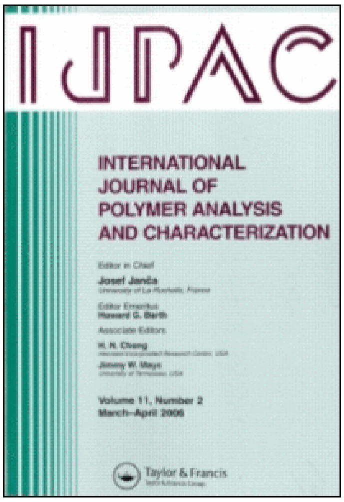

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Analysis and Characterization of Polycarbosilane

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Abstract: Polycarbosilane (PCS) synthesized at high temperature under high pressure from liquid polysilane was shown to be an organosilicon polymer with a Si–C backbone. M_W of the PCS with a softening point of 209°C was about 2861. Elemental analysis gave an empirical formula of $SiC_{1.86}H_{7.50}O_{0.02}$. IR and ^{29}Si-NMR showed the presence of SiC_4 and SiC_3H structural units. The H mole ratio for C–H bond to Si–H bond was about 9.83, and the Si mole ratio for SiC_3H to $SiC_4$was about 0.94. TG analysis showed the ceramic yield of the PCS at 1200°C in N_2 to be about 78.9%. β-SiC microcrystal was obtained when the PCS was pyrolyzed at 1250°C in N_2 with a grain size of about 35.9 Å.

Keywords: Analysis; Characterization; Liquid polysilane; Polycarbosilane

INTRODUCTION

In recent years, SiC fiber prepared from organic polymer precursor has attracted considerable attention.[1–3] SiC fiber was obtained through melt spinning from polycarbosilane (PCS), curing, and pyrolysis. It was thought that the composition, structure, and main physical chemistry

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characteristics of the preceramic precursor had a significant effect on the properties of the SiC fiber. Recent research on the precursor was therefore mainly focused on the synthesis of new precursors and PCS modification.

The process for the preparation of PCS under normal pressure (PCS-NP) via thermal decomposition of PDMS was developed in China in the 1980s. The molecular weight, softening point, and Si–H content of the PCS obtained, however, were lower than those reported by Yajima et al.[4,5] This meant that the composition and structure of the PCS-NP should be improved. In this study, PCS was synthesized at high temperature under high pressure (PCS-HP) by thermal decomposition of liquid polysilane (LPS), which was not previously reported. The composition, structure, and properties of the resulting PCS-HP were investigated.

EXPERIMENTAL SECTION

Preparation of LPS

An amount of polydimethylsilane (PDMS) was placed into a three-necked flask. It was then heated up to 420°C under a N_2 flow. PDMS was converted into colorless transparent LPS.

Synthesis and Refinement of PCS

A 200 g amount of LPS was placed in an autoclave, filled with N_2 at 1 atm. It was then heated up to 450°C and held for six hours. A crude PCS consisting of an admixture of yellow viscous and solid substance was obtained. The final pressure of the reaction system was about 2–5 MPa when cooled to room temperature.

The crude PCS was dissolved in xylene and the solution was filtered. By vacuum distillation at 350°C, the solvent and the fraction of lower molecular weight PCS were removed. The final product (PCS-HP) was yellowish and resin-like. The yield of the PCS was about 45%.

Characterization

Softening point was measured with an 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 carried out on three elements: Si (by a gravimetric method), C (by a combustion volumetric method), and O (by gas analysis). The content of H was obtained by difference.

IR spectra were obtained in the range 4000–400 cm^{-1} using a Nexus 670 Fourier-transform infrared spectrometer (FTIR) using the KBr pellet method. Si−H bond content of PCS, A_{Si-H}/A_{Si-CH_3}, was calculated from the absorbance ratio of characteristic absorption peaks of Si−H and Si−CH_3 at 2100 cm^{-1} and 1250 cm^{-1}, respectively. ^{1}H-NMR was carried out with a Varian Inova-300 nuclear magnetic resonance (NMR) spectrometer with C_6D_6 as solvent. ^{29}Si-NMR was carried out with $CDCl_3$ solvent.

Molecular weight distribution was measured with a Waters-1515 gel permeation chromatograph (GPC) with tetrahydrofuran eluant at a flow rate of 1.0 mL/min. Polystyrene standards were used for calibration.

