

Synthesis and Characterization of a Propargyl-Substituted Polycarbosilane with High Ceramic Yield

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ABSTRACT: A propargyl-substituted polycarbosilane (PCS), namely, propargyl-substituted hyperbranched hydrodipolycarbosilane (PHPCS), was prepared by a modified synthesis route, which involved Grignard coupling of partially methoxylated $\text{Cl}_3\text{SiCH}_2\text{Cl}$ and $\text{CH}\equiv\text{CCH}_2\text{Cl}$, followed by reduction with lithium aluminum hydride. The resultant PHPCSs were characterized by gel permeation chromatography, Fourier transform infrared (FTIR) spectroscopy, and NMR. Moreover, the thermal properties of the PHPCSs were investigated by thermogravimetric analysis. The ceramic yield of PHPCS at 1400°C was about 82.5%, which was about 10 wt % higher than that of hyperbranched

hydrodipolycarbosilane without the substitution of propargyl groups. The PHPCS-derived ceramics were characterized by X-ray diffraction (XRD), FTIR spectroscopy, and elemental analysis. The XRD and FTIR results indicate that the heat treatment significantly influenced the evolution of crystalline $\beta\text{-SiC}$. It can be convenient to get near-stoichiometric ceramics from PHPCS through the control of feed ratios of the starting materials. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3400–3406, 2011

Key words: crystallization; hyperbranched; pyrolysis; polymer synthesis and characterization; thermal properties

INTRODUCTION

The synthesis of silicon-based nonoxide ceramics via polymer pyrolysis offers attractive advantages in terms of processing temperatures, chemical purity, structural homogeneity, and achievable chemical and phase compositions.¹ It was the Yajima polycarbosilane (PCS) that marked the beginning of the new field of preceramic polymers for SiC ceramics.² In the intervening years, there has been much activity worldwide in this area. Recently, a liquid hyperbranched PCS has been studied extensively as a promising precursor to SiC because of its ideal processing and stoichiometric C/Si ratio; its study has involved the synthesis, modification, and polymer-to-ceramic conversion of this PCS.^{3–10} In a previous study, we successfully synthesized a hyperbranched allyhydridopolycarbosilane (AHPCS) by a one-pot synthesis with chloromethyltrichlorosilane ($\text{Cl}_3\text{SiCH}_2\text{Cl}$), chloromethylmethyldichlorosilane [$\text{Cl}_2\text{Si}(\text{CH}_3)\text{CH}_2\text{Cl}$], and allyl chloride as the starting materials, and we could control the composition of

this AHPCS by controlling the amounts of the starting materials.^{11,12} Subsequently, the polymer-to-ceramic conversion of this AHPCS for SiC-based ceramics was further studied.^{13–15} To obtain a stoichiometric SiC, we synthesized another hyperbranched ethynylhydridopolycarbosilane (EHPCS) and investigated its pyrolytic conversion to SiC, including the pyrolysis behavior, structural evolution, and crystallization behavior.¹⁶

Among the synthesis process of AHPCS and EHPCS,^{11,12,16} chlorosilanes underwent a side reaction with tetrahydrofuran (THF) used as a conventional solvent for the Grignard reaction; this resulted in the incorporation of oxygen derived from THF into the polymer chain. However, oxygen-containing polymeric precursors led to the generation of Si—O—C and Si—O—Si units in the final SiC ceramics. These units decomposed above 1200°C to evolve CO, CO_2 , and SiO gases; this led to a decrease in the strength of the ceramics.^{17,18} To obtain silicon-based nonoxide ceramics, it is necessary to prepare polymeric precursors containing no oxygen or low oxygen contents. On the basis of previous studies,^{11–16} a liquid hyperbranched hydrodipolycarbosilane (HPCS) with a low oxygen content was prepared by a modified synthesis route, which involved Grignard coupling of partially methoxylated $\text{Cl}_3\text{SiCH}_2\text{Cl}$ [$\text{Cl}_{1.25}\text{Si}(\text{OCH}_3)_{1.75}\text{CH}_2\text{Cl}$], followed by reduction with lithium aluminum hydride (LiAlH_4).¹⁹

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In this study, a partially propargyl-substituted hyperbranched hydrodipolycarbosilane (PHPCS) was prepared with $\text{Cl}_{1.25}\text{Si}(\text{OCH}_3)_{1.75}\text{CH}_2\text{Cl}$ and propargyl chloride ($\text{CH}\equiv\text{CCH}_2\text{Cl}$) as comonomers. On one hand, the side reaction between chlorosilanes with THF could be inhibited by the modified synthesis route with $\text{Cl}_{1.25}\text{Si}(\text{OCH}_3)_{1.75}\text{CH}_2\text{Cl}$ instead of $\text{Cl}_3\text{SiCH}_2\text{Cl}$ as starting materials. On the other hand, propargyl groups were introduced into the HPCS backbone to increase the ceramic yields of the polymeric precursor. The resultant PHPCSs were characterized by means of gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, NMR, and thermogravimetric analysis (TGA). Moreover, the effects of the introduction of propargyl groups on the ceramic yields and compositions of the final ceramics were investigated.

