and PCS-NP spectra, there were peaks at 2100 cm<sup>-1</sup> contributed to Si—H stretching, 1360 cm<sup>-1</sup> due to C—H stretching of Si—CH<sub>2</sub>—Si, and 1020 cm<sup>-1</sup>

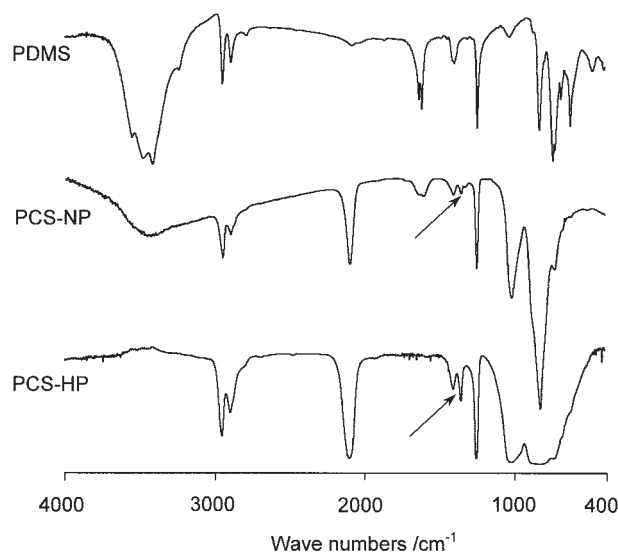
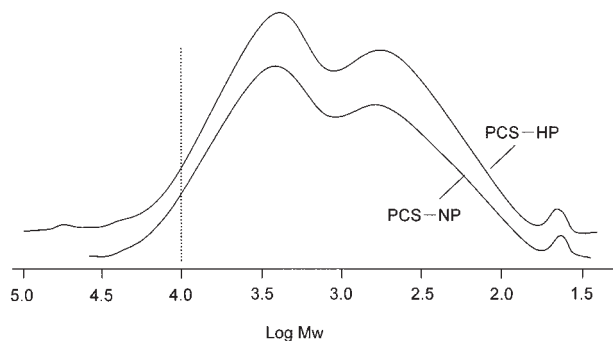


Figure 1 Infrared spectra of PDMS and PCS.



**Figure 2** The molecular weight distributions of PCS.

were  $\text{CH}_2$  wagging in  $\text{Si}-\text{CH}_2-\text{Si}$ . Therefore, there were  $\text{Si}-\text{CH}_3$ ,  $\text{Si}-\text{CH}_2-\text{Si}$ , and  $\text{Si}-\text{H}$  groups in the PCS molecule, which illuminated that PCS with  $\text{Si}-\text{C}$  backbone was obtained by thermal decomposition of PDMS at high temperature under high pressure.

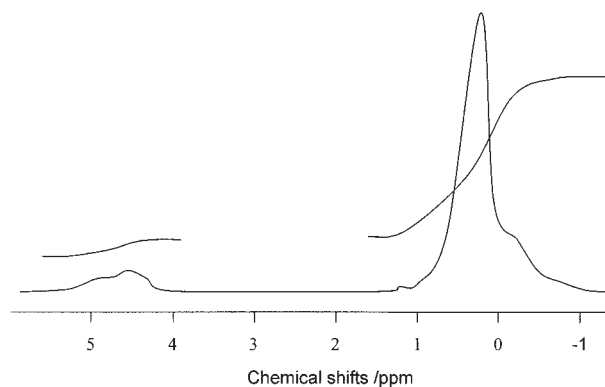
In the spectra of PDMS and PCS-NP, absorptions at 3400 and  $1600\text{ cm}^{-1}$  attributed to  $\text{O}-\text{H}$  stretching of  $\text{H}_2\text{O}$ , because PCS or KBr pellet was affected by dampness.

#### Molecular weight and distribution

The molecular weight distributions of the PCS-HP and PCS-NP measured by GPC were shown in Figure 2.  $M_n$ , the number average molecular weight of PCS-HP, was about 1587.  $M_w$ , the weight average molecular weight, was about 2752. The polydispersity index,  $M_w/M_n$ , was therefore about 1.73.  $M_n$  of PCS-NP was 1578 with  $M_w$  2642.  $M_w/M_n$  of PCS-NP was 1.67. The molecular weight of PCS-HP was higher and the molecular weight distribution was broader than those of PCS-NP respectively. It was because the reactive low molecular weight PCS evolved from the reaction system under normal pressure but participated in condensation under high pressure and increased the molecular weight. As a whole, the molecular weight of PCS-HP and PCS-NP were low and the polydispersity indexes were high. To increase the molecular weight and improve the spinnability of the PCS, optimum synthesis conditions should be further investigated.