Thermal gravimetric-differential thermal gravimetric-differential thermal analysis (TG-DTG-DTA) curves for PCS were recorded via a Netzsch STA 449C instrument up to 1600°C at a heating rate of 10°C/min in a N_2 flow.

X-ray diffraction pattern was obtained with a research-grade X-ray diffractometer using Cu Kα radiation. The grain size D was calculated by the following equation:

$$D = \frac{0.89 \cdot \lambda}{\beta \cdot \cos\theta}$$

where λ is 1.5406 Å, β is the half-height width of the diffraction peak, and θ is the angle in radians of the corresponding diffraction peak.

RESULTS AND DISCUSSION

Composition and Structure of PCS

Elemental Analysis

The average softening point of the PCS-HP ranged from 209° to 219°C. Elemental analysis of PCS-HP gave the following breakdown: Si, 48.24 wt%; C, 38.36 wt%; H, 12.92 wt%; and O, 0.48 wt%. The empirical formula was therefore $SiC_{1.86}H_{7.50}O_{0.02}$.

Because of the sensitivity of the PCS precursor to oxygen and moisture, absorption of oxygen or moisture could lead to higher oxygen content than expected. Oxygen could be introduced into the precursor polymer structure during synthesis. Variations in the synthesis conditions, such as the reaction temperature, would also affect the composition with a general decrease in the amount of carbon and hydrogen while the degree of polymerization of the PCS would increase. The experimental result showed that the mole ratio of carbon:silicon in the PCS-HP precursor was about 1.86. In comparison with PCS-NP

($SiC_{1.87}H_{7.10}O_{0.02}$) with a similar softening point,[5] PCS-HP had a higher H content and a lower C/Si ratio, both being beneficial for SiC fiber with high performance properties.

Infrared Spectra

The IR spectra of LPS, PCS-HP, and PCS-NP are shown in Figure 1. In Figure 1, the peaks at 2950 cm^{-1} and 2900 cm^{-1} correspond to C—H stretching in Si—CH_3, the peak at 2100 cm^{-1} to Si—H stretching, 1410 cm^{-1} to C—H stretching or CH_2 deformation in Si—CH_3, 1250 cm^{-1} to Si—CH_3 deformation, 1020 cm^{-1} to CH_2 wagging in Si—CH_2—Si, and 690–860 cm^{-1} to Si—CH_3 wagging and Si—C stretching. Thus, LPS was a mixture of low-molecular-weight carbosilane and polysilane.[6,7] Besides the peaks above, in the PCS-HP spectrum there was a peak at 1360 cm^{-1} due to C—H stretching of Si—CH_2—Si. Therefore, there were Si—CH_3, Si—CH_2—Si, and Si—H structural units in the PCS molecule, which indicated that PCS with Si—C backbone was obtained by thermal decomposition of LPS at high temperature and high pressure.

In the spectra of LPS and PCS, absorptions at 3400 cm^{-1} and 1600 cm^{-1} could be attributed to O—H stretching of H_2O or Si—OH, because PCS or KBr pellet was affected by moisture.

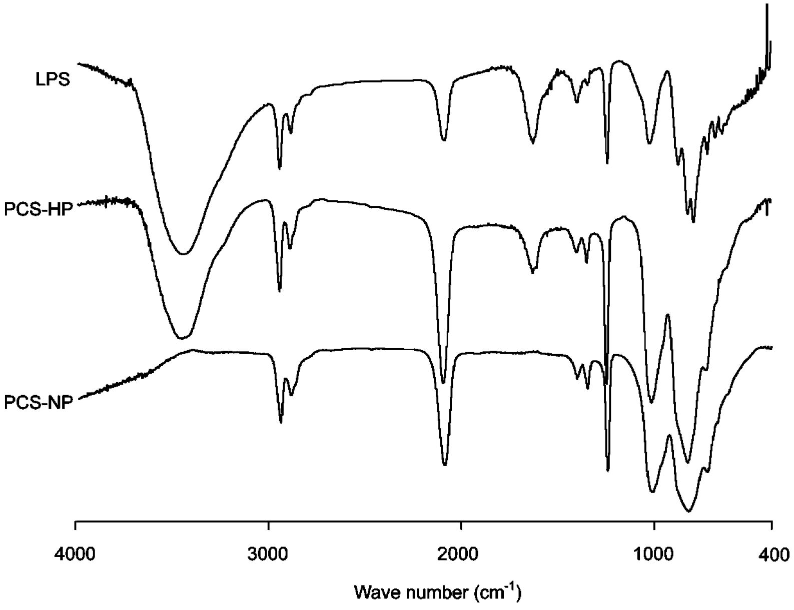

Figure 1. Infrared spectra of LPS, PCS-HP, and PCS-NP.

