

Preceramic Polymer as Precursor for Near-Stoichiometric Silicon Carbon with High Ceramic Yield

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ABSTRACT: Precursor polycarbosilane containing acetylenic and Si—H group (PCAS) has been successfully prepared by the reaction of dilithioacetylene with methyl dichlorosilane, and characterized by gel permeation chromatography, Fourier transform infrared spectroscopy, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and $^{29}\text{Si-NMR}$. Thermogravimetric analysis curve in nitrogen showed the temperature of 5 wt % weight losses (T_{d5}) was 613°C , while the ceramic yield of PCAS was 88% at 1000°C . Pyrolysis behavior and structure evolution of the cured PCAS were studied by means of X-ray diffraction, Raman, scanning electron microscope-energy dispersive X-ray spectrometer, transmission electron microscope (selected area electron diffraction and high resolution transmission electron microscope), and elemental analysis. The polymer to ceramic conversion was completed at 1600°C and the results revealed that the ceramic consisted of $\beta\text{-SiC}$ and $\alpha\text{-SiC}$. The composition of the ceramic was near-stoichiometric with molar ratio of Si/C (1.02 : 1) except rare and localized free carbon inclusions. The SiC ceramics exhibited high thermo-oxidation resistance at elevated temperatures in air atmosphere.
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INTRODUCTION

As high performance materials, advanced non-oxide ceramic such as silicon carbide (SiC) are gradually attracting more interest in the application. As is known to all, SiC is often used as a high temperature resistant material, due to its excellent resistance to oxidation, corrosion, and thermal shock. Nowadays, SiC is mostly used in fields such as aerospace, weapon systems, electronic, and photo electronic devices.^{1,2} SiC monolithic materials can be fabricated by a variety of techniques such as powder sintering, sol-gel, chemical vapor deposition, and polymer conversion.³ Among these methods, silicon-based polymers have been proved to be promising precursors for the production of advanced ceramic components.⁴ The most competitive advantage of polymer precursors is that ideal solubility or fusibility enables them to be shaped easily at moderate temperatures by conventional polymer processing techniques, so that they can yield various complex shapes such as fibers, coatings, and bulk bodies.⁵

It has been 40 years since the polycarbosilane (PCS) was studied as SiC precursors by Yajima, and a variety of PCSs have been reported. Although Yajima PCS resins have been widely studied and applied,⁶ the PCS encountered unavoidable drawbacks such

as high synthetic cost, low fluidability, foamable cure, and low ceramic yield.⁷

New synthetic methods were applied to SiC preceramic resins which have been studied in the past thirty years. The ideal PCS resins were expected to have low cure temperature, high ceramic yield, near stoichiometric elemental ratio, excellent thermal stability, good liquidity for material processing, and being convenient to use. The Grignard reaction between chlorosilane and dibromomethane was reported to obtain a novel liquid PCS.⁸ A hyperbranched polycarbosilane (HBPCS) derived from the Grignard coupling of (chloromethyl)trichlorosilane ($\text{Cl}_3\text{SiCH}_2\text{Cl}$), followed by reaction with lithium aluminum hydride (LiAlH_4), was reported by Interrante and coworker.⁹ In addition, the modification of HBPCS has also been of particular interest. A hyperbranched PCS of the type $[\text{R}_3\text{SiCH}_2-]_x[-\text{SiR}_2\text{CH}_2-]_y[-\text{SiR}(\text{CH}_2)_{1.5-}]_z[-\text{Si}(\text{CH}_2)_2-]_1$ ($\text{R}=\text{H}$, $-\text{CH}_2\text{CH}=\text{CH}_2$) has been prepared, which has been used as a precursor to inorganic solids with unusual microstructures and high ceramic yield.¹⁰ An improved preparation HBPCS was subsequently developed by Starfire Systems Inc., which yielded allylhydridopolycarbosilane (AHPCS) that was partially allyl-substituted.¹¹ Although the allyl groups as the side chains were shown to increase the ceramic yield, the free carbon residual was still relatively high.

Fang et al.¹² reported that partially ethynyl-substituted ethynyl-hydridopolycarbosilane (EHPCS) was carried out by the Grignard coupling of chloromethyltrichlorosilane, chloromethyldichlorosilane, and ethynylmagnesium bromide, followed by reduction with lithium aluminum hydride. Polyphenylcarbosilane as a novel preceramic polymer for SiC was synthesized by thermal rearrangement of polymethylphenylsilane at around 350–430°C. The average molecular weight (M_w) of the polyphenylcarbosilane synthesized was 2500, and it was found to easily dissolve in an organic solvent. The ceramic yield calculated from thermogravimetric analysis (TGA) is approximately 60% at 1000°C.¹³ Thermosetting polycarbosilane (PVCS) was prepared from PCS and 2,4,6, 8-tetravinyl-2,4,6,8-tetramethylcyclotrasiloxane. The results showed that PVCS containing Si—H and C—C reactive groups could cure at 200–350°C, the ceramic yield of PVCS at 1000°C in N₂ atmosphere was 78 wt %.¹⁴ A hybrid precursor of titanium-containing PCS was prepared by blending HBPCS and tetrabutyl titanate (TBT). The ceramic yield of HBPCS-TBT is 83% at 1400°C, and the characteristic peaks of β -SiC appear until 1600°C.¹⁵ Matsuda et al. reported crosslinked polycarbosilane (CLPCS) films with superior stability properties. CLPCS were prepared by spin-coating and thermal curing of hexylene-bridged disilacyclobutane (DSCB) rings. The resulting films were siloxane-free and hydrophobic, and present good thermal stability.¹⁶

