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Synthesis and characterization of novel preceramic polymer for SiC

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Abstract Polyphenylcarbosilane as a novel preceramic polymer for SiC was synthesized by thermal rearrangement of polymethylphenylsilane at around 350–430 °C. Characterization of the synthesized polyphenylcarbosilane was performed using ^{29}Si NMR, ^{13}C NMR and ^{1}H NMR spectroscopy, FT-IR spectroscopy and TG, XRD, and GPC analysis. From the FT-IR data, the band at 1035 cm^{-1} was very strong and was assigned to the CH_2 bending vibration in the Si–CH_2–Si group, indicating the formation of polyphenylcarbosilane. The average molecular weight (M_w) of the polyphenylcarbosilane synthesized was 2,500, and it was found to easily dissolve in an organic solvent. TGA data indicate that polyphenylcarbosilane is thermally stable up to 200 °C. However, rapid weight loss occurs above 200 °C because of the decomposition of polyphenylcarbosilane, and the diffraction peak of the pyrolysis residue at 1200 °C corresponds to β-SiC ceramic. The ceramic yield calculated from TGA is approximately 60%.

Introduction

Recently, various types of carbide and nitride ceramics have been prepared from preceramic polymeric precursors [1–7]. The most important advantage of using polymeric precursors is the ease of their preparation at low processing temperatures. Since preceramic polymers of moderate molecular weights are easily soluble in organic solvents such as cyclohexane, THF, and xylene, preceramic polymers can be easily coated on metal, ceramic, or graphite surfaces using spinning, dip-coating, and spray-coating methods to improve their anticorrosion and antioxidation properties. After cross-linking and thermal treatment, preceramic polymers are converted to amorphous ceramic at temperatures ranging from 600 to 900 °C, and to crystalline ceramic above 1200 °C. The derived ceramic microstructure and the chemical composition are strongly dependent on the composition of the polymer precursors used. Polycarbosilane is the most commonly used polymeric precursor for SiC ceramics and has been widely used since the pioneering study on SiC fiber of Yajima et al. [2].

In general, polycarbosilane is synthesized by thermal decomposition of polydimethylsilane under high pressure in an autoclave [1]. Si radicals are formed in the initiation step of the reaction, and polycarbosilane is synthesized from polydimethylsilane by Kumada rearrangement [1]. Kumada rearrangement of polydimethylsilane to polycarbosilane has been mostly studied under thermal decomposition at high temperature. However, this method has operational problems such as the generation of gaseous by-products including CH_4, Me_3SiH, and SiH_4. The gaseous by-products create extremely high pressures, generally higher than 100 atm inside the autoclave, which render the operation inconvenient and unsafe.

In order overcome these inherent limitations of the thermal decomposition process, Yajima et al. [2] adopted a catalytic process, wherein polycarbosilane was synthesized at normal pressure after the addition of a small amount of polyborodimethylsiloxane as a catalyst. Kim et al. [3] also

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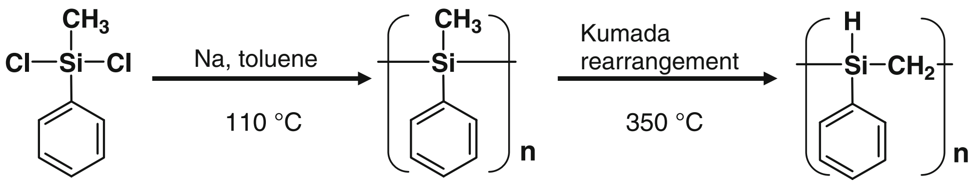

Fig. 1 Preparation process of polyphenylcarbosilane

attempted to synthesize polycarbosilane at low pressure by using zeolites as a catalyst such as ZSM-5, Zeolite A, and Zeolite Y as catalysts. Also, Hasegawa et al. [4] developed heterogeneous catalysts for this reaction such as $AlCl_3$, $MnCl_3$, $CrCl_3$, VCl_3, $TiCl_3$, and $GaCl_3$. However, the disadvantage of using the catalytic method for the preparation of polycarbosilane is the difficulty of catalyst separation, especially in the case of nano catalytic powder. Further contamination of the catalyst has deleterious effects on preceramic polymer properties.