From Figure 1, PCS-HP and PCS-NP had the same peaks, which indicates that PCS-NP contains the same structural units as PCS-HP. However, PCS-HP and PCS-NP had different absorption intensities. The content of Si–H bond for PCS-HP (according to A_{Si-H}/A_{Si-CH_3} in Figure 1) was 1.27, which was higher than 0.89 for the PCS-NP with the closest softening point.[2,4,5,8] It meant that the PCS-HP had a higher reactivity than PCS-NP during the curing process.

Molecular Weight Distribution

Previous work[4,5] showed that two steps could be discerned during the synthesis of PCS from LPS. First, LPS was converted into low-molecular-weight carbosilane with increasing temperature. Second, PCS was produced through dehydrogenation and condensation among the carbosilane moieties. The molecular weight of PCS increased gradually with increasing reaction temperature or reaction time. Different synthetic conditions, therefore, led to different molecular weight distributions of the resulting PCS. The molecular weight distributions of the PCS-HP and PCS-NP are shown in Figure 2.

From Figure 2, M_w, the weight-average molecular weight of the PCS-HP, was about 2861. The polydispersity index, M_w/M_n, was about 1.92, where M_n is the number-average molecular weight. The M_W of PCS-NP with similar softening point was about 2452 and M_w/M_n was about 1.8. The molecular weight of PCS-HP was higher and the molecular weight distribution broader than those of PCS-NP. This was because some lower molecular weight PCS that was formed under normal pressure was condensed under high pressure to increase the molecular weight.

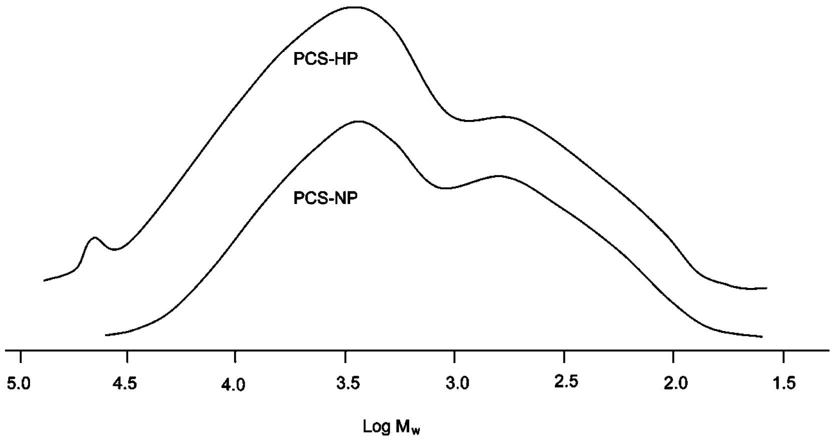

Figure 2. Molecular weight distribution of PCS-HP and PCS-NP.

NMR Analysis

^{1}H-NMR spectra of the PCS-HP and PCS-NP are shown in Figure 3. Chemical shifts (δ) are referenced to tetramethylsilane at 0 ppm as the internal standard. The peak at 4–5 ppm corresponds to the resonance of H in Si–H group. The broad peak around 0 ppm corresponds to the resonance of H in C–H bond, which was considered the overlap of three peaks. The peaks around 0.4 ppm, −0.1 ppm, and −0.6 ppm are the resonances of H in $Si-CH_3$, $Si-CH_2$, and Si–CH, respectively. They are all characteristic of carbosilane. From the C–H and Si–H resonance peak areas in ^{1}H-NMR spectra,[7–9] the H mole ratio between C–H and Si–H was calculated to be 9.83, which was lower than the 10.10 for PCS-NP. This means a high Si–H bond content, which was consistent with the results of IR analysis.

^{29}Si-NMR spectra of the PCS-HP and PCS-NP are shown in Figure 4. Chemical shifts are also based on tetramethylsilane as the internal standard. In Figure 4, the peak around −0.75 ppm was assigned to be the resonance of Si in the SiC_4 unit. The peak at −17.5 ppm was the resonance of silicon bonded to Si in the SiC_3H unit. This meants that there were SiC_4 and SiC_3H structures in the PCS molecule at the same time. From peak integrals, the ratio of SiC_3H to SiC_4 was about 0.94, which was higher than the 0.92 seen in PCS-NP. This meants that there are 48.4% (PCS-NP: 47.9%) of SiC_3H and 51.6% (PCS-NP: 52.1%) of SiC_4 in the PCS-HP structure, which implies low degrees of linearity for PCS-HP and PCS-NP,[7–9] and the degree of linearity for PCS-HP is yet a little higher.