EXPERIMENTAL

Materials

$\text{Cl}_3\text{SiCH}_2\text{Cl}$ and $\text{CH}\equiv\text{CCH}_2\text{Cl}$ were industrial grade and were distilled before use. Methanol (CH_3OH ; analytical-reagent grade) was obtained from Guoyao Shanghai Chemical Regents Center (Shanghai, China) and was distilled from calcium hydride before use. Magnesium (Mg; 99% purity) and LiAlH_4 (99% purity) were stored in an inert atmosphere. THF was distilled from sodium benzophenone ketyl before use. All other reagents were analytical grade and were used as received. All manipulations involving air- and/or water-sensitive compounds were performed under a nitrogen atmosphere with standard Schlenk technology.²⁰

Characterization

GPC measurements were performed at 35°C with THF as the eluent (1.0 mL/min) with an Agilent 1100 system (Santa Clara). The spectrum was calibrated with narrow polystyrene standards. FTIR spectra were recorded on a Nicolet Avatar 360 apparatus (Nicolet, Madison, WI) with KBr plates for liquid samples and KBr discs for solid samples. NMR experiments were carried out on a Bruker AV 300-MHz spectrometer (Bruker, Germany) operating at 300.13 MHz for hydrogen 1, 75.46 MHz for carbon 13 (^1H decoupling), and 59.63 MHz for silicon 29 (^1H decoupling), and the delay time was 30 s. The specimen used for NMR was dissolved in C_6D_6 solution. The ^1H , ^{13}C , and ^{29}Si chemical shifts all referred to tetramethylsilane. Thermal analysis of PHPCS was carried out on a thermogravimetric analyzer (Netzsch STA 409C, Netzsch, Germany) in argon gas with a ramping rate of 10°C/min ranging from room temperature to 1400°C. X-ray diffraction (XRD)

was carried out with a PANalytical, Netherlands X'Pert PRO diffractometer with $\text{Cu K}\alpha$ radiation. The specimens were continuously scanned from 10 to 90° (2 θ) at a speed of 0.0167°/s. Elemental analysis was carried out by a Horiba carbon/sulfur analyzer EMIA-320V (Horiba, Japan) for carbon and a Horiba oxygen nitrogen analyzer EMGA-620W for oxygen. Silicon was calculated by a difference, with the assumption that no other elements were present apart from these three.

Synthesis of PHPCS

Methoxylation of $\text{Cl}_3\text{SiCH}_2\text{Cl}$

According to the procedure in the literature,^{21,22} $\text{Cl}_3\text{SiCH}_2\text{Cl}$ (349.5 g, 1.90 mol) was added to a 2 L, three-necked flask with a reflux condenser, magnetic stirrer, and argon inlet. Then, 106.5 g (3.35 mol) of anhydrous CH_3OH was added dropwise through the dropping funnel while the reaction solution was stirred magnetically by the magnetic stirrer. Nitrogen gas continuously flushed the flask to purge the byproduct HCl gas, which was absorbed in the water in the plastic container. When the CH_3OH was completely added, the reaction mixture was stirred for 12 h at room temperature. This mixture had the average formula $\text{Cl}_{1.25}(\text{OMe})_{1.75}\text{SiCH}_2\text{Cl}$ and could be used directly in the following step without purification.

Grignard and reduction reactions

A series of experiments for synthesizing liquid PCSs were designed with different molar ratios of $\text{CH}\equiv\text{CCH}_2\text{Cl}$ to $\text{Cl}_{1.25}(\text{OMe})_{1.75}\text{SiCH}_2\text{Cl}$ of 0, 0.1, 0.15, and 0.2; the resultant polymers are abbreviated as HPCS, PHPCS1, PHPCS2, and PHPCS3, respectively.

One typical synthesis of PHPCS was achieved by the following procedure: dry THF (200 mL), $\text{Cl}_{1.25}(\text{OMe})_{1.75}\text{SiCH}_2\text{Cl}$ (68.7 g, 0.39 mol), and $\text{CH}\equiv\text{CCH}_2\text{Cl}$ (5.8 g, 0.078 mol) were added to a 1-L, three-necked flask with a reflux condenser, mechanical stirrer, and argon inlet. The Grignard reaction was carried out by the addition of 14.6 g of Mg powder (0.61 mol, 30% excess) to the three-necked flask gradually over 1 h under stirring in an argon atmosphere. The reaction started almost immediately and was controlled by occasional cooling of the three-necked flask in an ice-water bath. After the addition of Mg powder was complete, this solution was heated under argon at 60°C for 12 h.

Aqueous workup

The resulting solution was reduced by 9.6 g of LiAlH_4 (0.25 mol, 30% excess) with ice-water cooling under rapid stirring, and then, the resultant suspension was stirred under argon for 12 h at 60°C again.

