Novel Pyrolytic Conversion of Poly[(diisobutylsilylene)methylene] to Stoichiometric Silicon Carbide

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Silicon carbide ceramic (SiC) is a promising material because of its exceptional thermal and chemical stability and convenient mechanical properties. It is also known as a semiconductor having a wide band gap (2.2−3.0 eV). The excellent performance in high-temperature, high-power, high-frequency, and radiation-resistant systems makes SiC desirable especially for electronics applications.[1] To date, the fabrication of semiconductor-grade SiC thin films is implemented primarily by the use of modern deposition techniques[2] such as chemical vapor deposition (CVD), which often requires well-controlled deposition conditions and safety precautions. Largely due to the ease of processing, the preparation of stoichiometrically pure SiC from polycarbosilane precursors has continuously received much interest since the discovery of Yajima's polycarbosilane,[3] which can be pyrolytically transformed to SiC/C composites.[4] In the search for optimal preceramic materials, polymers possessing a 1:1 atomic ratio of Si:C are generally thought to be necessary to provide control of the purity of the resulting SiC. For example, the stoichiometric poly(silaethylene) represents the simplest polymer among the linear polycarbosilane family and its pyrolytic conversion gives satisfactory results in terms of high ceramic yield and low crystallization temperature of β-SiC.[5]

Unlike stoichiometric preceramic materials, the title polycarbosilane bearing isobutyl side chains contains many more carbon than silicon atoms. Our recent study[6] on the epitaxial growth of GaAs:Si using octa-*tert*-butyloctasilacubane as the source of Si dopant indicates that the elimination of bulky hydrocarbon groups in silanes may be efficient at elevated temperatures. This suggests the possibility of obtaining a stoichiometric SiC from a nonstoichiometric preceramic polymer.

As depicted in Scheme 1, the conversion of the disilacyclobutane to amorphous SiC (a-SiC) is achieved by the elimination of hydrocarbon side chains. The formation of SiC without the involvement of purification and the use of catalysts avoids tedious processes and any possible contamination, which are frequently encountered in the synthesis of polycarbosilanes. Moreover, this system provides a straightforward pathway to obtain soluble and stable polycarbosilanes containing SiH_2 moieties that can be readily spin coated onto a quartz substrate and pyrolyzed to SiC thin films.

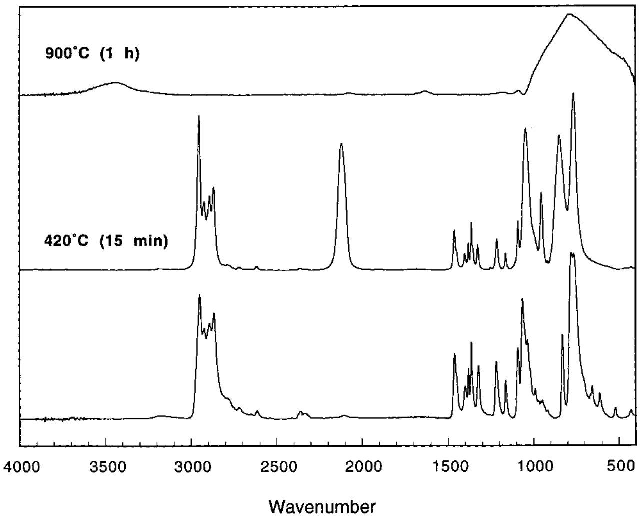
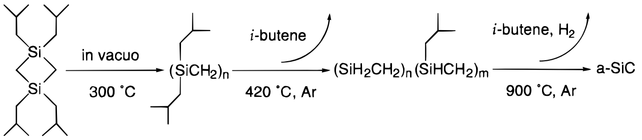


Figure 1. Infrared spectra of **1** (bottom) and pyrolyzed products after treatment at 420 °C for 15 min and at 900 °C for 1 h.

Scheme 1



Poly[(diisobutylsilylene)methylene] (**1**) is synthesized by thermal ring-opening polymerization[7] of the corresponding disilacyclobutane[8] at 300 °C. The resulting polymer (yield, 76%) is purified by precipitation from a hot toluene solution. Due to its limited solubility in common organic solvents, the determination of molecular weight by size exclusion chromatography was conducted at 135 °C in a *o*-dichlorobenzene solution and gave the $M_w = 5.3 \times 10^4$ relative to polystyrene standards and the polydispersity of 5.6. The ^1H, ^{13}C, and ^{29}Si NMR spectra of the polymer recorded at 90 °C in toluene-d_8 are consistent with the expected structure of **1**.[9] The DSC thermogram[10] of **1** exhibits a distinct melting endotherm centered at 221 °C; a weak exothermic reaction occurs at the onset of 265 °C and becomes significant beyond 320 °C. The pyrolysis behavior followed by thermogravimetric analysis (TGA) under a N_2 flow is in good agreement with the result of the DSC measurement. A fast and continuous weight loss is observed in the 320−520 °C region. Above 520 °C, there is almost no weight loss and a ceramic residue of 19% (calcd, 25.6%) is obtained at 900 °C. The volatile products carried by He flow during pyrolysis were examined by infrared spectroscopy. The spectrum is completely dominated by the typical vibrations of isobutene when the pyrolysis temperature reaches 350 °C or higher. The residue recovered after a thermal treatment at 420 °C for 15 min shows an intense absorption at 2119 cm^{-1}, characteristic of the Si−H vibration (Figure 1). It is evident that the elimination of isobutyl side chains involved in the decomposition of **1** at high temperatures is associated with the formation of Si−H bonds.