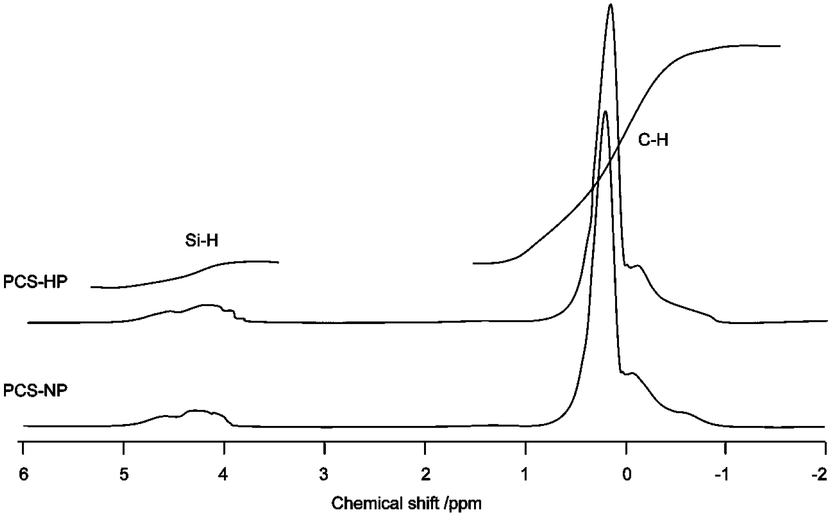

Figure 3. ^{1}H-NMR spectra of the PCS-HP and PCS-NP.

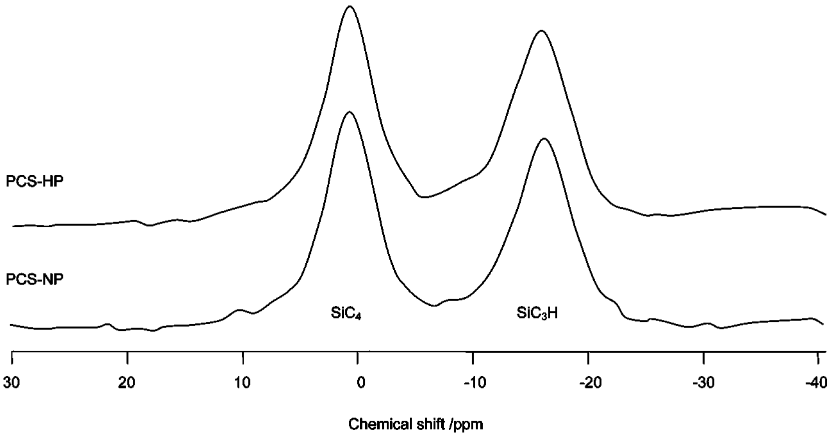

Figure 4. ^{29}Si-NMR spectra of the PCS-HP and PCS-NP.

According to the analysis above, PCS-HP is an organosilicon polymer with a Si—C backbone.[2,5,7–9] IR and NMR showed the presence of SiC_4 and SiC_3H structural units containing Si—CH_3, Si—CH_2—Si, and Si—H groups. From the results of NMR,[7–9] PCS contains about 10 C—H bonds per Si—H bond and one SiC_4 unit per SiC_3H unit. From the analysis above, a structural model of PCS-HP could be conceptualized as shown in Figure 5.

In summary, PCS-HP has a complicated structure with a low degree of linearity. Further research efforts in this area should attempt to increase the molecular weight as well as to increase the degree of linearity.

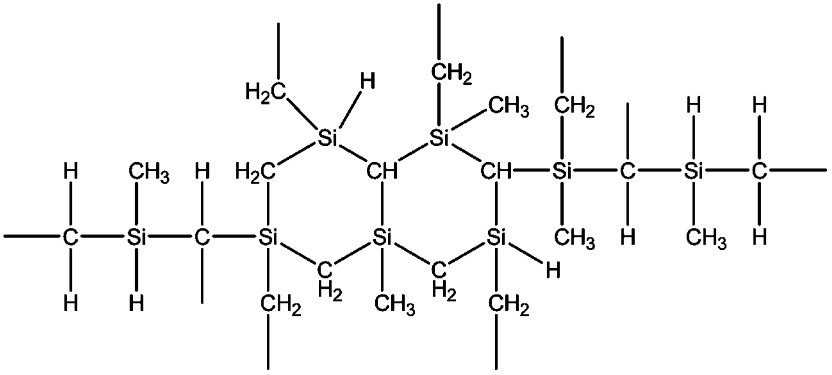

Figure 5. Structural unit model of the PCS-HP.

