

Synthesis, Characterization, and Properties of Silylene–Acetylene Preceramic Polymers

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ABSTRACT: A series of silylene–acetylene preceramic polymers **3a–e** were synthesized by polycondensation reaction of dilithioacetylene with dichlorosilane (H₂SiCl₂) or/and methylchlorosilane (MeSiHCl₂). Their structures were confirmed by infrared spectra (IR), and ¹H and ²⁹Si NMR spectroscopies. Differential scanning calorimetry (DSC) diagrams show exotherms centered at 200 to 233°C temperature range, attributed to crosslinking reaction of the acetylene and Si–H groups. After thermal treatment, the obtained thermosets **4a–e** possess excellent thermal stability. Thermogravimetric analysis (TGA) under nitrogen show the *T*_{d5s} (temperature of 5% weight loss) for all the thermosets are above 600°C, and the overall char yields are between 95.62% and 89.67% at 900°C. After pyrolysis at 1200°C, the obtained ceramic residues **5a–**

exhibit good thermo-oxidative stability with final weight retention between 98.76% and 91.66% at 900°C under air. In particular, perhydroploy(silylene)ethynylene **3a**, which has the highest Si/C ratio in silylene–acetylene polymers, has the highest char yield, and the derived ceramic material **5a** displays the best thermo-oxidative stability. Based on Scanning electron microscopy and its associated energy-dispersive X-ray microanalysis (SEM EDX) and ¹³C magic angle spinning nuclear magnetic resonance (MAS NMR) analysis, ceramic **5a** contains the highest SiC content. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 4064–4070, 2008

Key words: silylene–acetylene polymers; preceramic; thermosets; pyrolysis; thermal properties

INTRODUCTION

Rapid progress in the aerospace industry has created an ongoing need for materials with high thermal and thermo-oxidative stability. Silicon-containing polymers stand out as excellent candidates because their thermal degradation produce ceramics such as silicon carbide, which has excellent thermal and thermo-oxidative properties.^{1–5} In addition, soluble and meltable organosilicon polymers are processable and can be easily converted into products with different shapes. Among them, acetylene-containing organosilicon polymers have attracted much attention not only for their conducting and optical properties^{6–9} but also for their thermal properties.^{10–13} These polymers are stable under ambient conditions, but undergo crosslinking reactions without the evolution of volatiles during pyrolysis, thus exhibit high char yields.^{14–16} Organosilicon polymers containing an acetylene moiety as a part of the backbone or lateral chain have been reported.^{17–24}

However, all these preceramic polymers reported have a low Si/C ratio, so the resulting SiC ceramics contain a large excess of free carbon that are not suitable for the thermo-oxidative resistance materials.^{25,26} Research showed that the incorporation of Si–H groups can reduce the free carbon content in the pyrolysis residues as well as improve the char yields of organosilicon polymers.^{20,27–29} Moreover, organosilicon polymers containing Si–H group can be modified into various other useful polymers via hydrosilylation reactions.^{30,31}

To obtain ceramic materials that contain low-free carbon content and having good thermo-oxidative stability, a novel silylene–acetylene polymer, perhydroploy(silylene)ethynylene **3a**, which has the highest Si/C ratio in silylene–acetylene polymers, was synthesized in this paper. The precursor **3a** could be pyrolyzed to produce ceramic in high yield, and the derived ceramic contain high SiC content. However, we found the crosslinking reaction of polymer **3a** during heat treatment proceeds suddenly in a narrow temperature range. Therefore, control of the crosslinking process is very difficult. To improve the processability of polymer **3a**, as well as to investigate the relationship between structure and their thermal behavior, a series of copolymers **3b–d**, which contain different (methylsilylene)ethynylene

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concentrations, and poly(methylsilylene)ethynylene **3e** were also synthesized.

EXPERIMENTAL

Materials

Unless otherwise noted, all syntheses were performed under an atmosphere of dry nitrogen utilizing standard Schlenk techniques. *n*-Butyl lithium (2.5 M in hexane) was purchased from Acros Company and used as received. Dichlorosilane (H_2SiCl_2) was purchased from Kaihua Organosilicon factory and used as received. All other chemicals were purchased from Beijing Chemical Reagents Company. Trichloroethylene (TCE) and methylchlorosilane (MeSiHCl_2) were distilled before use. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from their deep purple solutions of sodium benzophenone/ketyl.