To explore the structure of pyrolysis intermediates and the elimination reaction, the samples heated at 420 °C for 15 and 30 min were investigated by NMR spectroscopy. The ^1H NMR of **1** shows a signal of the catenated CH_2 at 0.26 ppm and three signals of the isobutyl protons in the region from 0.5 to 2.1 ppm (Figure 2). No appreciable hydrosilane moiety is detected in the vicinity of 4 ppm, although a weak absorption of the Si−H vibration correlated to the slight loss of side chains during polymerization is found in the infrared spectrum (Figure 1). For the pyrolysis intermediates,[11] two additional resonances of the $-SiH_2CH_2-$ and $-SiH(\text{isobutyl})CH_2-$ moieties appear at the 4.2 and 4.4 ppm, respectively. With the progress of pyrolysis, the change in the relative intensity of the 4.2 and 4.4 ppm peaks indicates an increase in the content

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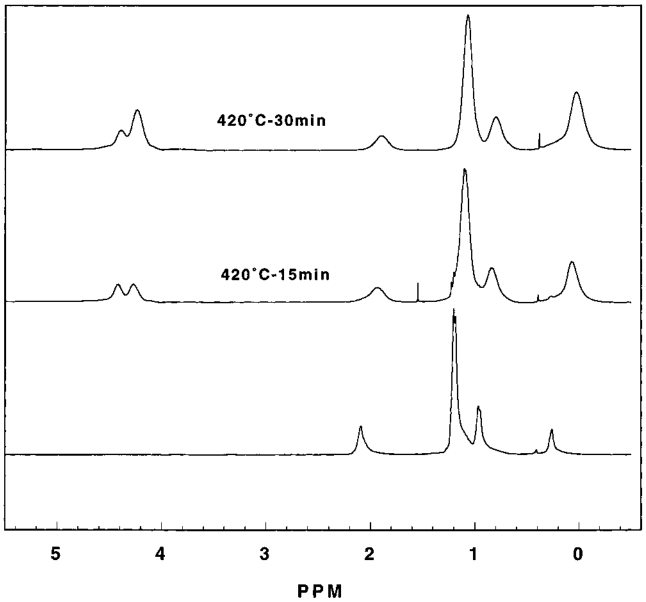

Figure 2. ^{1}H NMR spectra of **1** in toluene-d_8 at 90 °C (bottom) and pyrolyzed products in C_6D_6 with indicated pyrolysis conditions.

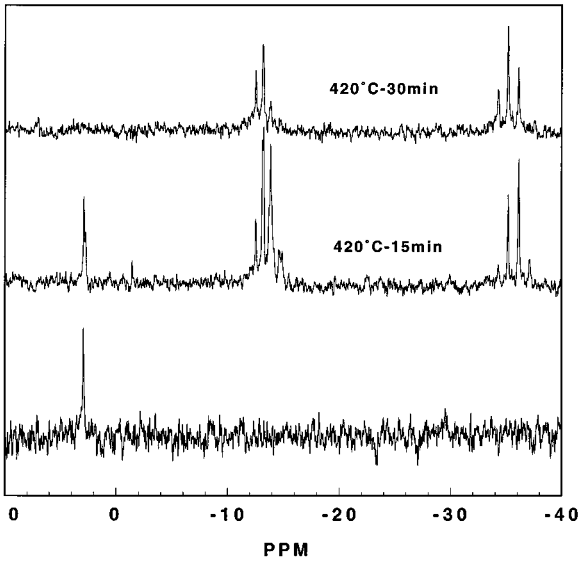

Figure 3. ^{29}Si NMR spectra of **1** in toluene-d_8 (bottom) and pyrolyzed products in C_6D_6 with indicated pyrolysis conditions.

of the SiH_2 moiety. In the ^{29}Si NMR spectra of the pyrolysis intermediates (Figure 3), the appearance of multiplets in the region of −13 and −35 ppm is consistent with the presence of SiH and SiH_2 groups. The assignment of the peaks in each multiplet is based on the possible sequences of triads;[12] the relative intensity of triads indicates a random arrangement of SiH and SiH_2 moieties in the pyrolysis intermediates. It is noteworthy that in the ^{29}Si NMR spectrum of the 30 min thermolyzed sample the signal at 2.9 ppm disappears, whereas it is evident in the sample thermally treated for only 15 min. In the absence of the dialkyl-substituted silylenemethylene moiety, an approximate estimation according to the integration result of the ^{1}H NMR spectrum suggests that the sample heated for 30 min had the structure $[SiH_2CH_2]_n[SiH(isobutyl)CH_2]_m$ where $n/m \sim 1$.