In our study, a new method of synthesizing the preceramic polymer for SiC at low pressure is proposed; this method involves the thermal rearrangement of polymethylphenylsilane (Fig. 1). The thermal decomposition of polymethylphenylsilane at temperatures above 350 °C generates liquidus by-products such as phenylsilane, methylphenylsilane, and diphenylsilane. Therefore, synthesis of polyphenylcarbosilane from polymethylphenylsilane using an autoclave with a condenser attached generates pressures less than 20 atm during the reaction. Therefore, polyphenylcarbosilane can be synthesized under considerably milder conditions than those used for the synthesis the polycarbosilane. The prepared polyphenylcarbosilane and the by-products obtained during thermal conversion were characterized by ^{29}Si NMR, ^{13}C NMR, ^{1}H NMR, FT-IR, TG, XRD, GPC, and GC analysis to understand their properties and structures.

Experimental

Preparation of polymethylphenylsilane

Polymethylphenylsilane was synthesized through the reaction of methylphenyldichlorosilane with sodium metal in toluene solvent at 110 °C. Forty grams of metallic sodium was cut into small pieces and transferred into 100 ml toluene under an inert atmosphere. At 110 °C, after sodium had entirely dispersed into the toluene solvent, 100 g of methylphenyldichlorosilane was added dropwise and refluxed for 7 h. After the reaction, the unreacted sodium metal was removed by adding methanol. In order remove NaCl and lower molecular weight of polymethylphenylsilane, the solid product was washed thoroughly with deionized water and acetone. The final product of a white precipitate was dried under vacuum.

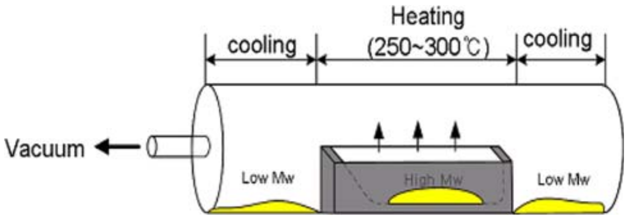

Fig. 2 Apparatus for purification of polyphenylcarbosilane

Preparation and purification of polyphenylcarbosilane

For the preparation of polyphenylcarbosilane, 20 g of polymethylphenylsilane was loaded into a 300 ml autoclave reaction vessel with an attached condenser. After purging the sample with nitrogen gas, the temperature was increased to 350 °C and kept for 6 h for Kumada rearrangement to occur. The temperature was raised to 430 °C, and the sample was kept for another 6 h to increase the molecular weight of the polyphenylcarbosilane. During synthesis, the pressure in the autoclave did exceed 20 atm.

After the reaction, a yellow viscous solid was obtained. The product was dissolved in cyclohexane, and the solution was filtered to remove the insoluble products. Thereafter, cyclohexane was evaporated using a rotary evaporator. A yellow–brown viscous product was obtained. Purification was done by heating under vacuum at 250 °C for 30 min to remove the low molecular weight products (Fig. 2). A yellow–brown solid remained in the middle of the furnace, and a clear liquid by-product accumulated at both the sides of the furnace.

Characterization

NMR spectra were obtained using a Varian Unity Inova spectrometer at 200 MHz (^{29}Si), 125 MHz (^{13}C), and 500 MHz (^{1}H). For ^{29}Si solid NMR spectroscopy, the CP/MAS technique was applied to obtain better signal-to-noise ratios. $CDCl_3$ was used as the solvent in ^{13}C NMR and ^{1}H NMR spectroscopy, and trimethylsilane (TMS) was used for the chemical shift reference. FT-IR spectra were obtained using an FTS-175C spectrometer in the range of 400–4000 cm^{-1}. FT-IR spectra were obtained using pellets made from the mixture of the solid sample and dried KBr. The molecular weight distribution of polyphenylcarbosilane was determined by a gel permeation chromatography

(Agilent) with a Styragel column using THF as the solvent. Polystyrene standard was used for calibration.

The sample was analyzed for silicon, carbon, and hydrogen. Carbon and hydrogen contents were determined using a thermal combustion method. About 1 mg of the sample was placed in a container and heated in an oxygen atmosphere to 1800 °C. The amounts of carbon and hydrogen were measured as CO_2 and H_2O, respectively using GC. In order determine the Si content, 10 mg of the sample was fused in a mixture of KOH and KNO_3 in a nickel crucible at 650 °C to release Si as a silicate, which was then detected by atomic adsorption [5]. Thermal decomposition of the polyphenylcarbosilane up to 1200 °C was measured by an STA-MS-Skimmer thermal gravimetric analysis (TGA) instrument under nitrogen atmosphere. XRD analysis of the powder after pyrolysis was carried out using a KFX-987228-SE MAC Science X-ray diffractometer with a Cu target ($K_\alpha = 1.54$ A).