Facile and cost efficient synthetic methods for PCS is promising, and attracting a lot of research interests. It was reported that side chains such as allyl, butyl, and hexyl should be avoided to get a ceramic composition close to 1 : 1(C : Si). Although these functionalities could increase the ceramic yield, the free carbon residual will be high. In this article, a novel PCS containing acetylenic and Si—H group has been synthesized and its characterization, properties, thermal cure, and pyrolytic conversion to SiC were also investigated. The substitution of ethynyl and Si—H groups were sufficient to promote thermal crosslinking of PCAS and improve the final ceramic yield. Moreover, the resulting ceramic composition was near-stoichiometric.

EXPERIMENTAL

Materials

Tetrahydrofuran, diethyl ether, and trichloroethylene were all purchased from Sinopharm Chemical Reagent Company. *n*-BuLi (2.4M in *n*-hexane) was obtained from J&K Chemical Reagent Company. All reagents were analytical grade except methyl dichlorosilane. Methyl dichlorosilane was industrial grade and distilled before use. All equipments involving air and/or water sensitive compounds were under nitrogen atmosphere using standard Schlenk techniques.

Characterization

Gel permeation chromatography (GPC) measurements were recorded with THF as the eluent at 1 mL/min using a Waters 1515 system. The rheological property was monitored with a Brookfield CAP 2000+ Rheometer at 25°C. Fourier transform infrared spectroscopy (FTIR) spectra in the range of 4000–400 cm⁻¹ were obtained with the KBr plates using Nicolet 5700. NMR was recorded on Bruker AVANCE 500 using CDCl₃ as the solvent. Differential scanning calorimetry (DSC) analysis

was conducted on a NETZSCH DSC 200 F3 in nitrogen atmosphere at a heating rate of 10°C/min. TGA was studied on NETZSCH STA409PC in nitrogen atmosphere at a heating rate of 10°C/min. X-ray diffraction (XRD) was conducted by using a D/max2550V. The elemental analysis was performed by EL on Vario EL III. Scanning electron microscope (SEM) measurements were made on a JSM-6360LV. SEM integrated with energy dispersive X-ray spectrometer (EDS). Raman scattering spectrum was conducted by using a Renishaw Invia Reflex. High resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED) measurements were made on a JEM-2100.

Synthesis of PCAS Resin

The precursor was synthesized from *n*-BuLi, trichloroethylene, and methyl dichlorosilane under a nitrogen atmosphere using standard Schlenk techniques. Typically, *n*-BuLi (2.4M in *n*-hexane, 0.2 mol) and trichloroethylene (0.067 mol, 6 mL) were placed in a flask, which was cooled for 2 h with stirring. Then methyl dichlorosilane (0.13 mol, 14 mL) was added and aged for 2 h. After the addition was completed, a highly air-sensitive, yellowish white solution, containing amounts of lithium chloride was obtained. At last, this solution was reduced by lithium aluminum hydride (LiAlH₄) with an ice/water bath and rapid stirring. The resulting solution was poured into water and extracted with ether. The organic layer was separated, dried over magnesium sulfate. The solvent in the solution was removed by rotary evaporation and a red-brown, viscous resin was obtained in 75% yield.

Thermal Cure of PCAS

PCAS was cured in a vacuum oven according to the following procedure: 120°C/1 h → 150°C/1 h → 180°C/1 h → 200°C/2 h → 230°C/2 h → 250°C/2 h → 280°C/2 h → 300°C/2 h. After thermal cure, PCAS was converted into a dark and shiny brittle nonporous monolith.

Pyrolysis of the Cured Precursor

The pyrolysis was conducted in a tube furnace under argon atmosphere as the following heating schedule: firstly, being heated up from room temperature to 1200°C under the heating rate of 5°C/min, and then being kept at the target temperature for 1 h. Then continued to heat it up to 1600°C under the heating rate of 2°C/min, and kept it at the target temperature for 30 min. After the pyrolysis, the black ceramic solids without visible pores were obtained.

Thermal Oxidation of the Pyrolyzed PCAS

The studies of oxidation resistance were investigated by the TGA and the muffle furnace in air. Preliminary study of the oxidation behaviors of the ceramics was carried out in TGA under dry air at 1200°C with the rate 10°C/min. Meanwhile, the long-time oxidation study of the pyrolyzed PCAS was implemented at 1000°C in the muffle furnace for 200 min under the air atmosphere.