At last, the LiAlH_4 /polymer slurry was hydrolyzed with a mixture of 4 M HCl (270 mL) and hexane (250 mL) in an ice bath. The organic phase was then separated and washed with dilute 1M HCl. Then, the organic layer was dried over powder sodium sulfate under an argon atmosphere for 2 h. The solvent was stripped off at 60°C *in vacuo* to give a viscous, transparent, pale yellow oil with a yield of 47.1% (9.5 g).

Pyrolysis of PHPCS

Thermal curing of the PHPCS was carried out in an argon atmosphere with 1-g samples in a Schlenk flask placed in a 170°C oil bath. The liquid transformed into a compact pale orange rubbery solid immediately, and this temperature was then retained over 6 h. These solids were used both for TGA and for a macroscopic pyrolysis. In the macroscopic pyrolysis experiment, the cured PHPCS was put in an alumina pan and heated to 900°C at a rate of $5^\circ\text{C}/\text{min}$; it was then kept at this temperature for 1 h in a glass silica tube under an argon atmosphere. For pyrolysis temperatures above 900°C , the sample (prepyrolyzed at 900°C) was put in a graphite crucible and heated in a tube furnace. The prepyrolyzed sample was heated rapidly to the pyrolysis temperature at a rate of $40^\circ\text{C}/\text{min}$ and kept at this temperature for 10 min.

RESULTS AND DISCUSSION

Synthesis and characterization of PHPCS

Viscous liquid products were obtained via the Grignard coupling of $\text{Cl}_{1.25}(\text{OMe})_{1.75}\text{SiCH}_2\text{Cl}$ and $\text{CH}\equiv\text{CCH}_2\text{Cl}$, followed by reduction with LiAlH_4 . The weight-average molecular weight and polydispersity index of the resulting polymers were measured by GPC. Figure 1 shows the GPC curve of PHPCS3. The weight-average molecular weight and polydispersity index of PHPCS ranged from 1300 to 7500 and from 2.6 to 7.2, respectively. The results

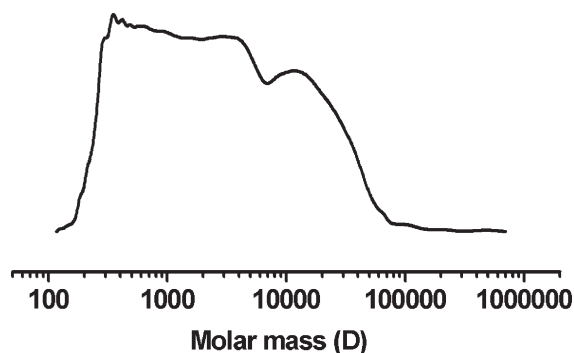
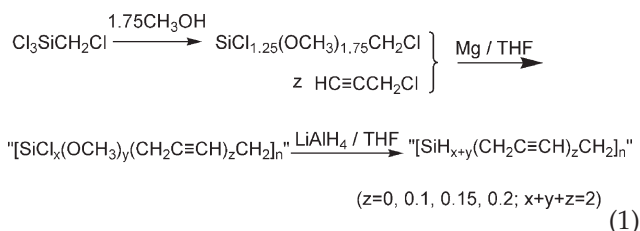


Figure 1 Typical GPC traces of the liquid PHPCSs.

reveal that the polymers had wide molecular distributions.

The reaction sequence of the PHPCS is shown in eq. (1). A precedent for the cleavage of ethers by halosilanes to form alkoxy silanes is well established, having been known for over 100 years.³ In a previous study, we investigated the side reactions of THF solvent and Si—Cl bonds in chlorosilanes in detail.¹² It is supposed that oxygen-containing units, such as $\text{Si—O}(\text{CH}_2)_4\text{—Si}$ and $\text{Si—O}(\text{CH}_2)_4\text{—Cl}$, are introduced into AHPCS and EHPCS because of the side reaction. Therefore, in this study, $\text{Cl}_3\text{SiCH}_2\text{Cl}$ was partially methoxylated to reduce the amount of active Si—Cl bonds; this was expected to inhibit the side reaction. According to some articles,^{3,12,16} we supposed that the initial step in the polymerization was the formation of the intermediate $\text{R}_3\text{Si—CH}_2\text{MgCl}$ ($\text{R}=\text{Cl}$, OMe, or another CH_2SiR_3 group) and $\text{CH}\equiv\text{CCH}_2\text{MgCl}$. The complicated branched structure was formed by the coupling reaction of the intermediate $\text{R}_3\text{Si—CH}_2\text{MgCl}$ and $\text{CH}\equiv\text{CCH}_2\text{MgCl}$ with the remaining SiCl or SiOMe groups because the Grignard reagents could couple with both the methoxy and Cl groups on the Si atoms.¹⁰ Then, the intermediate product $[\text{SiCl}_x(\text{OCH}_3)_y(\text{CH}_2\text{C}\equiv\text{CH})_z\text{CH}_2]_n$ was generated and used to further the reaction without separation.^{21,22} Finally, the target polymer $[\text{SiH}_{x+y}(\text{CH}_2\text{C}\equiv\text{CH})_z\text{CH}_2]_n$ was obtained after the reduction reaction of $[\text{SiCl}_x(\text{OCH}_3)_y(\text{CH}_2\text{C}\equiv\text{CH})_z\text{CH}_2]_n$.