Synthesis

Synthesis of dilithioacetylene ($\text{LiC}\equiv\text{CLi}$)²¹

To a flame-dried 500 mL three-necked flask (equipped with a reflux condenser, a pressure-equalized dropping funnel, a gas inlet tube and a magnetic stirring bar and flushed with N_2) 100 mL of a 1 : 1 mixture of freshly distilled Et_2O and THF and 0.24 mol of *n*-butyl lithium was added. After cooling to -78°C , 0.08 mol TCE in 20 mL Et_2O was added dropwise over 20 min to the stirred solution. Then the -78°C bath was removed and the mixture was stirred at room temperature for 2 h. The resulting dilithioacetylene was used without further purification.

Synthesis of perhydropoly(silylene)ethynylene **3a**

Into a flame-dried 500 mL three-necked flask (equipped with a reflux condenser, a pressure-equalized dropping funnel, a gas inlet tube and a magnetic stirring bar, and flushed with N_2), H_2SiCl_2 (8.08 g, 0.08 mol) was carefully dissolved in 60 mL of Et_2O which was cooled to -70°C . The as-prepared dilithioacetylene was cannulated into the dropping funnel and added slowly under vigorous stirring. After completion of addition, the cold bath was kept for 2 h, then the mixture was stirred at room temperature for 15 h. The reaction mixture was poured into cool dilute hydrochloric acid and extracted with ether. The ethereal extract was washed with iced water until neutral, and the organic layer was dried with anhydrous magnesium sulfate and then filtered. After evaporation of the solvent, red-brown liquid **3a** (3.91 g, 90.5%) was obtained.

Synthesis of copolymers **3b-d**

The procedure for preparation of these copolymers was similar to that of used for **3a**. For each copoly-

mer, the following quantities of H_2SiCl_2 and MeSiHCl_2 was used in preparation: 5.39 g (0.053 mol) H_2SiCl_2 and 2.8 mL (0.027 mol) MeSiHCl_2 produced **3b**, 4.46 g (yield 96.75%); 4.04 g (0.04 mol) H_2SiCl_2 and 4.2 mL (0.04 mol) MeSiHCl_2 produced **3c**, 4.21 g (yield 86.11%); 2.73 g (0.027 mol) H_2SiCl_2 and 5.6 mL (0.053 mol) MeSiHCl_2 produced **3d**, 4.54 g (yield 89.82%).

Preparation of ploy(methylsilylene)ethynylene **3e**²⁸

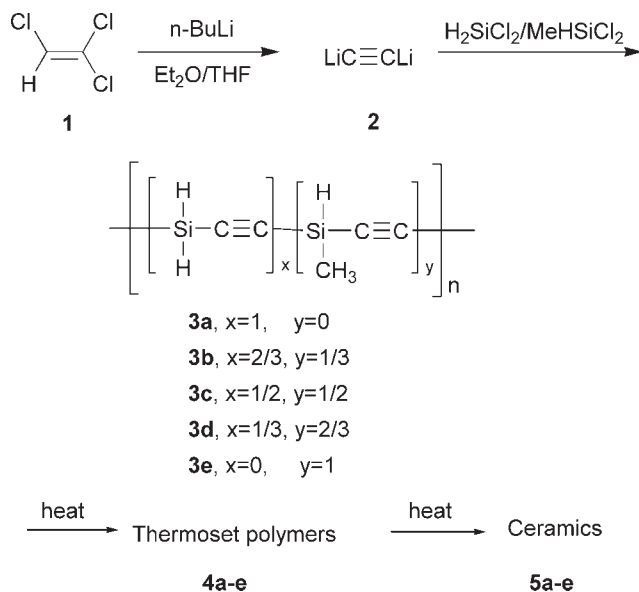
TCE (0.08 mol) was converted to dilithioacetylene by 0.24 mol *n*-butyl lithium using the procedure mentioned earlier, and MeSiHCl_2 (0.08 mol) was added dropwise for 10 min at -70°C . Then the reaction mixture was warmed to room temperature and stirred for 12 h. The reaction mixture was poured into cool dilute hydrochloric acid and extracted with ether. The ethereal extract was washed with iced water until neutral and the organic layer was dried with anhydrous magnesium sulfate and then filtered. After evaporation of the solvent, red-brown liquid **3e** (4.94 g, yield 90.57%) was obtained.