In order to characterize the by-product, the crystal that precipitated out of the low molecular weight product, which is a clear solution, was coated with paratone oil and mounted onto a cryo-loop pin. The data for the small sized single crystals were collected with a Bruker APEX II detector with synchrotron radiation at beamline 11.3.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory. All data were collected at 150 K by using the w scan mode and integrated by using SAINT V7.34. Absorption correction was done with SADABS. The structures were determined by a direct method and refined with the SHELXS package [8, 9].

Results and discussion

West et al. [10] have synthesized polymethylphenylsilane (known as polysilastyrene) from the copolymerization of dimethyldichlorosilane and phenylmethyldichlorosilane. However, this polymer itself is not suitable as a SiC precursor, because it is unstable; while it decomposes at high temperatures, it generates gaseous by-products, including CH_4, Me_3SiH, and SiH_4. The gaseous by-products, especially silane gas, render the operation inconvenient and unsafe. In order obtain a more stable SiC precursor, West et al. [11] tried to crosslink this polymer by photolysis using ultraviolet radiation at 350 nm, and Krishnan et al. [12] crosslinked the polymer chemically by using divinylbenzene. Although the ceramic yield obtained by crosslinking increased approximately 40%, the polymer that was finally obtained was an insoluble white powder.

Preceramic polymers soluble in organic solvent can be coated on metal, ceramic, or graphite surfaces. Spinning, dip-coating, and spray-coating methods can be applied at room temperature; heat treatment after these coating techniques converts the polymer to amorphous ceramic, thereby, improving its anticorrosion and antioxidation properties [13, 14]. Thus, the SiC precursor used to prepare the SiC that is coated on various substrates must satisfy two requirements: (1) it should be soluble, and (2) it should have a high ceramic yield.

In order produce a soluble SiC precursor with high ceramic yield, we prepared polyphenylcarbosilane from polymethylphenylsilane by thermal rearrangement at 350°C for 6 h; thereafter, the temperature was raised to 430°C for 6 h to increase the molecular weight of the polyphenylcarbosilane (Fig. 1). Polymethylphenylsilane was prepared by dechlorination and polymerization of methylphenyldichlorosilane using sodium metal.

Formation of polymethylphenylsilane was confirmed by FT-IR and ^{29}Si solid NMR. Figure 3a shows the FT-IR spectrum of the prepared polymethylphenylsilane. The bands at around 2950 and 3066 cm^{-1} are assigned to C–H stretching vibration in the methyl group and phenyl group, respectively. The adsorptions seen at 1098 and 1248 cm^{-1} represent Si-phenyl stretching in phenyl group and Si–CH_3 deformation, respectively. All the other peaks are in agreement with those reported in the literature [15].

Figure 4 shows the ^{29}Si solid NMR spectra of polymethylphenylsilane. A singlet peak assigned to Si–Si appears at −37 ppm suggesting that all the Si species are in identical environments.

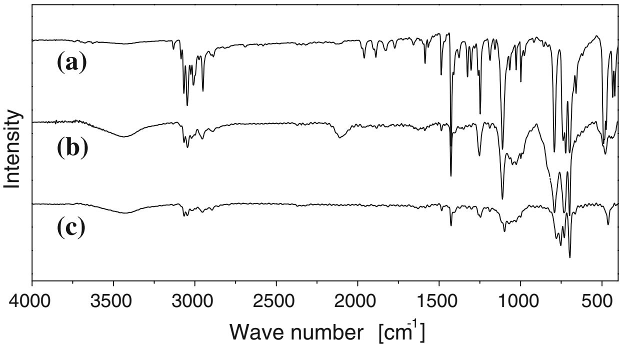

Fig. 3 FT-IR spectroscopy of (*a*) polymethylphenylsilane (*b*) polyphenylcarbosilane (*c*) methyltriphenylsilane