The as-synthesized polymers were characterized by means of FTIR spectroscopy and NMR. As shown in Figure 2, the functional groups in PCS, including Si—CH₂—Si, Si—H, and C≡CH, were identified by FTIR spectroscopy as follows: 3310 cm^{-1} (w, ≡C—H stretching), $1900\text{--}1930\text{ cm}^{-1}$ (m, C≡C stretching), 2920 cm^{-1} (s, CH₂ stretching), 2130 cm^{-1} (vs, Si—H stretching), 940 cm^{-1} (vs, Si—H bending), 1355 cm^{-1} (s, Si—CH₂—Si deformation), 1050 cm^{-1} (vs, Si—CH₂—Si stretching), and 850 cm^{-1} (vs, Si—C stretching).

Herein, the intensity ratios of the peaks at $1900\text{--}1930\text{ cm}^{-1}$ (C≡C) to 1050 cm^{-1} (Si—CH₂—Si) are denoted as $A(\text{C}\equiv\text{C})/A(\text{Si—CH}_2\text{—Si})$ and indicate the C≡C contents shown in Figure 3. With increasing molar ratio of $\text{CH}\equiv\text{CCH}_2\text{Cl}$ in the feed, the value of $A(\text{C}\equiv\text{C})/A(\text{Si—CH}_2\text{—Si})$ increased significantly. Moreover, a relatively linear relationship was found

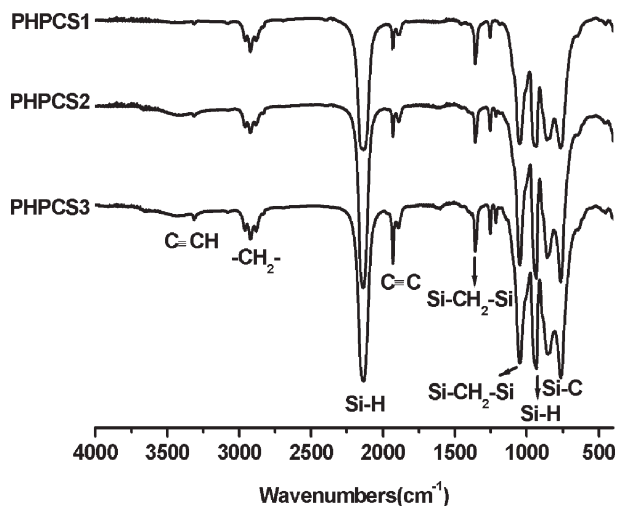


Figure 2 FTIR spectra of the PHPCSs.

between the $\text{CH}\equiv\text{CCH}_2\text{Cl}$ contents in the feed and the factual $\text{C}\equiv\text{C}$ contents in PHPCS. Thus, the $\text{C}\equiv\text{C}$ contents of PHPCS could be readily controlled by variation of the amount of $\text{CH}\equiv\text{CCH}_2\text{Cl}$ used; this was facile to control the compositions of PHPCS and the final ceramics.

The NMR result was taken to further confirm the structure of the liquid PHPCS. In the $^1\text{H-NMR}$ spectra (Fig. 4), the groups of signals around 0 ppm were assigned to the various Si-CH_2 functionalities. The three peaks ranging from 3.5 to 4.5 ppm were attributed to the proton absorption of Si-H_x (where $x = 3, 2, \text{ or } 1$) groups. The signals at 4.3 and 1.6 ppm were assigned to the protons of $\text{SiCH}_2\text{C}\equiv\text{CH}$ and $\text{SiCH}_2\text{C}\equiv\text{CH}$, respectively. Moreover, intensities of the signals of $\text{SiCH}_2\text{C}\equiv\text{CH}$ at 4.3 and 1.6 ppm increased with increasing amount of $\text{CH}\equiv\text{CCH}_2\text{Cl}$ in the feed; this was consistent with the FTIR results.

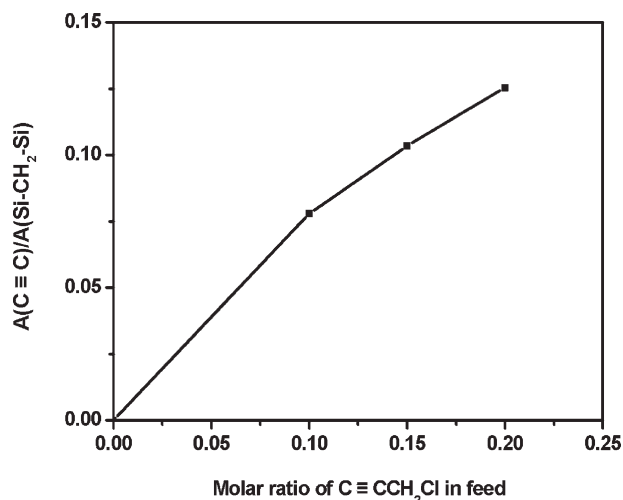


Figure 3 Dependence of the contents of the $\text{C}\equiv\text{C}$ groups on the amount of $\text{CH}\equiv\text{CCH}_2\text{Cl}$ in the feed.