Crosslinking, pyrolysis of polymers **3a-e**

The samples were weighted in alumina boats and placed into the tubular furnace. Then, polymers **3a-c** were slowly heated ($2^\circ\text{C}/\text{min}$) in a sequence at 120°C (2 h), 150°C (2 h), 170°C (4 h), 200°C (4 h), 250°C (2 h), and polymers **3d-e** were heated ($5^\circ\text{C}/\text{min}$) in a sequence at 170°C (2 h), 200°C (4 h), 250°C (4 h), 300°C (2 h) in a flowing of nitrogen, hard, brown thermosets **4a-e** were obtained. Further heating the thermosets to 1200°C at a heating rate of $5^\circ\text{C}/\text{min}$ with a final plateau of 2 h gave the blue-black ceramic materials **5a-e**.

Characterization

Fourier transform infrared spectra (FTIR) were recorded between 4000 and 400 cm^{-1} with a Perkin-Elmer 2000 IR spectrometer. ^1H NMR were run on a Bruker AV 600 instrument and referenced to the internal solvent peak. ^{29}Si NMR were performed in CDCl_3 solution with 0.1% $\text{Cr}(\text{acac})_3$ as relaxation agent on a Bruker DMX 300 instrument using tetramethylsilane as an external standard. ^{13}C magic angle spinning nuclear magnetic resonance (MAS NMR) was carried out by a Bruker AV 300 instrument. NMR frequency, 75.47 MHz; recycling delay 5 s; contact time 1 ms; spinning rate 5 kHz. Gel permeation chromatography (GPC) was conducted in THF (1 mL/min) at 35°C on four Styragel columns (HR 0.5, HR 0.5, HR 1, HR 4) that were connected to a Waters 1515 Isocratic HPLC pump and Waters 2414 refractive index detector. Molecular



Scheme 1 Synthesis of preceramic polymers **3a–e** and further thermal treatment to ceramic materials.

weights are reference to polystyrene standards. Differential scanning calorimetry (DSC) experiments were performed by using a heating rate of $10^\circ\text{C}/\text{min}$ on a Mettler Toledo 822^e instrument with a N_2 flowing rate 50 mL/min. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA409PC TGA instrument at a heating rate of $10^\circ\text{C}/\text{min}$. X-ray powder diffraction (XRD) measurements were obtained using $\text{Cu-K}\alpha$ radiation (40 KV, 200 mA, $\lambda = 0.154056$) with a Rigaku D/MAX 2400 diffractometer. The average size of the crystallites L_m was calculated from the Scherrer formula $L_m = K\lambda/D\cos\theta$, where K is a constant taken as 0.9, λ is the $\text{CuK}\alpha$ wavelength, θ is the bragg angle ($\theta = 17.8^\circ$), and D is the width at midheight in radius of the $\beta\text{-SiC}$ (111)]. Scanning electron microscopy (SEM) and its associated energy-dispersive X-ray microanalysis (SEM-EDX) measurements were carried out on a HITACHI S-3000 instrument.

RESULTS AND DISCUSSION

Synthesis and characterization

The preparation of polymers **3a–e** is shown in Scheme 1. All the polymers are liquid at room temperature and soluble in various organic solvents, such as THF, toluene, and CHCl_3 . The structures of polymers **3a–e** were characterized by FTIR and NMR spectroscopies (Figs. 1–3). As shown in Figure 1, all polymers show strong absorptions around 2170 cm^{-1} attributed to the Si–H stretch and bands at 3282 and 2048 cm^{-1} due to the C–H and $\text{C}\equiv\text{C}$ stretches of the acetylene groups (The bands in **3e** are very weak because its molecular weight is very

large, and the concentration of $\equiv\text{C-H}$ moiety is very low). Additional bands at $2865 \sim 2968\text{ cm}^{-1}$ (C–H stretch), 1403 cm^{-1} (in-plane bending of Si– CH_3), and 1258 cm^{-1} (out-plane bending of Si– CH_3) in polymers **3b–e** are assigned to Si– CH_3 groups of the (methylsilylene)ethynylene moiety. It can be observed that the relative intensities of the Si– CH_3 peaks ($\sim 1250\text{ cm}^{-1}$) to the Si–H peaks ($\sim 2170\text{ cm}^{-1}$) in the spectrums of the polymers **3b–e** are proportional to the concentration of (methylsilylene)ethynylene linkage. IR spectra for all polymers show absorptions at $1070 \sim 1096\text{ cm}^{-1}$, indicating the presence of Si–O unit, which would be formed from hydrolysis of the Si–Cl groups retaining in the resulting polymers during work up.