RESULTS AND DISCUSSION

Synthesis and Characterization of PCAS

A viscous and rufous resin was prepared by organic lithium reaction of *n*-BuLi, Cl₂C=CHCl, and Cl₂Si(CH₃)₂H, followed by the

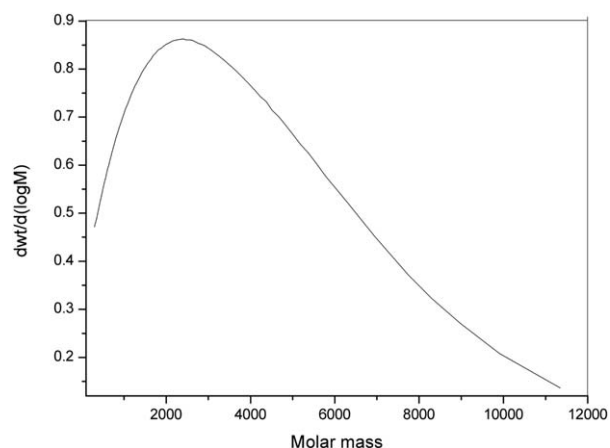
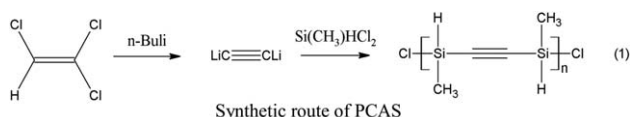


Figure 1. GPC curve of PCAS in tetrahydrofuran: $M_n = 1175$, $M_w = 2648$.

reduction with LiAlH_4 . The dilithioacetylene ($\text{LiC}\equiv\text{CLi}$) was prepared via the coupling reaction of trichloroethylene with $n\text{-BuLi}$. The polymer with ethynyl groups on the backbone was prepared by the polycondensation of dilithioacetylene with methyl dichlorosilane. The synthesis was performed according to eq. (1).



Finally, the residual chlorine groups were reduced into Si-H . The synthesis of PCAS was based on the following transformation [eq. (2)]. The couple reaction of dichloro-oligosilanes with dimetalated π -conjugated compounds was a typical way to synthesize the polymer of oligosilylene units and π -units, in general, the molecular weights of the polymers produced were relatively low.¹⁷ In Figure 1, the GPC measurement indicated the number-average molecular weight (M_n), the mass-average molecular weight (M_w), and polydispersity index of this resin were 1175, 2648, and 2.25, respectively. The rheometer viscosity of the resin at 25°C was 0.6 Pa s, indicating excellent fluidity.

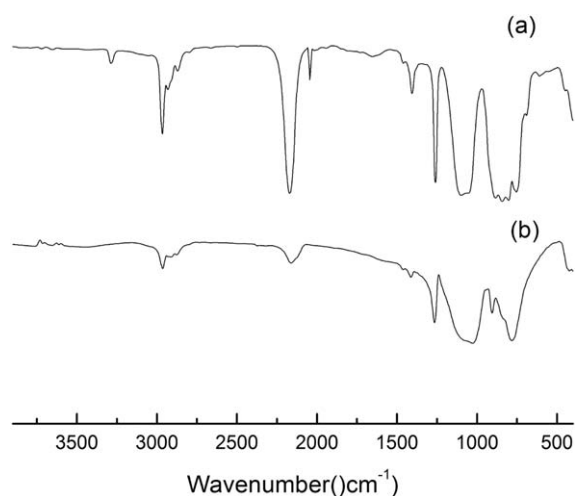


Figure 2. FTIR spectrum of PCAS: (a) the spectrum of PCAS; (b) the spectrum of PCAS without LiAlH_4 reduction.