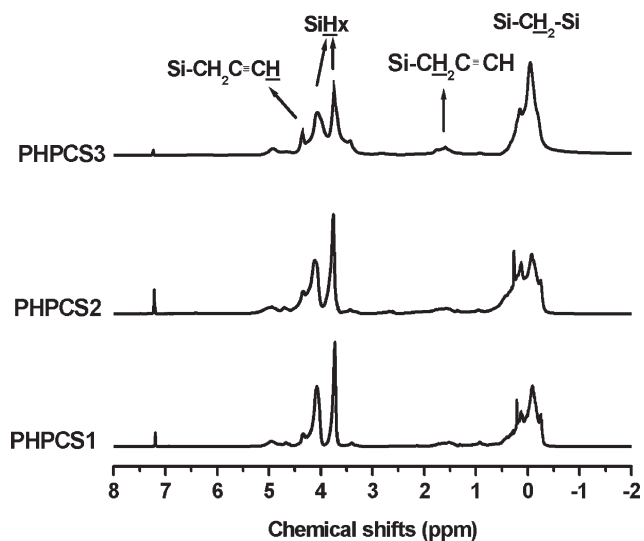


Figure 4 $^1\text{H-NMR}$ spectra of the PHPCSs in C_6D_6 .

In our previous study, oxygen-containing units, such as $\text{Si-O}(\text{CH}_2)_4\text{-Si}$ and $\text{Si-O}(\text{CH}_2)_4\text{-Cl}$, were introduced into AHPCS and EHPCS because of the side reaction. This was confirmed by the $^1\text{H-NMR}$ results, in which multiplets ranging from 1.5 to 2 ppm assigned to the methylene protons of $\text{SiOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ segments derived from THF were observed.^{11,12,16} No proton signals derived from the side reaction were detected by $^1\text{H-NMR}$ in this system; this indicated that the side reaction was efficiently inhibited by the replacement of $\text{Cl}_3\text{SiCH}_2\text{Cl}$ with $\text{Cl}_{1.25}\text{Si}(\text{OCH}_3)_{1.75}\text{CH}_2\text{Cl}$.

On the other hand, the molecular structure of the polymer was also characterized by $^{13}\text{C-NMR}$, as presented in Figure 5. The complex multiplets from -15 to 5 ppm were assigned to $\text{Si-CH}_2\text{-Si}$ chains

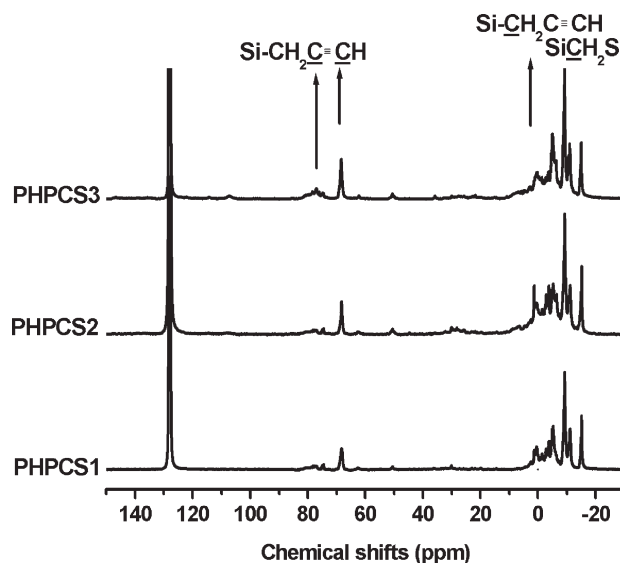


Figure 5 $^{13}\text{C-NMR}$ spectra of the PHPCSs in C_6D_6 .