NMR spectra for polymers **3a–e** were also measured to confirm the structure. In ^{29}Si NMR (Fig. 2), the perhydropoly(silylene)ethynylene (**3a**) has resonances with chemical shift of $-84.0 \sim -85.4\text{ ppm}$. For poly(methylsilylene)ethynylene (**3e**), a peak at -62.7 ppm was observed. Copolymers **3b–d** display resonances characteristic of both **3a** and **3e**, with individual intensities proportional to specific copolymer compositions. The compositional changes of the copolymers **3b–d** were also observed in ^1H NMR (Fig. 3) spectra. The C–H protons resonate in the $0.33\text{--}0.45\text{ ppm}$ range, and the Si–H protons resonate in the $4.27\text{--}4.34\text{ ppm}$ region. These resonances were also observed to show appropriate growth and collapse as the polymer composition was varied.

Weight-average molecular weights in the range of $M_w = 1072\text{--}4860$ relative to polystyrene standards were determined by GPC (Fig. 4). A weight-average molecular weight of 1072 in the case of **3a** corresponds to a polymerization degree of about $n_w = 19$ (19 silyleneethynylene units on average). A total of 71 units have been found in the case of the

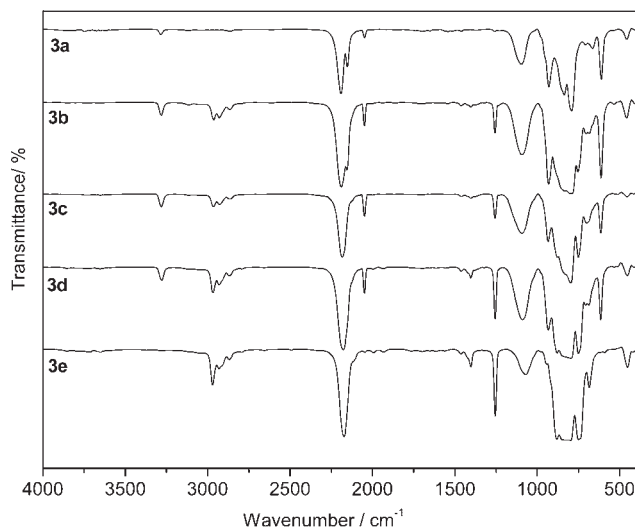


Figure 1 IR spectra of the preceramic polymers **3a–e**.

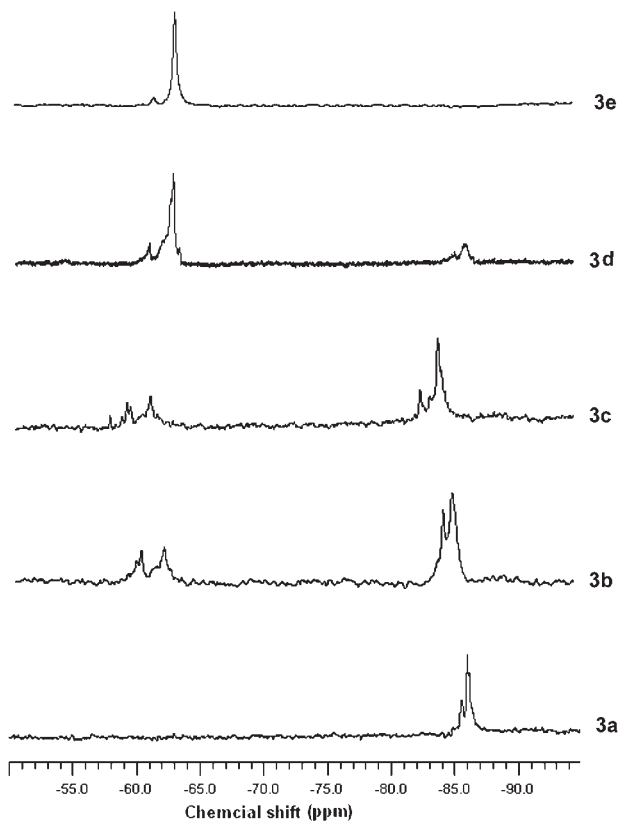


Figure 2 ²⁹Si NMR spectra of the preceramic polymers 3a-e.