#### NMR analysis

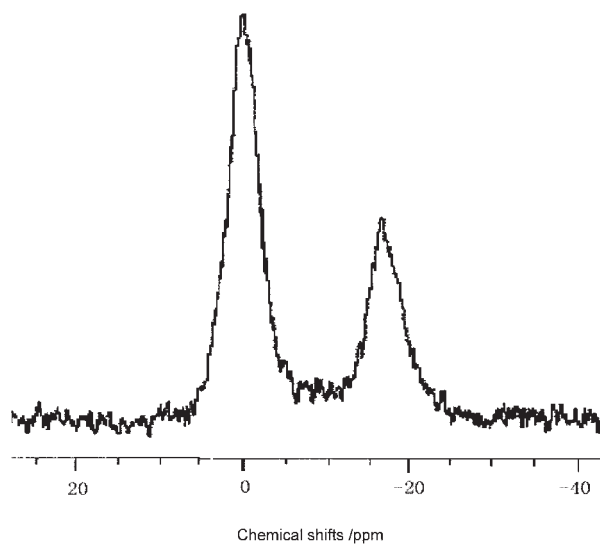
$^1\text{H}$  NMR spectrum of PCS-HP was shown in Figure 3. Chemical shifts  $\delta$  were based on 0 ppm of tetramethylsilane for the internal standard. The peak at 4–5 ppm corresponded to the resonance of H in  $\text{Si}-\text{H}$  bond. The broad peak around 0 ppm corresponded to the resonance of H in  $\text{C}-\text{H}$  bond, which was considered the overlap of three peaks. The peaks around 0.2,  $-0.1$ , and  $-0.6$  ppm were the resonance of H in  $\text{Si}-\text{CH}_3$ , H in  $\text{Si}-\text{CH}_2$ , and H in  $\text{Si}-\text{CH}$ , respectively.



**Figure 3**  $^1\text{H}$  NMR spectrum of PCS-HP.

They were all characteristics of carbosilane. From the ratio of  $\text{C}-\text{H}$  and  $\text{Si}-\text{H}$  resonance peak areas in  $^1\text{H}$  NMR spectra,<sup>6,7</sup> the value of  $\text{C}-\text{H}/\text{Si}-\text{H}$  was 8.84. The ratio of  $\text{C}-\text{H}/\text{Si}-\text{H}$  of PCS-NP was 9.12.<sup>3,4</sup> The content of  $\text{Si}-\text{H}$  bonds in PCS-HP was a little higher than that of PCS-NP, which meant a higher  $\text{Si}-\text{H}$  bonds reaction activity in the curing process.

$^{29}\text{Si}$  NMR spectrum of PCS-HP was shown in Figure 4. Chemical shifts  $\delta$  were also based on tetramethylsilane for the internal standard. In Figure 4, the peak around  $-0.75$  ppm was assigned to be the resonance of silicon bonded to four carbons ( $\text{SiC}_4$ ). The signal at  $-17.5$  ppm was the resonance of silicon bonded to hydrogen and three carbons ( $\text{SiC}_3\text{H}$ ). From peak integral, the ratio of  $\text{SiC}_3\text{H}$  to  $\text{SiC}_4$  was about 0.51, a little lower than 0.53 of PCS-NP,<sup>3,4</sup> which indicated a slightly lower linear degree than PCS-NP. It also meant that there were 34% of  $\text{SiC}_3\text{H}$  and 66% of  $\text{SiC}_4$  in the  $\text{Si}-\text{C}$  structure of PCS-HP.<sup>6,7</sup> So pressure might accelerate the disorderly rearrangement and condensation among the PCS molecules.