Properties of the PCS

Thermal Decomposition of the PCS

TG-DTA curves of the PCS-HP and PCS-NP in N_2 up to 1200°C are shown in Figure 6. Four stages could be observed during the conversion process of the PCS-HP. At the first stage (from room temperature to 360°C), the weight loss was only about 0.4% as the result of evaporation of low-molecular-weight fractions. No obvious change occurred in this stage. At the second stage (from 360° to 585°C), the TG curve fell off rapidly as the result of evaporation of low-molecular-weight fractions and evolution of H_2 and CH_4 due to dehydrogenation and dehydrocarbonation condensation among the PCS molecules. A weight loss of about 11.4% took place. At this stage, the network structure gradually formed by thermal curing and partial pyrolysis of PCS. At the third stage (from 585° to 820°C), the DTA curve exhibited a large endothermic peak. The weight loss was 7.4%. The reaction at this stage consisted mainly of thermal decomposition of the side chains such as Si–H, $Si-CH_3$, and C–H in $Si-CH_2-Si$ of the PCS. Thermal decomposition of the main chains hardly occurred because of the low weight loss. At the last stage (>820°C), the weight loss was about 1.9% and the DTA curve showed an exothermic peak at 1034°C due to the crystallization of β-SiC accompanied by evolution of residual C and H,[10,11] which showed that

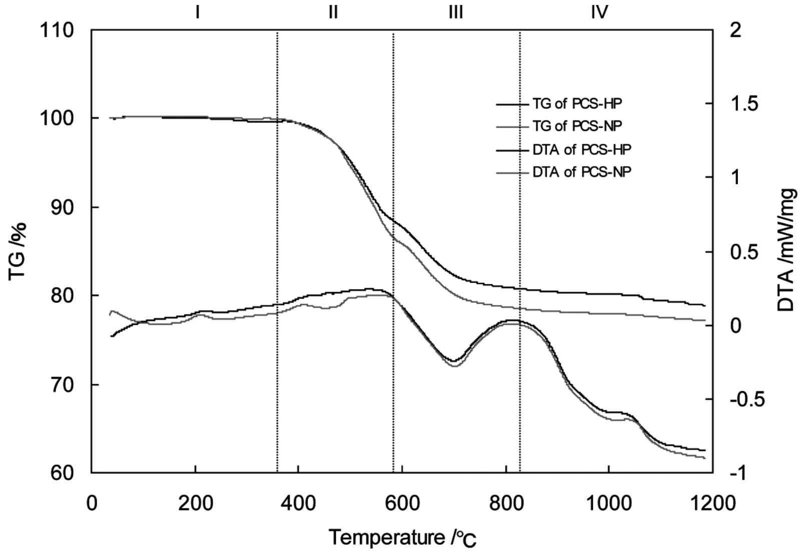

Figure 6. TG- DTA curves of the PCS-HP and PCS-NP in a N_2 flow.

the conversion of the PCS to the inorganic state was almost complete. The crystal structure would be unchanged with further increase in temperature. The ceramic yield of PCS-HP at 1200°C was about 78.9%.

From Figure 6, PCS-NP[5] had a conversion process similar to that of PCS-HP. The weight losses of PCS-NP at the four stages were 0.1%, 13.4%, 7.9%, and 1.4% respectively. The ceramic yield of PCS-NP at 1200°C was about 77.2%.

The difference of weight loss at the first and second stages between PCS-HP and PCS-NP was due to the different molecular weight distributions. During the pyrolysis process, more low-molecular-weight gases evaporated from the PCS with a low degree of linearity. So the weight loss at the third stage of PCS-NP was higher than that of PCS-HP, showing that the degree of linearity of PCS-HP was higher, which is consistent with the results of ^{29}Si-NMR. The ceramic yield of PCS-NP at 1200°C was a little lower than that of PCS-HP, showing that the molecular weight of the latter is higher.