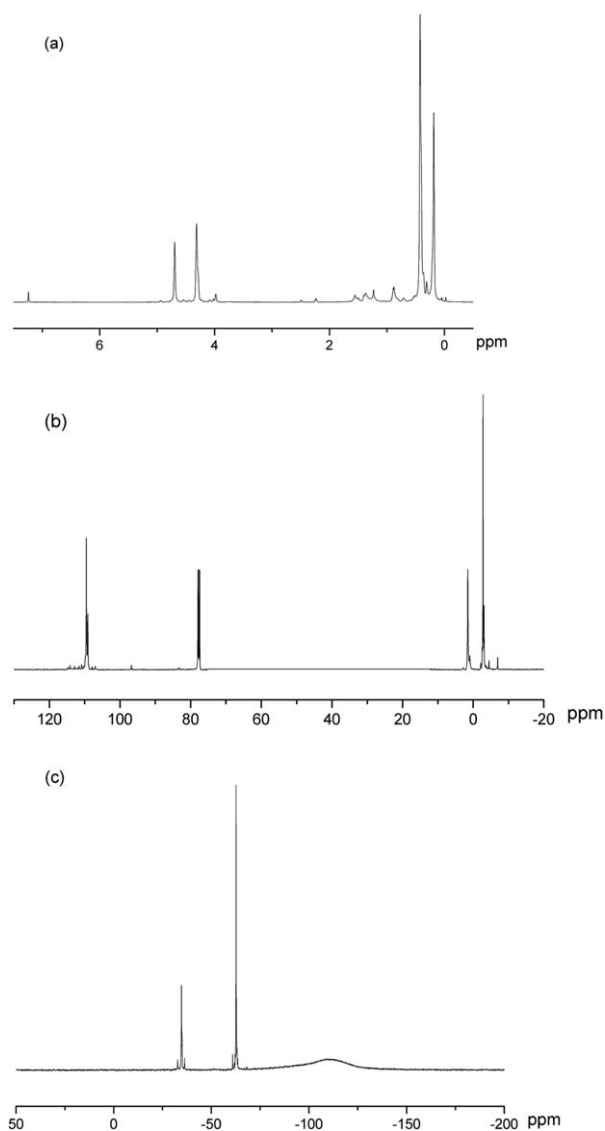
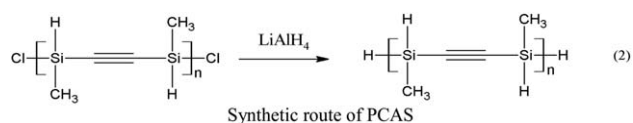


Figure 3. NMR spectra (CDCl_3) of PCAS: (a) ^1H -NMR spectrum; (b) ^{13}C -NMR spectrum; (c) ^{29}Si -NMR spectrum.

Furthermore, the precursor was well soluble in acetone, toluene, and tetrahydrofuran (THF), etc. The good liquidity and solubility was conducive to the application process by now.



The product was confirmed as PCAS by FTIR (Figure 2) and NMR (Figure 3). In Figure 2(a), the existence of Si-CH_3 was indicated by the deformation band at around 1250 cm^{-1} and the stretching band at 2950 cm^{-1} . The strong band at 2170 cm^{-1} was assigned to the Si-H group, while it did not show in Figure 2(b). The absorption at 800 cm^{-1} was attributed to Si-CH_3 rocking and Si-C stretching. The absorptions at 3286 cm^{-1} and 2044 cm^{-1} suggested that the ethynyl groups had been introduced into PCAS chains.

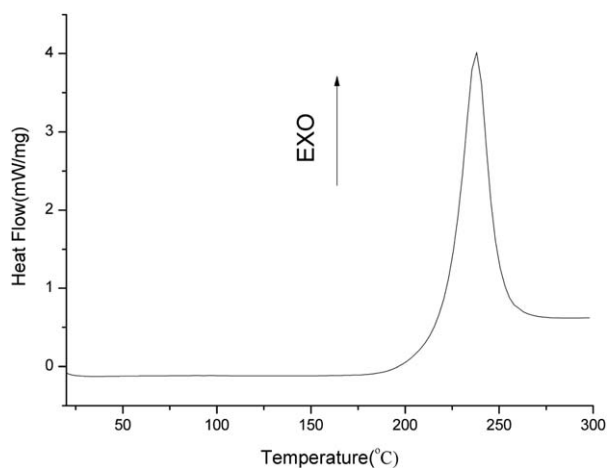


Figure 4. DSC curve (10°C/min under nitrogen atmosphere) of the PCAS.

The structure of PCAS was also characterized by NMR. In the $^1\text{H-NMR}$ spectrum shown in Figure 3(a), the information in $^1\text{H-NMR}$ was highly consistent with the FTIR results: the product revealed the main peak at 0.18–0.42 ppm assigned to Si-CH_3 , while the broad peak at 4.0–4.7 ppm was assigned to Si-H , Si-H_2 .^{12,18,19} In Figure 3(b), the main peak from –3 ppm to 1.5 ppm shown in the $^{13}\text{C-NMR}$ spectrum indicated the existence of Si-CH_3 . Moreover, the signal at about 109.5 ppm was attributed to $-\text{C}\equiv\text{C}-$. In the $^{29}\text{Si-NMR}$ spectrum shown in Figure 3(c), two peaks indicated that silicon links with different functional groups. The signals at –35 ppm and –60 ppm were attributed to the existence of C_2SiH_2 and C_3SiH . The spectrogram provided the evidence of the structure of PCAS.