**Figure 4**  $^{29}\text{Si}$  NMR spectrum of PCS-HP.

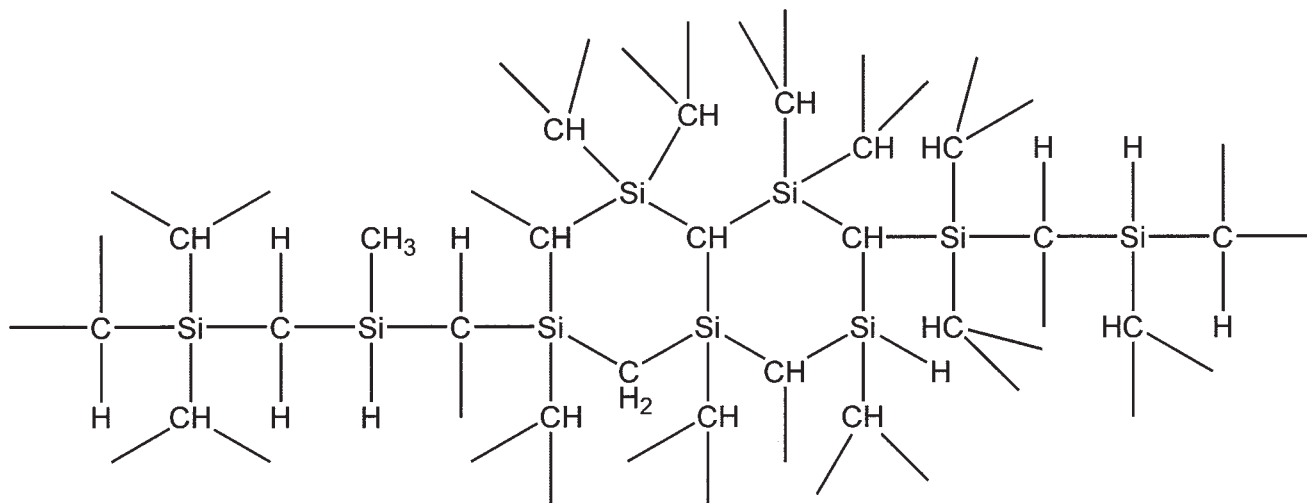


Figure 5 Structure unit model of PCS-HP.

According to these analyses, the PCS-HP was the general term for organosilicon polymers with a Si—C backbone.<sup>3,6-8</sup> IR and NMR showed the presence of SiC<sub>4</sub> and SiC<sub>3</sub>H structure units containing Si—CH<sub>3</sub>, Si—CH<sub>2</sub>—Si, and Si—H groups. From the results of NMR,<sup>6-8</sup> PCS-HP contained nine C—H bonds with one Si—H bond and two SiC<sub>4</sub> units with one SiC<sub>3</sub>H unit. The structure unit model of PCS-HP, inferred from the analysis above, is shown in Figure 5. PCS-HP had a complicated structure with low linear degree,

which was a disadvantage for the melt-spinning of PCS. Suitable synthesis condition of PCS under high pressure should be optimized.

#### The properties of PCS

The thermal decomposition of PCS-HP

TG-DTG-DTA curves of PCS-HP in a N<sub>2</sub> flow up to 1200°C were shown in Figure 6. From Figure 6, four