corresponding methylated polymer 3e. Changing hydrogen atoms to methyl groups results in a significant increase of the polymerization degree. This may be due to the reactivity of dichlorosilane is lower than that of methylchlorosilane, which is similar to the report that the reactivity of

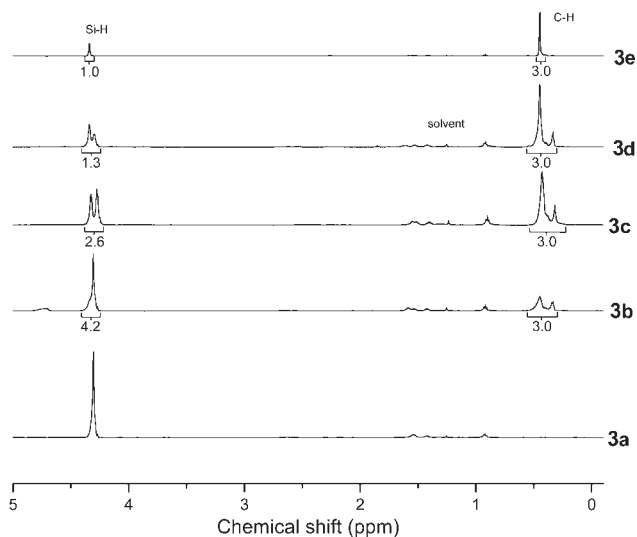


Figure 3 ¹H NMR spectra of the preceramic polymers 3a-e.

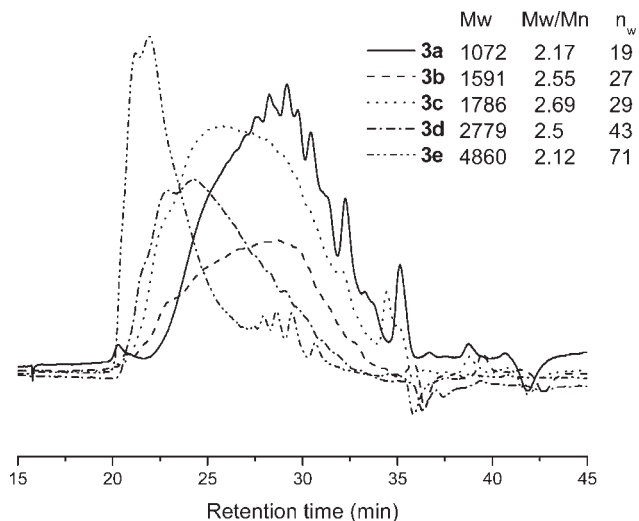


Figure 4 GPC curves for the preceramic polymers 3a-e.

methylchlorosilane is lower than that of dimethylchlorosilane.²⁸

Thermal properties

The thermal properties of the precursor polymers 3a-e were studied by DSC analysis. The DSC diagrams of all the polymers (Fig. 5) show exotherms centered at 200 ~ 233°C, characteristic of the acetylene crosslinking reaction. Polymer 3a displays a sharp and strong exothermic peak and the integration of this exothermic area corresponds to 1169 J/g, which indicates a fast crosspolymerization reaction. So, a heating rate of 2°C/min was used in the curing cycle to avoid explosive polymerization. To slower the crosspolymerization reaction of polymer 3a, the (methylsilylene)ethynylene linkage was introduced. As displayed in Figure 5, the exothermic peak width

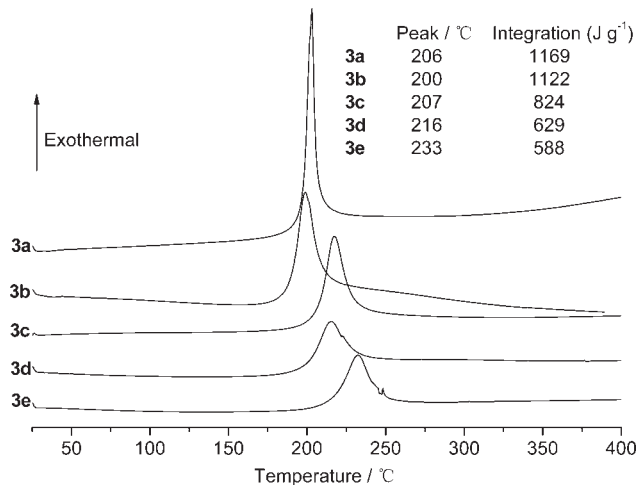


Figure 5 DSC thermograms of the preceramic polymers 3a-e.