Curing of PCAS

In the thermal treatment process of PCS precursors, the crosslinking of the organic groups on the Si backbone of the polymer contribute to the better ceramic yield.²⁰ In order to comprehend the crosslinking behavior of the cured PCAS, the thermal behavior was illustrated by DSC (Figure 4) and FTIR (Figure 5). As shown in Figure 4, an exothermic peak which began at 194°C and reached a maximum at 240°C suggested the Diels–Alder reaction between $-\text{C}\equiv\text{C}-$ and $-\text{C}\equiv\text{C}-$ [eq. (3)],

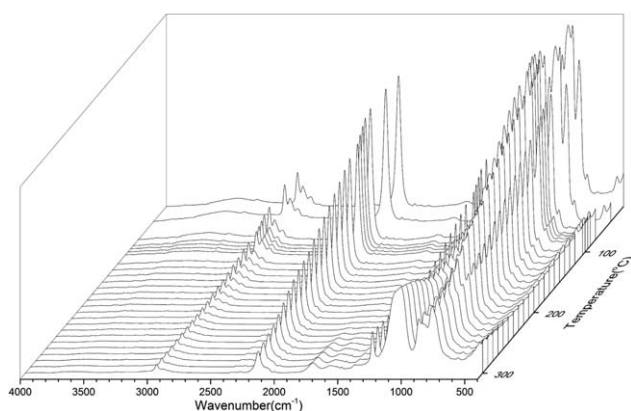
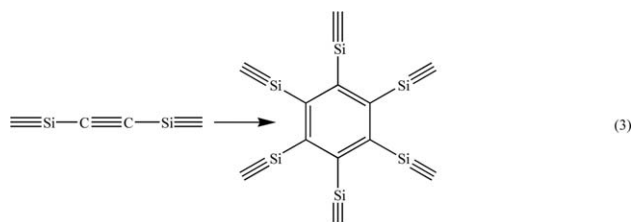


Figure 5. FTIR spectra of PCAS at the different curing temperatures.

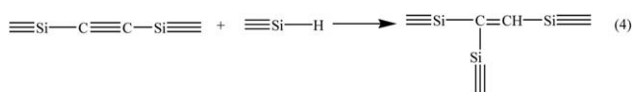
Table I. The $\text{C}\equiv\text{C}$ and Si-H Reaction Degree of PCAS Calculated During the Curing Process

T (°C)	120	150	180	200	230	250	280	300
$P_{\text{C}\equiv\text{C}}$	0.03	0.2	0.59	0.98	1	1	1	1
$P_{\text{Si-H}}$	0.01	0.03	0.41	0.76	0.77	0.79	0.82	0.83

the hydrosilylation reaction between $-\text{C}\equiv\text{C}-$ and Si-H [eq. (4)]. After curing, the resin was converted from liquid to solid state, and the specific heat of the material changed that baseline deviation. As shown in Figure 5, at 300°C, the absorption at 1621 cm^{-1} and 1721 cm^{-1} were assigned to the cycloalkenyl group, while the peak at 1038 cm^{-1} increased significantly, suggesting cycloalkenyl group had been produced in the cured PCAS. The peak at 790 cm^{-1} increased significantly, indicating the existence of trisubstituted alkene in the cured product. The evidence of IR indicated the Diels–Alder reaction and the hydrosilylation reaction. The PCAS was cured at 150–300°C to gain a black hard monolithic solid. The solid was insoluble in various solvents such as toluene and THF indicating the formation of network structures among the polymer chains. The crosslinking reaction made contribution to the network structure, corresponding to thermal and oxidative property of PCAS.



The Diels–Alder reaction and the hydrosilylation reaction



The Diels–Alder reaction and the hydrosilylation reaction

Figure 5 shows the FTIR absorption variations of PCAS during the cure reaction. The change of acetylenic group at 2044 cm^{-1} and Si-H at 2170 cm^{-1} could be successfully used to supervise the cure reaction. The Si-H reaction degree ($P_{\text{Si-H}}$) of the polymer was measured through the characteristic peak's ratio of Si-H to Si-CH_3 in FTIR spectra.²¹ Likewise, the $\text{C}\equiv\text{C}$ reaction degree ($P_{\text{C}\equiv\text{C}}$) of the polymer was calculated through the characteristic peak's ratio of $\text{C}\equiv\text{C}$ to Si-CH_3 . The $P_{\text{Si-H}}$ and $P_{\text{C}\equiv\text{C}}$ were calculated according to eqs. (1) and (2) and the calculation results are listed in Table I. In the initial stage of cure, no obvious change of absorptions was observed which indicated acetylenic and Si-H group still remained dormant until 120°C. Compared with Si-CH_3 group at 1250 cm^{-1} , with the reaction proceeding, the absorption of acetylenic and Si-H group apparently decreased due to the occurrence of cure reaction. At