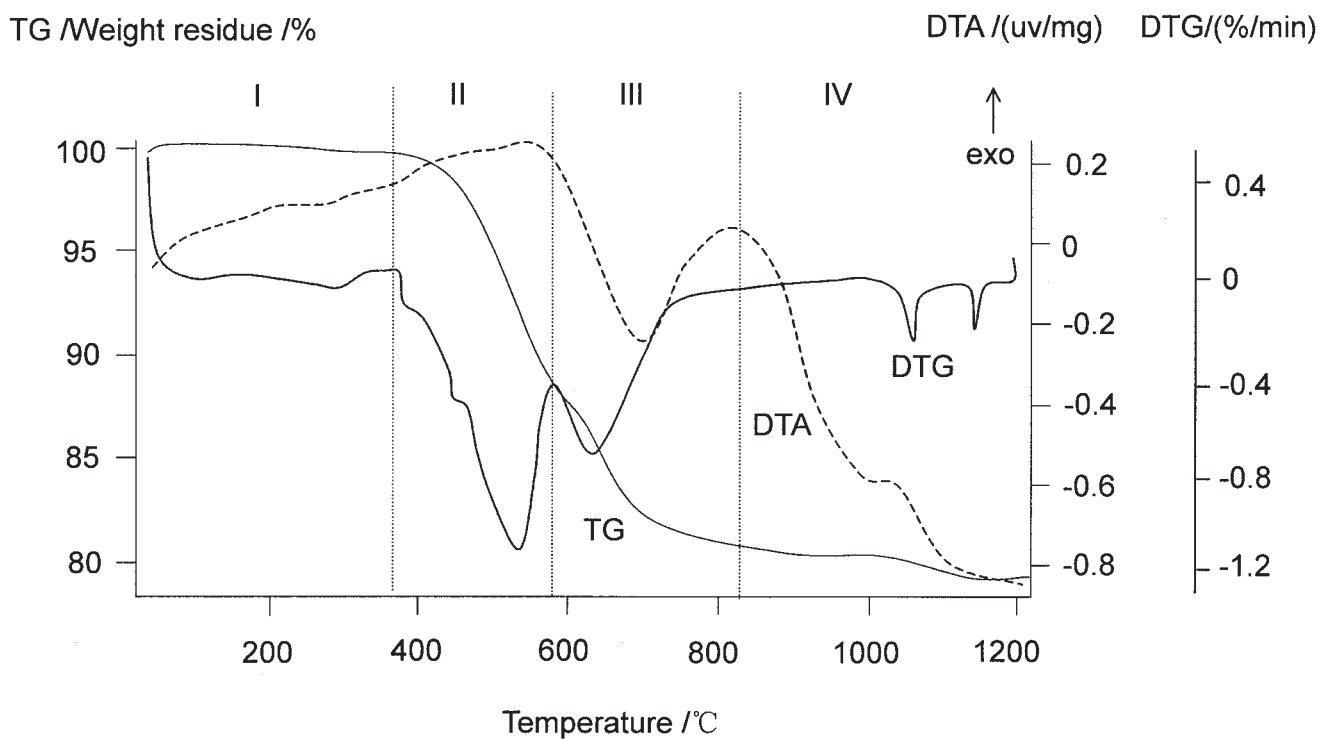


Figure 6 TG-DTG-DTA curves of PCS-HP in a N<sub>2</sub> flow.

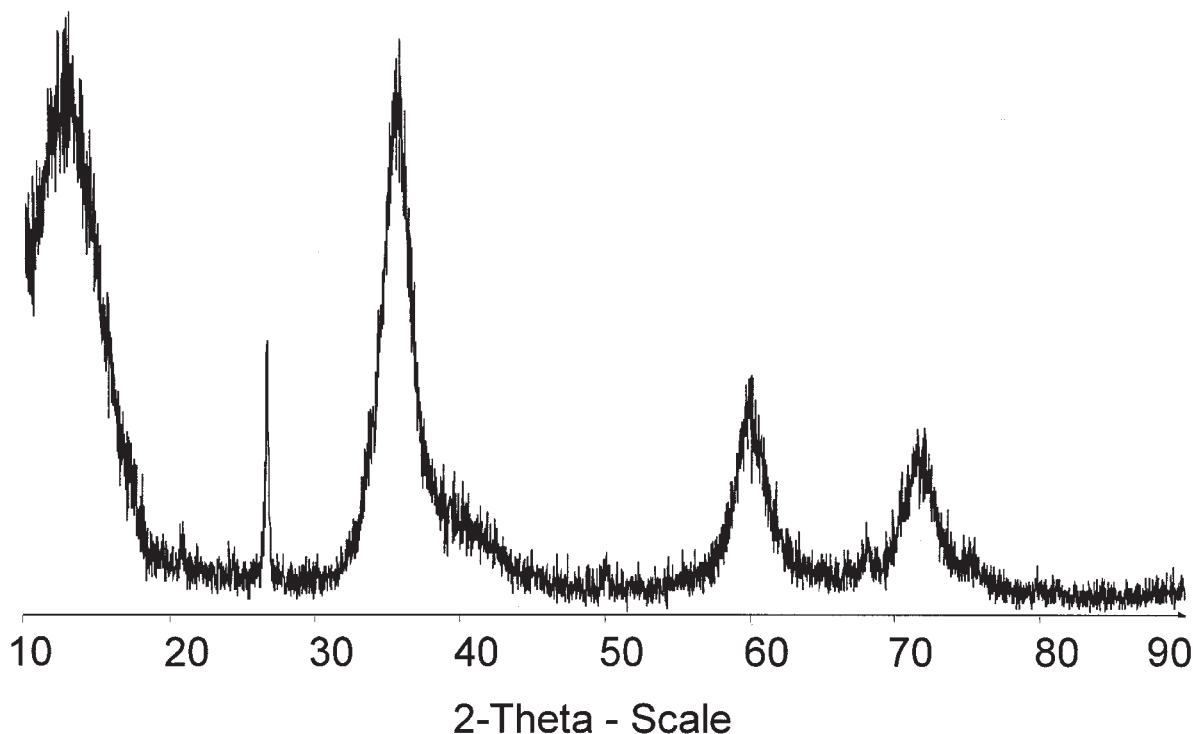


Figure 7 XRD pattern of the pyrolysis product of PCS-HP.