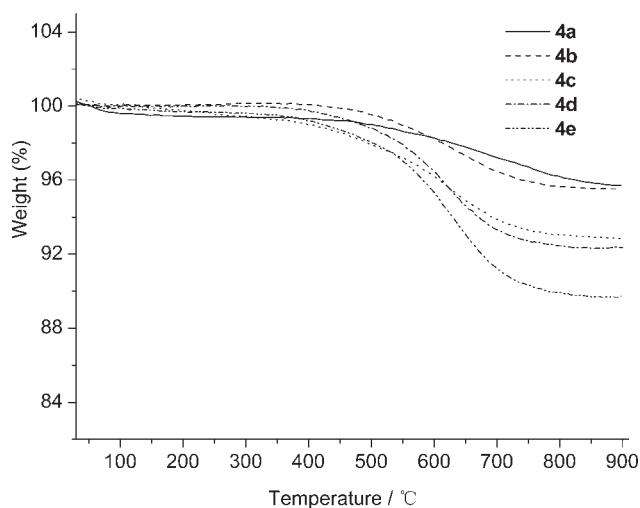


Figure 6 TGA thermograms to 900°C in N₂ of the thermosets **4a–e**.

increases with increasing concentration of the (methylsilylene)ethynylene linkage, and the average exothermic energy decreases simultaneously, which means the processability of polymer **3a** was improved. As the average exothermic energy decreases with decreasing concentration of the Si–H group, we presume that the Si–H groups, as well as the C≡C groups, were also partly involved to form a crosslinking structure in the curing process. Our hypothesis was also confirmed by FTIR spectra, which show the peaks near 3282 cm⁻¹ and 2048 cm⁻¹ arising from ≡C–H bond vanished completely after the completion of each curing cycle, whereas the absorption due to Si–H groups (2170 cm⁻¹) became broader as well as a new peak at 1635 cm⁻¹ attributed to C=C stretch appeared.

The TGA traces (Fig. 6) show that the thermosets **4a–e** have outstanding thermal stability, and almost no weight loss occurred when heated to 400°C under N₂. The *T*_{d5} (temperature of 5% wt loss) of all the thermosets under N₂ are above 600°C (*T*_{d5} for **4c–e** are 645.6°C, 639.0°C, and 607.7°C, respectively). Especially, the *T*_{d5} of **4a** and **4b** under N₂ are above 900°C. The char yields are also high, and the weight residues at 900°C under N₂ are 95.62%, 95.58%, 92.87%, 92.37%, and 89.67%, respectively. These results proved that introduction of the Si–H groups enhanced the char yields of the polymers, which is consistent with Shim and coworkers report.²⁸

The oxidative stability of ceramic materials **5a–e** was also examined. It was found by TGA (10°C/min, air) that the ceramics possess excellent thermo-oxidative stability. Heating the ceramic residues **5a–e** in air to 900°C, gave final weight retention of 98.76%, 97.68%, 96.29%, 94.97%, and 91.66%, respectively, (Fig. 7). That is, the precursor which has the highest concentration of Si–H group (or Si/C ratio) resulted ceramic with the

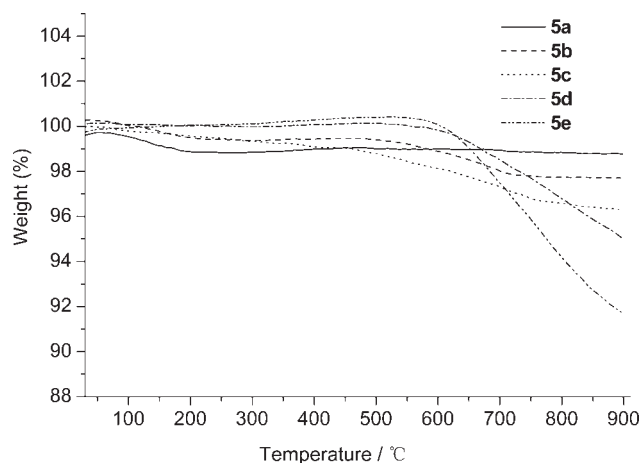


Figure 7 TGA thermograms to 900°C in air of the ceramics **5a–e**.

best oxidative stability. This is due to the SiC content in the ceramic materials increases with increasing –SiH₂– units incorporated in the starting precursors. This is confirmed by the results of SEM EDX as shown in Table I.