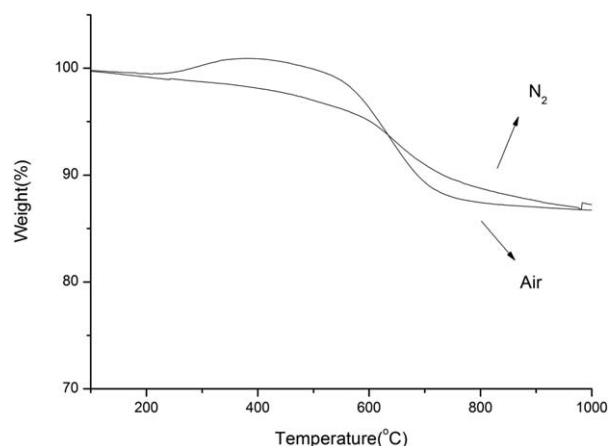


Figure 6. TGA curves ($10^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere and air atmosphere) of the cured PCAS.

temperatures $\geq 230^{\circ}\text{C}$, the acetylenic group completely disappeared while the Si—H group was essentially unchanged with the residual of nearly 20%, which indicated the completion of Diels–Alder reaction [eq. (3)] and the hydrosilylation reaction [eq. (4)].

$$P_{\text{Si-H}} = \frac{(A_{2170}/A_{1250})_{\text{uncured}} - (A_{2170}/A_{1250})_{\text{cured}}}{(A_{2170}/A_{1250})_{\text{uncured}}} \quad (1)$$

$$P_{\text{C}\equiv\text{C}} = \frac{(A_{2044}/A_{1250})_{\text{uncured}} - (A_{2044}/A_{1250})_{\text{cured}}}{(A_{2044}/A_{1250})_{\text{uncured}}} \quad (2)$$

Thermal and Oxidative Property of PCAS

The thermal and oxidative stability of PCAS were determined by TGA study under a flow of N_2 and air. The TGA curves of thermoset (Figure 6) provided valuable information regarding its thermal and oxidative property. As shown in Figure 6, the thermoset exhibited excellent heat resistant property in nitrogen. When heating rate was $10^{\circ}\text{C}/\text{min}$, the ceramic yield of the cured PCAS at 1000°C was 88% and T_{d5} was 613°C . The cured PCAS, due to the formation of a complete network crosslinked structure, was almost no loss of small molecules at low temperatures. For comparison, it was reported that the char yield of PCS was only 57% at 1000°C by TGA,¹⁴ the cured AHPCS,¹¹ EHPCS,¹² and PVCS¹⁴ were 60%, 70%, and 78%, respectively. Therefore, the ceramic yield was significantly enhanced by the introduction of ethynyl groups and Si—H into molecular chains. Surprisingly, the ceramic yield of the cured PCAS at 1000°C in air was 87% and T_{d5} was 603°C , which was attributed to the oxidation of silicon to SiO_2 upon exposure to oxidizing atmosphere at elevated temperatures and the formation of a protective layer on the sample. However, most organic-based systems were usually observed to undergo catastrophic weight losses in the 500 – 600°C temperature range upon exposure to air.

The cured PCAS was put into the muffle furnace at 1000°C for 5 h in air, and a black and dense solid was obtained with the residual rate of 87%. The thermal oxidation result was in accordance with the TGA at 1000°C under air atmosphere. From aforementioned, the high heat resistance and good oxidative stability of PCAS make it potentially useful as precursor for ceramic.

Pyrolysis and Ceramic Conversion of PCAS

A better ceramic yield was ascribed to the organic groups on the backbone of the polymer, in the process of the pyrolysis of precursor.²⁰ The analytical information of the SiC ceramic obtained from the pyrolysis which was carried out in a tube furnace under argon atmosphere of the cured PCAS at 1600°C was performed by SEM-EDS. The result for the SiC ceramic obtained from pyrolysis of the cured PCAS at 1600°C (PCAS-1600) under argon atmosphere is shown in Figure 7. While the data is shown in Table II, EDS spectrum of PCAS-1600 showed that the material consists of 70.77 wt % [Si], 28.84 wt % [C], and 0.39 wt % [O], corresponding to a chemical formula of $\text{SiC}_{0.95}\text{O}_{0.01}$.

Moreover, the information revealed by element analysis conformed to the EDS result. The element analysis of the annealed ceramic sample showed the material consisted of 69.58 wt % [Si] and 30.32 wt % [C] with a chemical formula of $\text{SiC}_{1.02}\text{O}_{0.003}$. The result indicated that the SiC had near-stoichiometric C : Si ratio of 1.02, while the C : Si ratio of EHPCS-derived SiC was 1.55.¹²

Raman scattering spectroscopy is a sensitive method for the characterization of the different modification of carbon. The Raman spectrum of SiC ceramic derived from PCAS is shown in Figure 8. In the first-order Raman spectra of SiC powder, the two major peaks at 796 cm^{-1} and 970 cm^{-1} were attributed to SiC, due to a good crystallization state.²² The obvious peak at 1360 cm^{-1} (D-peak) was assigned to the unorganized carbon involving lattice defects, while the sharp peak at 1560 cm^{-1} (G-peak) was attributed to the E_{2g} symmetric mode vibration in graphite.²³ Tuinstra and Keenig reported that the intensity ratio I_D/I_G was sensitive characterization of the amorphous carbon and related to the cluster diameter or in-plane correlation length, L_w of the free carbon domains ($I_D/I_G \propto L_w^{-1}$).²⁴ The I_D/I_G of 0.74 indicated that L_w was large at the high annealing temperature and the free carbon domains in the ceramics had been orderly at 1600°C . The sharp peak at 2710 cm^{-1} was the second-order Raman spectra of graphite carbon, which indicated orderly graphite crystals. The Raman spectrum indicated the microscopic structure change in the process of the pyrolysis and the sharp peaks show the highly crystalline and few crystal defects.