In a stream of Ar, the polycarbosilane was heated to 900 °C and held for 1 h. A lustrous black ceramic was obtained after the pyrolysis. Its X-ray diffraction pattern shows weak and broad diffractions, indicative of the amorphous nature for the ceramic product. Due to the refractory nature of SiC, the composition of this ceramic was determined by electron probe microanalysis (EPMA). The averaged composition of the surface region is found to be $SiC_{1.01}O_{0.17}$. Although the corresponding infrared spectrum (Figure 1) gives a broad band centered at 820 cm^{-1}, the existence of small amounts of oxygen is manifested by the weak ν(Si−O) absorptions above 1000 cm^{-1}.[13] The compositional depth profile measured by Auger electron spectroscopy shows that the oxygen impurity is highly concentrated at the surface and that carbon and silicon are homogeneously distributed throughout the sample.

It is known that β-silyl groups stabilize carbonium ions mainly by the hyperconjugative effect.[14] In this polycarbosilane system, the β-hydrogen in the isobutyl substitutent is expected to undergo facile migration with the aid of steric protection. The formation of Si−H bonds associated with the evolution of isobutene and the existence of stoichiometric SiC after pyrolysis indicate that the loss of organic components during pyrolysis is accomplished by the elimination of side chains, although some depolymerization may occur and account for the lower ceramic yield. The confirmation of the SiH_2-containing polycarbosilanes as the pyrolysis intermediates suggests a ceramization process analogous to that involved in the pyrolysis of poly(silaethylene).[5,15]

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(8) The 1,1,3,3-tetraisobutyl-1,3-disilacyclobutane was prepared according to the described method.[16] The coupling of diisobutyl(chloromethyl)chlorosilane in the presence of Mg metal gave a colorless liquid (bp 90 °C/0.3 Torr) in 65% yield. ^{1}H NMR (toluene-d_8): $\delta = 0.16$ (s, 4H, $-SiCH_2Si-$), 0.79 (d, 8H, $SiCH_2-$), 1.02 (d, 24H, $-CH_3$), 1.92 (sept, 4H, $-CH(CH_3)_2$); ^{13}C{H} NMR (toluene-d_8): $\delta = 1.6$ ($-SiCH_2$-Si−), 25.7 ($-CH(CH_3)_2$), 26.5 ($-CH_3$), 28.5 ($SiCH_2-$). ^{29}Si{H} NMR (toluene-d_8): $\delta = 5.1$.

(9) The NMR assignments for poly[(diisobutylsilylene)methylene] are as follows. ^{1}H NMR: $\delta = 0.26$ (2H, $-SiCH_2Si-$), 0.96 (4H, $SiCH_2-$), 1.20 (12H, $-CH_3$), 2.09 (2H, $-CH(CH_3)_2$); ^{13}C{H} NMR (toluene-d_8): $\delta = 4.0$ ($-SiCH_2Si-$), 26.1 ($-CH(CH_3)_2$), 27.7 ($-CH_3$), 30.2 ($SiCH_2-$). ^{29}Si{H} NMR (toluene-d_8): $\delta = 2.9$.

(10) The DSC thermogram was recorded at a heating rate of 5 °C/min from 25 to 350 °C.

(11) The intermediates prepared at 420 °C for 15 and 30 min are fully soluble in common organic solvents. With the thermal treatment longer than 30 min, insoluble and gel-like elastomer was found in the pyrolyzed products, indicating the occurrence of cross-linking reaction.

(12) The ^{29}Si chemical shifts for the possible triad sequences in random copolymers are assigned as follows: 2.8 ($\mathrm{SiR_2{-}\mathit{Si}R_2{-}SiR_2}$), −12.5 ($\mathrm{SiH_2{-}\mathit{Si}RH{-}SiH_2}$), −13.2 ($\mathrm{SiH_2{-}\mathit{Si}RH{-}SiRH}$), −13.9 ($\mathrm{SiRH{-}\mathit{Si}RH{-}SiRH}$), −14.7 ($\mathrm{SiR_2{-}\mathit{Si}RH{-}SiRH}$), −34.3 ($\mathrm{SiH_2{-}\mathit{Si}H_2{-}SiH_2}$), −35.2 ($\mathrm{SiRH{-}\mathit{Si}H_2{-}SiH_2}$), −36.1 ($\mathrm{SiRH{-}\mathit{Si}H_2{-}SiRH}$), −37.1 ($\mathrm{SiR_2{-}\mathit{Si}H_2{-}SiRH}$), where R = isobutyl.

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