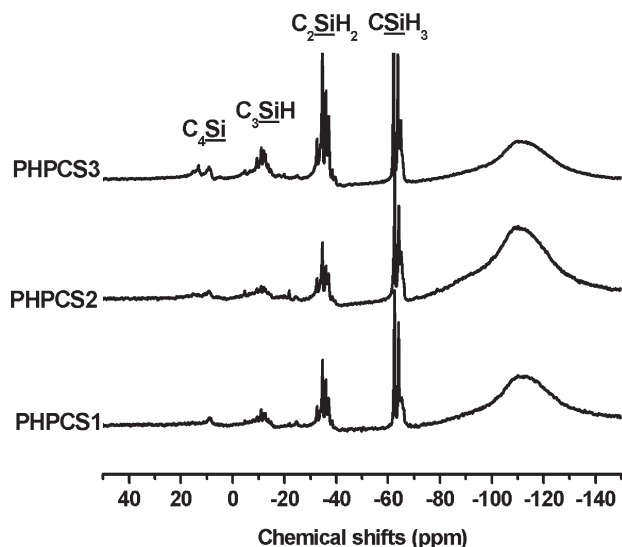
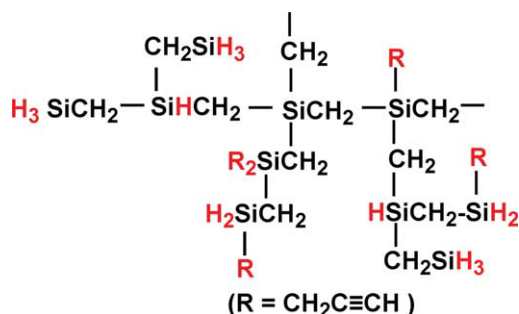


Figure 6 ^{29}Si -NMR spectra of the PHPCSs in C_6D_6 .

because of the numerous environments around the silicon element. The signals at 68 and 76 ppm were attributed to carbons from $\text{CH}_2\text{C}\equiv\text{CH}$ and $\text{CH}_2\text{C}\equiv\text{CH}$, respectively. The assignment of the ^1H -NMR signal at 4.3 ppm and that of the ^{13}C -NMR signal at 68 ppm were due to proton and carbon derived from $\text{CH}_2\text{C}\equiv\text{CH}$; this was supported by the ^1H - ^{13}C Heteronuclear Multiple Quantum Coherence (HMQC) spectrum (not shown), in which cross signals at 4.3 and 68 ppm were clearly observed. The results indicate the existence of propargyl groups introduced into the HPCS backbone. Moreover, the groups of signals from 30 to 70 ppm, attributed to the methylene carbons derived from $\text{Si}-\text{O}(\text{CH}_2)_4-\text{Si}$ and $\text{Si}-\text{O}(\text{CH}_2)_4-\text{Cl}$ units, were hardly observed in the ^{13}C -NMR spectra. This indicated that the side reaction was significantly inhibited.

The ^{29}Si -NMR spectra of the PHPCSs are shown in Figure 6. The signal around -110 ppm was due to the silicon of the sample tube. The multiplets from -55 to -65 ppm were assigned to the CSiH_3 groups. The peaks from -28 to -38 ppm were attributed to C_2SiH_2



Scheme 1 Molecular structure of PHPCS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

units in the polymer main chain, whereas the peaks between -8 and -15 ppm presumably came from the C_3SiH units. The signal at about 10 ppm was due to the SiC_4 units. These tetracarbo-silicon, tricarbo-silicon, dicarbo-silicon, and monocarbo-silicon units were further evidence of a branched structure.^{3,6}

In conclusion, the resultant polymers were confirmed as propargyl-substituted PCSs by means FTIR spectroscopy and NMR. On the basis of these findings, the molecular structure of PHPCS is given in Scheme 1.

Thermal properties of PHPCS

Generally speaking, ceramic yield is an important factor in the value a polymeric precursor. Thus, TGA was used to study the thermal behavior and mass residue of PHPCS during the heat-treatment process. Froehling⁴ reported that a previous cross-linking treatment before pyrolysis could improve the final ceramic yield of a branched PCS. The liquid PHPCSs were crosslinked at 170°C for 6 h under an argon atmosphere to gain compact yellow solids, and then, the solids were used for TGA (Fig. 7). In comparison with PHPCS, HPCS was crosslinked under the same conditions to give a viscous liquid used for TGA.

For HPCS, the weight losses were 17.5 wt % (25– 400°C), 7.4 wt % (400– 900°C), and 1.6 wt % (900– 1400°C), with an overall value of 73.5 wt % at 1400°C . Correspondingly, the PHPCSs revealed ceramic yields of 82.5 wt % at 1400°C with weight losses of 1.5 wt % (25– 400°C), 14.5 wt % (400– 900°C), and 1.5 wt % (900– 1400°C). No obvious weight loss was observed in the range 900– 1400°C ; this indicated that the polymer-to-ceramic conversion was complete at about 900°C . Careful examination showed that the majority of weight loss

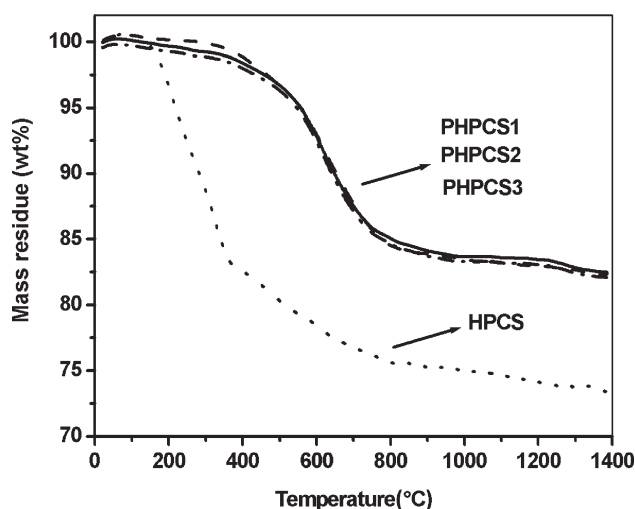


Figure 7 TGA curves of the PHPCSs and HPCS.