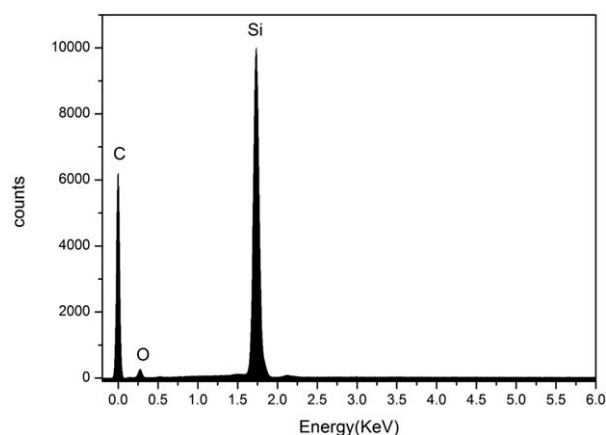
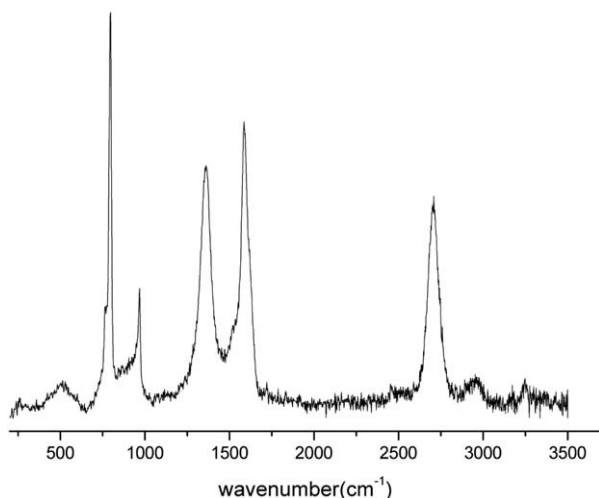


Figure 7. EDS spectrum of the SiC powder pyrolyzed at 1600°C .

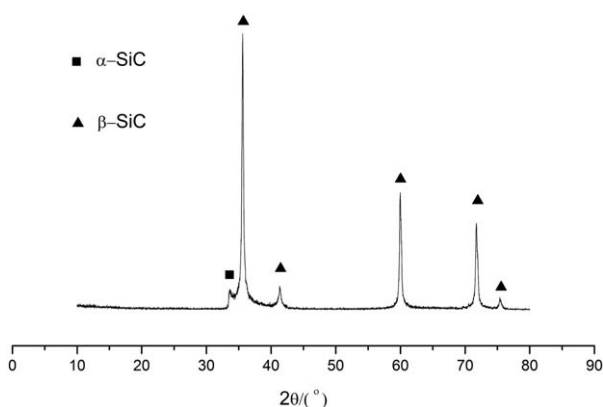
Table II. Chemical Composition of the PCAS-1600

No.	Test method	Si (wt %)	C (wt %)	O (wt %)	C : Si	Ceramic composition
PCAS-1600	EDS	70.77	28.84	0.39	0.95	$\text{SiC}_{0.95}\text{O}_{0.01}$
	Element analysis	69.58	30.32	0.1	1.02	$\text{SiC}_{1.02}\text{O}_{0.003}$