stages could be divided during the pyrolysis process of PCS-HP. In the first stage (from RT to 360°C), the weight loss was only 0.4% as a result of evaporation of low molecular weight components. No remarkable change occurred in the stage. In the second stage (360–585°C), the TG curve fell off rapidly as a result of evaporation of low molecular weight components and evolution of H<sub>2</sub> and CH<sub>4</sub> because of the dehydrogenation and dehydrocarbonation condensation among the PCS molecules. The weight loss was about 11.4%. In this stage, the network structure was gradually formed by thermal curing. In the third stage (585–820°C), the DTA curve exhibited a large endothermic peak. The weight loss was 7.4%. The reaction in this stage was mainly the thermal decomposition of the side chains such as Si—H, Si—CH<sub>3</sub>, and C—H in Si—CH<sub>2</sub>—Si of the PCS. Thermal decomposition of the main chains hardly occurred, because the weight loss was low. In the last stage (from 820°C to 1200°C), the conversion of the PCS into the inorganic state was almost terminated at about 820°C and completed with further increase in temperature, accompanied by weight loss of 1.9% because of evolution of residual C and H. DTA curve showed the exothermic peak at 1034°C because of the crystallization of β-SiC.<sup>6–9</sup>

#### X-ray diffraction analysis

The X-ray diffraction pattern of the pyrolyzed product of PCS-HP at 1250°C in a N<sub>2</sub> flow is shown in Figure

7. The pyrolysis product was β-SiC crystallite. The peaks at  $2\theta = 36^\circ, 60^\circ, 72^\circ$  were contributed to the (111), (220), and (311) diffraction lines, respectively. From the (111) line, the grain size was found to be 37.5 Å. The peak at  $2\theta = 26.5^\circ$  was due to a (101) diffraction line of α-quartz, which showed a high oxygen content.<sup>8</sup> The peak at 12.5° due to the small angle diffraction could be ignored.

#### Oxidative reaction activity

Si—H bond content of PCS molecule could be calculated on the basis of molecular weight ( $M_n = 1587$ ) and structure unit content of PCS (SiC<sub>3</sub>H/SiC<sub>4</sub> = 0.51). According to the calculation, there were eight Si—H bonds per PCS-HP molecule.<sup>6–8</sup>

PCS green fiber must be cured to avoid melting in the pyrolysis process. PCS green fiber was cured for 2–10 h at 190°C in air. Si—H bonds in the PCS molecule would react with oxygen during the curing process. Si—O—Si bonds and network structure were therefore produced.<sup>8,9</sup> The weight, Si—H bonds reaction degree, gel content, and oxygen content of PCS fiber changed with the increase of curing time. The results are shown in Table II.

The weight, Si—H bond reaction degree, and gel content of the PCS fiber all increased with increase in curing time because of the introduction of oxygen. The oxygen content and Si—H bond reaction degree of the PCS-HP were lower than those of PCS-NP under the



TABLE II  
Influence of Curing Time on the Properties of PCS Fiber

Sample	Curing time (h)	Si—H bond reaction degree (%)	Si—H bond reaction number per PCS	Weight increase (%)	Gel content increase (%)	Oxygen content of PCS fiber (mass fraction, %)
PCS-HP	2	4.75	0.38	5.53	1.22	7.78
	3	11.84	0.95	6.91	6.12	8.82
	4	20.15	1.61	7.10	26.43	11.90
	5	28.16	2.25	7.96	31.28	10.17
	6	35.15	2.81	8.15	52.52	12.57
	7	39.41	3.15	10.83	74.85	13.42
	8	43.05	3.44	11.40	72.38	14.92
	10	47.10	3.79	11.36	74.00	15.57
PCS-NP	4	57.03	3.99	10.11	77.98	13.14

same curing condition, which showed that the Si—H bond content of PCS-HP was higher than that of PCS-NP. So PCS-HP green fiber could be cured with less oxygen. It was consistent with the result of  $^1\text{H}$  NMR analysis.