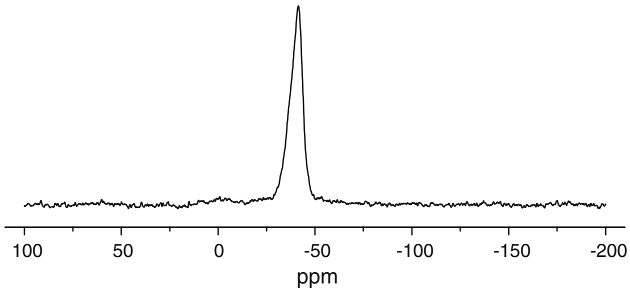

Fig. 4 ^{29}Si-NMR spectroscopy of polymethylphenylsilane

Characterization of polyphenylcarbosilane

The formation of polyphenylcarbosilane from polymethylphenylsilane is confirmed from the FT-IR spectrum. As shown in Fig. 3b, the FT-IR spectrum of the synthesized polyphenylcarbosilane exhibits vibration bands at around 1035 cm^{-1}, which is very strong; these bands are assigned to CH_2 bending vibration in the $Si–CH_2–Si$ group, indicating the formation of polyphenylcarbosilane. Except for the peaks assigned to Si-phenyl stretching (1098 cm^{-1}) and C–C stretching in phenyl (1486 cm^{-1}), the other peaks are in agreement with those of polycarbosilane reported in the literature [2]. The quantitative chemical analysis data are consistent with the formulation of $SiC_{9.4}H_{11.3}$ for polyphenylcarbosilane. The number average of the molecular weight (M_w) of the polyphenylcarbosilane determined by GPC is 2,500, and up to 30 wt% of polyphenylcarbosilane is easily soluble in organic solvents such as cyclohexane, THF, and xylene.

Figure 5 shows the ^{29}Si MAS NMR spectrum of as-synthesized polyphenylcarbosilane from polymethylphenylsilane. The ^{29}Si MAS NMR spectrum of the synthesized sample shows three split peaks at around 0, −17, and −38 ppm. In general, the peak at around 0 ppm is assigned to SiC_4. However, this peak is split as several peaks because the neighboring SiC_xSi_{4-x} species originated from the residual Si–Si bonds in the structure. The peak at −17 ppm is attributed to SiC_3H, and also, this peak is split as several peaks because of the residual $SiC_{x-1}HSi_{4-x}$ species in the structure. Figure 5 also exhibits small peaks at around −37 ppm corresponding to residual Si–Si species.

Figure 6 shows the ^1H NMR spectra of polylphenylcarbosilane. The peaks at 0.85, 1.28, and approximately 7.5 ppm are assigned to CH_3, CH_2, and the phenyl group, respectively. Figure 7 shows ^{13}C NMR spectra of polyphenylcarbosilane. The peaks at 1.28, 29.96, and approximately 130 ppm are assigned to CH_3, $CH_{2,}$ and the phenyl group, respectively. The ratio of CH_3, CH_2 and phenyl group content can be calculated from the integral value of the peaks from ^1H NMR and ^{13}C NMR spectra data. Figure 8 shows the proposed structure of polyphenylcarbosilane, as derived from NMR and GPC data.

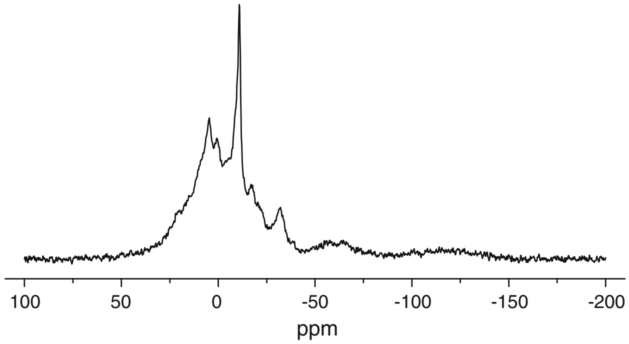

Fig. 5 ^{29}Si-NMR spectroscopy of polyphenylcarbosilane

The TGA curve reveals a large amount of weight loss up to 600 °C. This implies that the organic groups of the polyphenylcarbosilane undergo decomposition in this temperature range (Fig. 9). Weight loss of the polyphenylcarbosilane occurs rapidly above 400 °C under nitrogen atmosphere because of pyrolysis of polyphenylcarbosilane to SiC ceramic. However, the behavior of the TGA curve of polyphenylcarbosilane under an oxygen atmosphere was different from the TGA curve under nitrogen atmosphere because of the reaction that occurs between the oxygen and the residual silicon from polyphenylcarbosilane at around 300 °C.