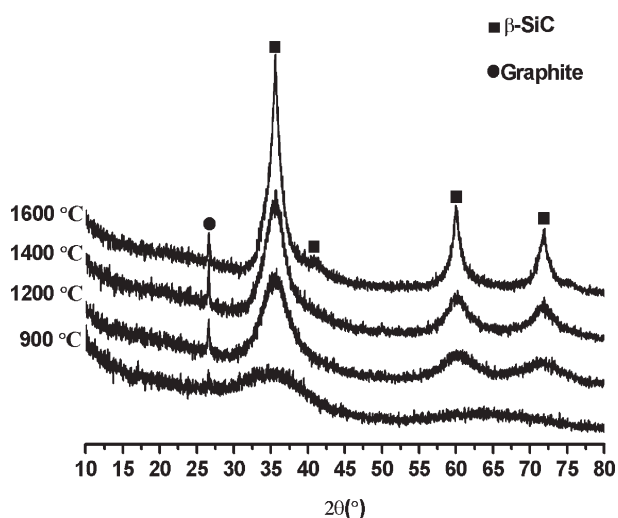


Figure 8 XRD patterns of PHPCS3-derived ceramics at different temperatures.

happened between 25 and 400°C for HPCS and between 400 and 900°C for PHPCS. A detailed study of the linear polymer relative of HPCS, $[\text{SiH}_2\text{CH}_2]_n$ (polysilaethylene) indicated that the main crosslinking mechanism involved the 1,1-elimination of molecular hydrogen from SiH_n ($n > 2$) groups, and the resultant H_2 evolution rate increased rapidly above 425°C.²³ This might have been due to the vaporization of low-molecular-weight oligomers in the range 25–400°C. In comparison with HPCS, 10–20 mol % substitution of propargyl groups was sufficient to improve the crosslinking of oligomers via the conventional hydrosilation involving Si-H and unsaturated groups; this was responsible for the difference in the weight loss (25–400°C). According to the literature, the weight loss between 400 and 900°C is due to the release of gaseous products, such as CH_4 and H_2 , during the polymer-to-ceramic conversion.²⁴ We observed that the weight loss of PHPCS was higher than that of HPCS with the average formula $[\text{SiH}_2\text{CH}_2]_n$; this might have been due to the decomposition of propargyl side groups of PHPCS in the range 400–900°C. The observation was consistent with reports on a Yajima PCS, $[\text{Si}(\text{CH}_3)\text{HCH}_2]_n$, in which the decomposition of methyl side groups occurred above 600°C.^{24,25} On the basis of the TGA results, the substitution of propargyl groups contributed to about a 10 wt % higher ceramic yield of PHPCS in comparison with HPCS. In comparison with AHPCS, PHPCS had lower oxygen contents and higher ceramic yields; it is more promising for use as a precursor for the SiC matrix and coating.

Characterization of PHPCS-derived ceramics

Figure 8 shows the XRD patterns of the pyrolytic residues of crosslinked PHPCSs pyrolyzed at 900,

1200, 1400, and 1600°C in argon. The 900°C ceramic was amorphous and highly disordered. Further heating at 1200°C caused a broad peak at 36°; this indicated the incomplete crystallization and the formation of a local order SiC. At 1400°C, the intensity of broad peak at 36° increased; this indicated that the resultant SiC was more ordered in comparison with that at 1200°C. The characteristic peaks of β -SiC appeared until 1600°C. Among these peaks, the three major peaks at $2\theta = 36^\circ$ (111), 60° (220), and 72° (311) were attributed to β -SiC.²⁶ These XRD patterns also indicated that the heat treatment significantly influenced the evolution of crystalline β -SiC.

To further investigate crystallization behavior of the final ceramics, FTIR spectroscopy was performed at various temperatures (Fig. 9). At 900°C, only one broad peak was retained around 780 cm^{-1} ; this was attributed to the amorphous SiC framework structure.²⁶ Further heating to 1200, 1400, and 1600°C led to a sharpening of the SiC band and a shift in its position from 780 to 850 cm^{-1} ; this was consistent with the formation of crystalline SiC.²⁷ In summary, the FTIR spectroscopy results agreed well with the XRD results.