The relationship between Si—H bond reaction degree and PCS fiber weight increase is shown in Figure 8. The weight increase of the PCS fiber was positive in proportion to the Si—H bond reaction degree, which meant that the weight increase was mainly due to the oxidative reaction of Si—H bonds and production of Si—O—Si bonds. Network structure was therefore gradually produced among the PCS molecules. The PCS became infusible in xylene with increase in reaction degree. The gel content of the PCS fiber was gradually increased with the increase of Si—H bond reaction degree. The relationship between Si—H bond reaction degree and PCS fiber gel content is shown in Figure 9.

When the Si—H bond reaction degree was about 15%, one coupling point was produced per PCS

molecule and the network structure appeared. Three to four coupling points were produced when the Si—H bond reaction degree was about 40%. So the three-dimensional network structure was formed theoretically.

## CONCLUSIONS

1. PCS-HP was the polymer with a Si—C backbone with the number average molecular weight about 1587. The result of chemical analysis showed that the experimental formula was  $\text{SiC}_{1.87}\text{H}_{7.13}\text{O}_{0.03}$ . IR and NMR showed the presence of  $\text{SiC}_4$  and  $\text{SiC}_3\text{H}$  structure units containing Si— $\text{CH}_3$ , Si— $\text{CH}_2$ —Si, and Si—H groups. The value of C—H/Si—H was about 8.84 with  $\text{SiC}_3\text{H}/\text{SiC}_4$  about 0.51. The inferred model showed that the PCS-HP had a complicated structure with a low linear degree.
2. The TG curve showed that the ceramic yield of PCS-HP at 1200°C in a  $\text{N}_2$  flow was 78.9%.  $\beta$ -SiC

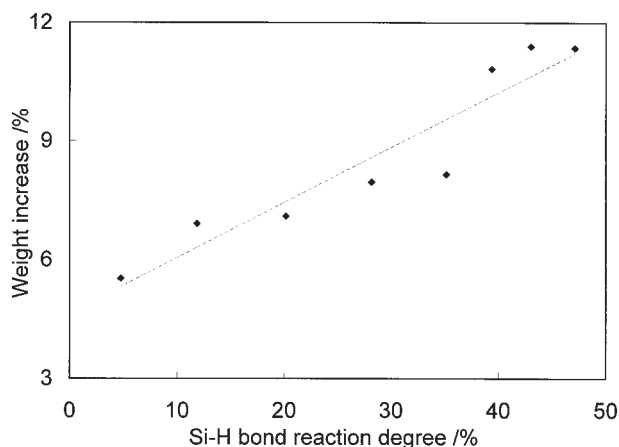


Figure 8 Relationship between Si—H bond reaction degree and PCS fiber weight increase.

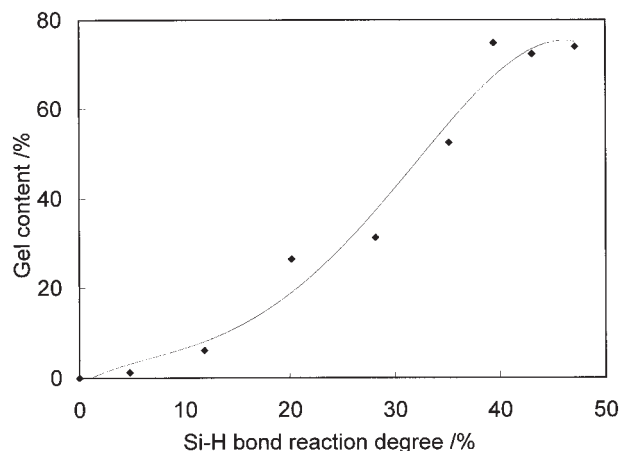


Figure 9 Relationship between Si—H bond reaction degree and PCS fiber gel content.

microcrystal could be obtained when PCS-HP was pyrolyzed at 1250°C with the crystal size about 37.5Å. The Si—H bond reaction degree of PCS-HP fiber was about 20% after curing for 4 h at 190°C, which showed that PCS-HP had high Si—H bond content and reaction activity.

3. PCS-HP had a similar experimental formula, higher molecular weight, higher Si—H bond content and reaction activity, but a lower linear degree than PCS-NP. Suitable synthesis conditions should be further studied.

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