When polyphenylcarbosilane was pyrolyzed at 1200 °C under N_2 atmosphere without prior curing, it became soft at around 100 °C, and finally, a black expanded foam product was obtained. This highly porous structure is foamed due to the loss of organic oligomer and gaseous by-product during pyrolysis. The ceramic yield calculated from TGA is about 60% under N_2 atmosphere. The pyrolysis residue obtained after heat treatment was crushed into a powdered form, and analyzed by XRD. Figure 10 shows the XRD results of the sample after heat treatment at 1200 °C for 1 h under N_2 atmosphere. The diffraction peak around 35°, 60°, and 73° corresponded to β-SiC. All the diffraction peaks were quite broad, which indicated that the sample was in the early stage of crystallization at the heat treatment temperatures. The chemical compositions of the ceramic residue were $SiC_{3.63}$ and $SiC_{3.45}$ after pyrolysis at 1200 and 1400 °C for 1 h under N_2 atmosphere, respectively.

Characterization of triphenylmethylsilane

From the GPC data (Fig. 11), it is understood that the synthesized sample is composed of a preceramic polymer of high molecular portion (Mw = ~2,500) and an unpolymerized monomer part (Mw = ~250).

The unpolymerized monomer is composed of triphenylmethylsilane, diphenyldimethylsilane, and diphenylmethylsilane, which could not polymerize because of their steric hindrance.

The synthesized sample was purified by heating under nitrogen atmosphere at 250 °C for 30 min to remove the low molecular weight products (Fig. 2). A yellow–brown solid which was identified as polyphenylcarbosilane remained in the middle of the furnace, and clear liquid was collected as a by-product at both the sides of the furnace. A single crystal can be grown from the clear liquid. The large crystals can be grown from the clear liquid, and the tiny ones on the wall of the vial have same crystal structure. Structure refinement was carried out in space group $P2_1/c$ with cell parameters a = 18.524(6) Å, b = 9.544(2) Å,

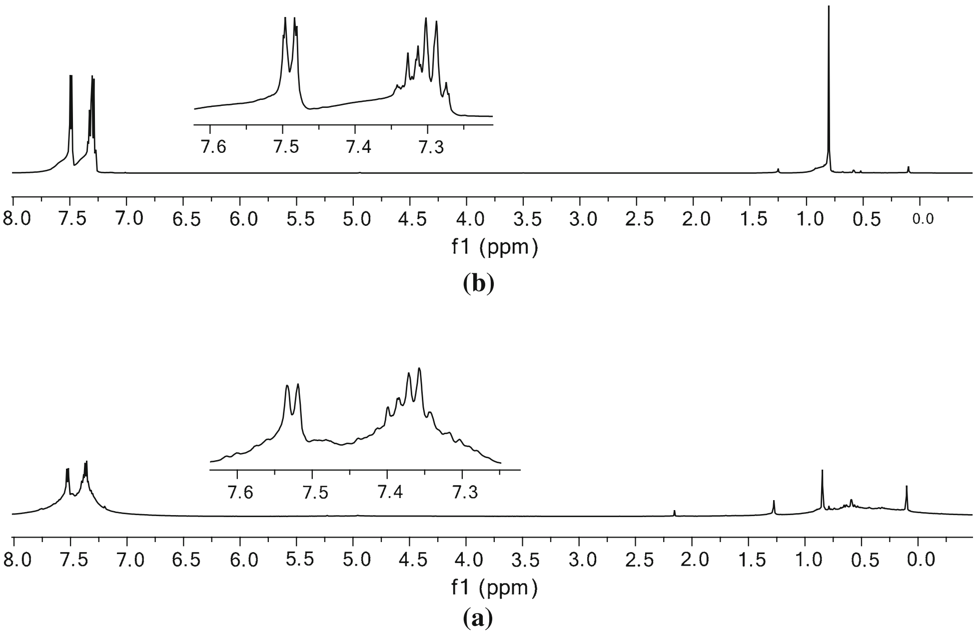

Fig. 6 ^{1}H NMR spectra of the polylphenylcarbosilane and methyltriphenylsilane. **a** H-NMR of Polyphenylcarbosilane (δ, $CDCl_3$, 300MHz) 7.53(*d*, 10H, Ph), 7.40(*t*, 5H, Ph), 7.86(*t*, 10H, Ph), 1.28(*s*, 2H, CH_2), 0.85(*s*, 4H, Me), 0.10(*s*, 3H, Me), **b** H-NMR of methyltriphenylsilane (δ, $CDCl_3$, 300MHz) 7.49(*d*, 6H, Ph), 7.33(*t*, 3H, Ph), 7.29(*t*, 6H, Ph), 0.80(*s*, 1H, Me)