To investigate the influence of the $\text{CH}\equiv\text{CCH}_2\text{Cl}$ amount on the composition of the PHPCSs and their final ceramics, elemental analysis was performed, and the results are given in Figure 10. A series of PHPCSs with different carbon contents ranging from 28.2 to 33.8 wt % were synthesized through the variation of the molar ratio of $\text{CH}\equiv\text{CCH}_2\text{Cl}$ to $\text{Cl}_{1.25}(\text{O-Me})_{1.75}\text{SiCH}_2\text{Cl}$ in the feed. We expected that the carbon contents of PHPCSs would increase with increasing $\text{CH}\equiv\text{CCH}_2\text{Cl}$ amount. Subsequently, SiC ceramics were obtained after the pyrolysis of the cured PHPCS. The C/Si ratios of the final ceramics derived from PHPCSs were in the range 0.93–1.21. It

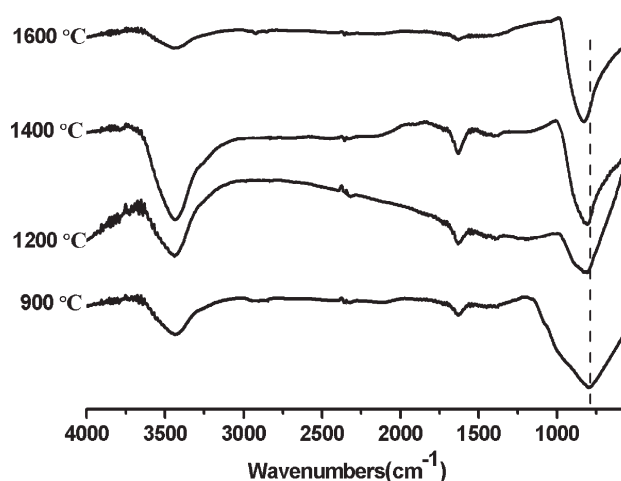


Figure 9 FTIR spectra of PHPCS3-derived ceramics at different temperatures.

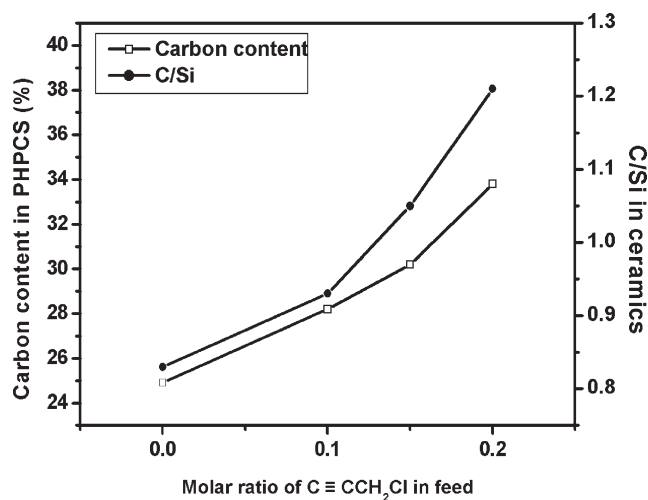


Figure 10 Dependence of the carbon contents of the PHPCSs and the C/Si ratios of the ceramics on the amount of $\text{CH}\equiv\text{CCH}_2\text{Cl}$ in the feed.

is generally accepted that SiC has quite different properties with different C/Si ratios.²⁸ As is well-known, near-stoichiometric SiC has excellent mechanical properties and heat resistance at high temperatures. Many efforts have been devoted to obtaining near-stoichiometric SiC via the polymeric precursor method.^{29,30} About 10–20 mol % substitution of propargyl groups was found to be sufficient for promoting the ceramic yield without incorporating a substantial excess of carbon on pyrolysis in this study. Near-stoichiometric SiC with C/Si = 1.05 was gained with a molar ratio of $\text{CH}\equiv\text{CCH}_2\text{Cl}$ to $\text{Cl}_{1.25}(\text{OMe})_{1.75}\text{SiCH}_2\text{Cl}$ of 0.15. As a result, the compositions of the final ceramics could be tailored by the control of the compositions of the PCS precursors. Therefore, it could be convenient to obtain near-stoichiometric ceramics from the PHPCS through the control of the feed ratios of the starting materials.

CONCLUSIONS

A propargyl-substituted PCS, namely, PHPCS, was prepared by a modified synthesis route, which involved Grignard coupling of partially methoxylated $\text{Cl}_3\text{SiCH}_2\text{Cl}$ and $\text{CH}\equiv\text{CCH}_2\text{Cl}$, followed by reduction with LiAlH_4 . The resultant PHPCSs were characterized by GPC, FTIR spectroscopy, and NMR. Moreover, the thermal properties of the PHPCSs were investigated by TGA. The ceramic yield of PHPCS at 1400°C was about 82.5%; this suggested that the PHPCSs have great potential to be promising precursors to SiC. The XRD and FTIR results indicated that the heat treatment significantly influenced the evolution of crystalline β -SiC. It could be convenient for getting near-stoichiometric ceramics

from PHPCS through the control of the feed ratios of the starting materials.

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