Composition analysis of ceramics

The crystalline phase of ceramics derived from various precursors at 1200°C were identified by XRD (Fig. 8). In each case, the three broad peaks which are observed at 2θ = 35.6°, 60.0°, and 71.8° correspond to the(111), (220) and (311) planes of β-SiC, respectively. From the (111) line, the average size of the SiC crystallites were found to be 16.7 Å, 18.6 Å, 19.7 Å, 20.9 Å, and 22.3 Å. The peak at 2θ = 26.5° was due to the (101) diffraction line of α-quartz.³² The oxygen was thought to be introduced during the curing and pyrolysis process.

To confirm the SiC/C ratios, and gain a better understanding of the relationship of structures and compositions, ceramics derived from perhydropoly (silylene)ethynylene (**5a**) and poly(methylsilylene)ethynylene (**5e**) were investigated comparatively by ¹³C MAS NMR (Fig. 9). Both showed two main

TABLE I
Chemical Compositions^a of Ceramic Materials **5a–e**

Ceramic materials	SiC (mol %)	SiO ₂ (mol %)	Excess C (mol %)
5a	80.26	9.42	10.32
5b	63.72	4.73	31.55
5c	49.79	7.66	42.55
5d	43.02	4.51	52.47
5e	41.92	3.65	54.44

^a Original EDX analysis provided only elemental composition. We presume the ceramics only consist of SiC, SiO₂, and free C.

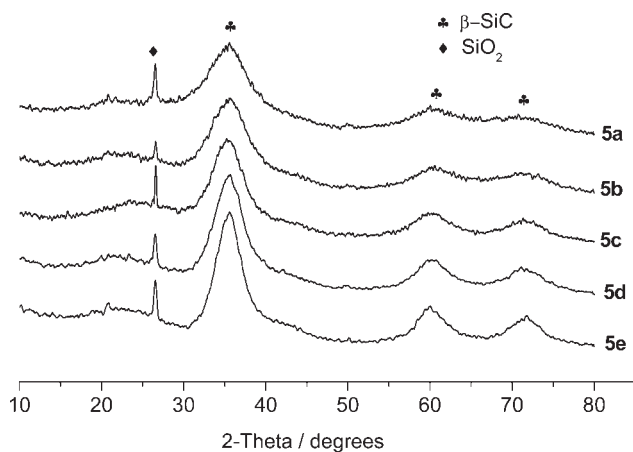


Figure 8 XRD powder patterns of the ceramics **5a–e**.

peaks centered around 19 and 130 ppm, which were assigned to the SiC and free C, respectively. According to their relative intensities, ceramic **5a** have a higher SiC content than ceramic **5e**. This is consistent with the TGA (under air) results.

SEM showed that both thermosets **4a–e** and their resulting ceramics **5a–e** were smooth and pore free. The micrographs of **4b**, **4d**, **5b**, and **5e** were selected as an example and are shown in Figure 10. To determine the chemical composition of the ceramics, EDX were performed on the specimen and provided a quantitative elemental composition. Presuming that

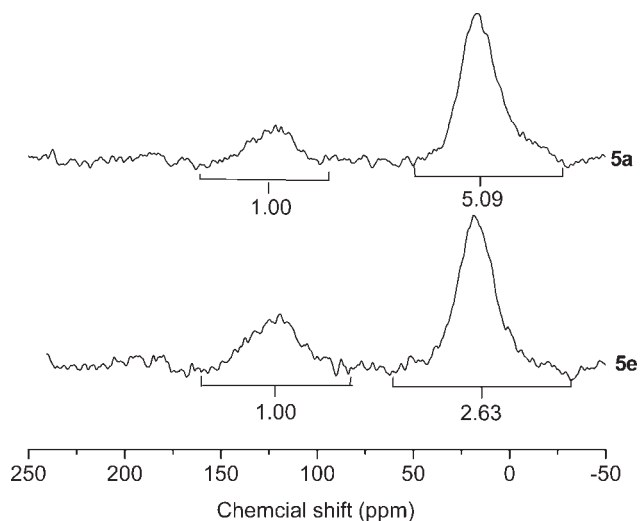


Figure 9 ^{13}C MAS NMR of ceramics **5a** and **5e**.