X-ray Diffraction Analysis

The X-ray diffraction pattern of PCS and the derived ceramics pyrolyzed at 1250°C in N_2 is shown in Figure 7. According to the data, PCS-HP and PCS-NP are amorphous. The pyrolysis products were shown to contain β-SiC crystallite. The peaks at 36°, 60°, and 72° were attributed to the

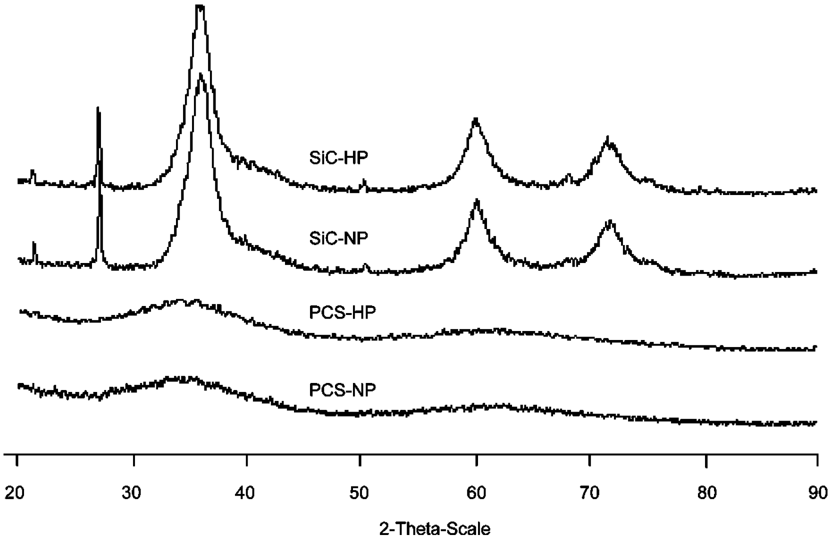

Figure 7. XRD patterns of PCSs and the derived ceramics pyrolyzed at 1250°C in N_2 gas.

Table I. Composition, structure, and properties of PCS-HP and PCS-NP

Sample	Empirical formula	A_{Si-H}/A_{Si-CH_3}	M_w	M_w/M_n	$C-H/Si-CH_3$	$Si-CH_3/Si-CH_4$	Ceramic yield	Grain size
PCS-HP	$SiC_{1.86}H_{7.50}O_{0.02}$	1.27	2861	1.92	9.83	0.94	78.9	35.9
PCS-NP	$SiC_{1.87}H_{7.10}O_{0.02}$	0.89	2452	1.80	10.10	0.92	77.2	34.4

(111), (220), and (311) diffraction lines, respectively. From the (111) line, the grain sizes were found to be 35.9 Å (PCS-HP) and 34.4 Å (PCS-NP), respectively. The peak at 26.2° was due to diffraction of graphite. This means that the pyrolysis product is a somewhat carbon rich, which is consistent with the elemental analysis result. The peak at 12.5° due to small-angle diffraction could be ignored.

From the above observations, the composition, structure, and properties of PCS-HP and PCS-NP were compared and are summarized in Table I.

Previous investigations[1–3,7] showed that PCS should contain high Si–H bond content and high molecular weight. Compared to the PCS-NP, the PCS-HP showed obvious advantages as a precursor for SiC fiber. Increasing the molecular weight of the PCS was beneficial to the properties of SiC fiber. Melt spinnability, however, decreased gradually with increasing molecular weight and decreasing degree of linearity. Further research should be focused on increasing the molecular weight with high degrees of linearity.

CONCLUSIONS

PCS-HP with a softening point of 209°–219°C was shown to have a Si–C backbone with weight-average molecular weight of about 2861. Elemental analysis gave the empirical formula $SiC_{1.89}H_{4.81}O_{0.05}$. IR and NMR showed the presence of SiC_4 and SiC_3H structural units containing $Si{-}CH_3$, $Si{-}CH_2{-}Si$, and Si–H groups. The ratio of C–H/Si–H was about 9.83, with SiC_3H/SiC_4 about 0.94. The data showed that the PCS-HP had a complicated structure with a low degree of linearity.

The TG curve showed that the ceramic yield of the PCS-HP at 1200°C was about 78.9%. β-SiC microcrystal was obtained when PCS-HP was pyrolyzed at 1250°C in a N_2 flow with a grain size of about 35.9 Å.

With a higher molecular weight, higher Si–H bond content, and higher ceramic yield, PCS-HP is more suitable as the precursor for SiC fiber than PCS-NP.

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