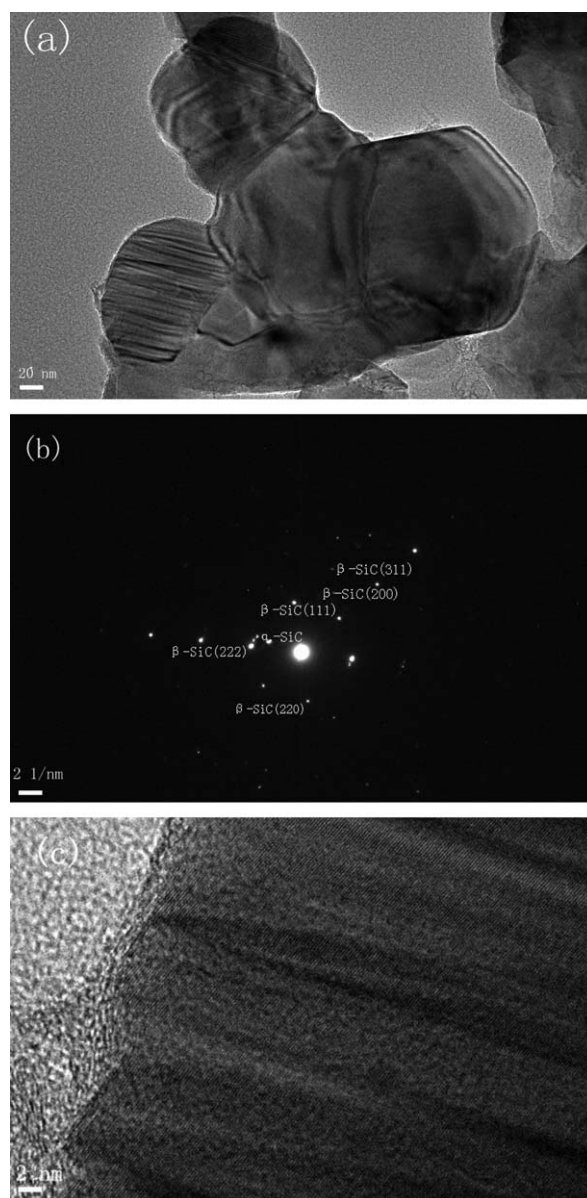
**Figure 8.** Raman spectrum of PCAS pyrolyzed at 1600°C.

In order to understand the crystallization of the ceramic char derived from the pyrolyzed PCAS, the sample powder was also measured by XRD. As shown in Figure 9, the XRD pattern of PCAS-1600 indicated several typical peaks of α -SiC and β -SiC. The primary peaks at 35.6°(111), 41.4°(200), 60.0°(220), 71.8°(311), and 75.5°(222) represented the diffraction of β -SiC, while the shoulder of 33.7° was assigned to α -SiC. Such stacking faults were usually observed in precursor-derived SiC materials after crystallization and this part of the XRD pattern resembles quite closely that observed for PCS-derived SiC after heating to 1600°C. Thus, there was strong evidence for the presence of both β -SiC and α -SiC and the strong and sharp peaks stated clearly the crystallization behavior after 1600°C annealing.

In Figure 9, the sharp XRD peaks and the Raman spectrum suggested a high crystallinity of SiC. The microstructural features

**Figure 9.** XRD spectra of PCAS heat-treated at 1600°C.

of β -SiC grains were carefully discussed with the information in Figure 10. As shown in Figure 10(c), under HRTEM, it was found that the atoms join together in regular arrays. In addition to the well crystallized grains, β -SiC containing volumes of

**Figure 10.** Structural features of the prepared SiC ceramic heated at 1600°C under nitrogen. (a) Bright field image investigated by HRTEM; (b) SAED pattern collected from the area in (a); (c) HRTEM image collected from the grain in (a).

stacking faults was also common in the ceramic, as shown in Figure 10(a). A large amount of light-and-dark stripes, which show a periodic variation of phase contrast, could be observed, implying the existence of plane defects in the lattices. The significant spots, as suggested by the FFT pattern in Figure 10(c), also implied the existence of stacking faults. The information was implied by the SAED pattern in Figure 10(b) within the area in Figure 10(a). Bright diffraction points, with the grain spacing $d = 0.2518$ nm, 0.2180 nm, 0.1541 nm, 0.1315 nm, 0.1267 nm, indicate a large amount of β -SiC grains. A diffraction point with $d = 0.2671$ nm denotes the existence of α -SiC in the SAED pattern. The interplanar spacing of the SiC grains also correspond with the value calculated by the Scherrer equation, using the FWHM value of the β -SiC and α -SiC diffraction peaks in Figure 9. The HRTEM images indicated that crystallization of the SiC components occurred after heating to 1600°C.

CONCLUSION

In this article, a novel procarbosilane with the high ceramic yield and excellent properties as SiC precursor was prepared. The ideal structure of PCAS and the main chain contains ethynyl and hydrogenated were confirmed by FTIR and NMR.

The ethynyl group was brought into the main chain in favor of the curing of PCAS. As a result, the crosslinking of PCAS could be carried out when the temperature was above 230°C, which promoted high yield and excellent thermal property. It was considered that the hydrosilylation and the Diels–Alder reaction between ethynyl groups were involved in the crosslinking of PCAS. TGA curve in nitrogen showed the T_{d5} was 613°C and the ceramic yield was 88% at 1000°C. There were only 0.5 wt % weight loss in the thermal oxidation test of the ceramic, which shows the excellent thermal oxidation resistance. The near-stoichiometric SiC ceramic with the C/Si ratio of 1.02 and good oxidative stability was obtained in the polymer–ceramic conversion of the cured PCAS. It was proved that a high crystallinity of SiC, the well crystallized grains, and the ceramic was composed of β -SiC and α -SiC. The PCAS has a great advantage as precursor for its excellent liquidity and high ceramic yield. The PCAS with satisfactory properties and excellent ceramic will be applicable to the existing production process and a better application as a precursor to SiC ceramic.

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