the ceramics only consist of SiC, SiO₂, and free C, we gave quantitative data as shown in Table I. As expected, polymer **3a**, which has the highest Si/C ratio in silylene-acetylene polymers, has the highest SiC content in its resulting ceramic materials **5a**, whereas polymer **3e** gave ceramics which contain the highest free C. The results confirmed that induction of Si–H bond reduced the free-carbon content effectively.

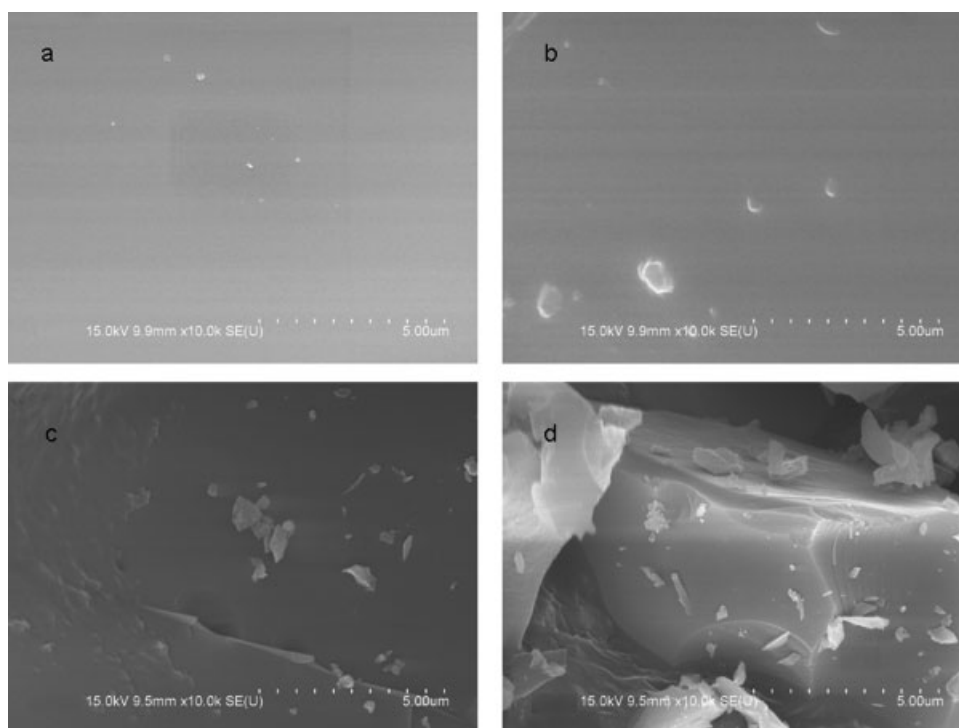


Figure 10 SEM micrographs of (a) thermoset **4b**, (b) thermoset **4d**, (c) ceramic **5a**, and (d) ceramic **5d**.

CONCLUSIONS

Processable silylene-acetylene precursor polymers **3a-e** containing perhydrosilylene and/or methylsilylene units in the polymer backbone were synthesized and characterized using FTIR and NMR spectroscopies. After thermal crosslinking, the obtained thermosets **4a-e** show exceptional thermal stability and the T_{d5S} (temperature of 5% weight loss) under nitrogen are all above 600°C. When heating to 1200°C with the final temperature maintained for 2 h, ceramics **5a-e** were obtained. XRD analysis shows β -SiC crystallites were formed in the progress. ^{13}C MAS NMR and SEM EDX of the ceramics showed the ceramic derived from perhydropoly(silylene)ethynylene **3a** to have the highest SiC content. Thermal gravimetric analysis of the ceramics **5a-e** in air indicated good oxidative stability. Especially, the thermal and oxidative stability increased with increasing concentration of Si-H group, and the thermoset **3a** has the highest char yield, and the resulting ceramic **5a** has the best oxidative stability. However, the rapid curing rate and huge curing exotherm made it difficult to process. And introduction of methylsilylene linkage can improve the processability of polymer **3a**. These polymers have a potential application as matrix materials for advanced composites and ceramic precursors.

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