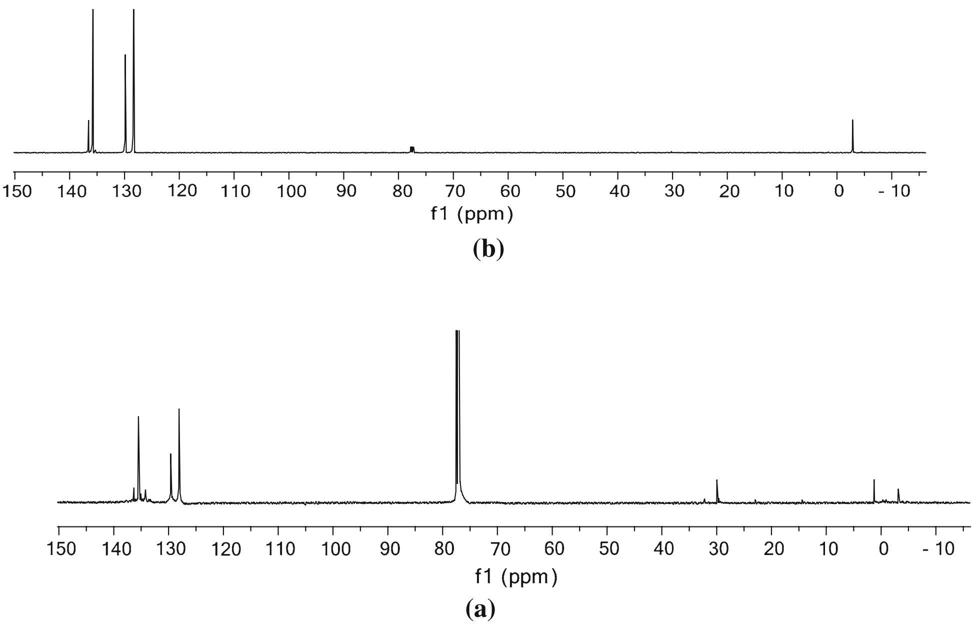

Fig. 7 ^{13}C NMR spectra of the methyltriphenylsilane and polyphenylcarbosilane. **a** C-NMR of Polyphenylcarbosilane (δ, $CDCl_3$, 300MHz) 136.39(*i*-Ph), 135.58(*o*-Ph), 129.70(*p*-Ph), 128.16(*m*-Ph), 29.96(CH_2), 1.28(Me), −3.14(Me), **b** C-NMR of methyltriphenylsilane (δ, $CDCl_3$, 300MHz) 136.54(*i*-Ph), 135.74(*o*-Ph), 129.86(*p*-Ph), 128.33(*m*-Ph), −2.86(Me)

and c = 18.346(2) Å, and $\beta = 107.80(1)°$. The building unit is a Si monomer with three phenyl rings and one methyl group. Its structure was reported in the literature [16].

As shown in Fig. 3, the FT-IR spectrum of triphenylmethylsilane is in agreement with that of triphenylmethylsilane purchased chemical reagent. The number average of the molecular weight (M_w) of the triphenylmethylsilane determined by GC is 277.

Figure 6b shows the ^{1}H NMR spectra of methyltriphenylsilane. The peaks at 0.80 and approximately 7.5 ppm are assigned to CH_3 and the phenyl group, respectively. Figure 7b shows the ^{13}C NMR spectra of methyltriphenylsilane. The peaks at −2.86 and approximately 130 ppm

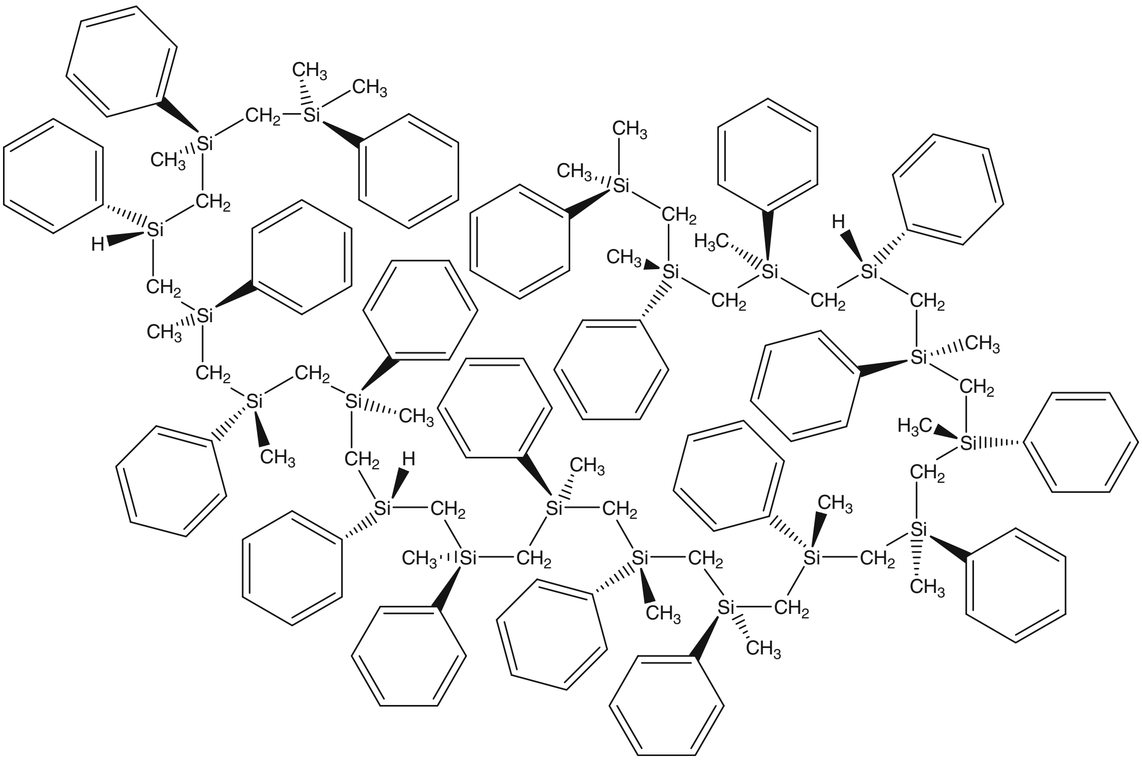

Fig. 8 Proposed structure of Polyphenylcarbosilane, as derived from NMR and GPC data

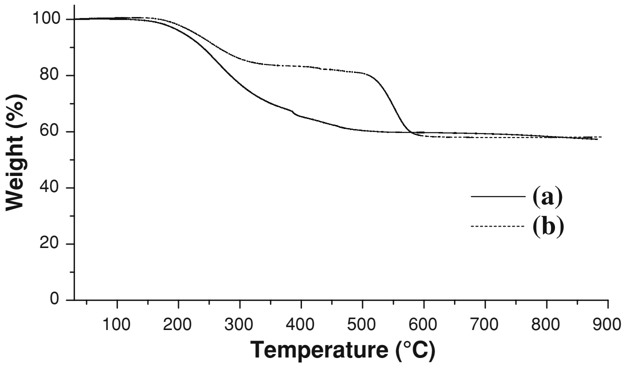

Fig. 9 TGA curve of Polycarbosilane under (*a*) N_2 (*b*) air atmosphere

are assigned to CH_3 and the phenyl group, respectively. From the integral value of the peaks from ^1H NMR and ^{13}C NMR spectra data, the ratio of the CH_3 and phenyl group can be calculated.

Conclusion

We reported the synthesis and characterization of polyphenylcarbosilane, which is a suitable precursor for SiC ceramic. Polyphenylcarbosilane can be synthesized under much milder conditions than those used for synthesizing polycarbosilane because of the liquidus type rather than volatile type thermal by-products generated. Purification was done by heating under vacuum at 250 °C for 30 min to remove the low molecular weight products. The number average of the molecular weight (M_w) of purified polyphenylcarbosilane is 2,500, and polyphenylcarbosilane is easily soluble in organic solvents. The diffraction peak of the pyrolysis residue at 1200 °C corresponds to *β*-SiC ceramic. The ceramic yield calculated from TGA is approximately 60%. The obtained polyphenylcarbosilane has a good solubility in organic solvent and is a suitable precursor for coating by a solution process.

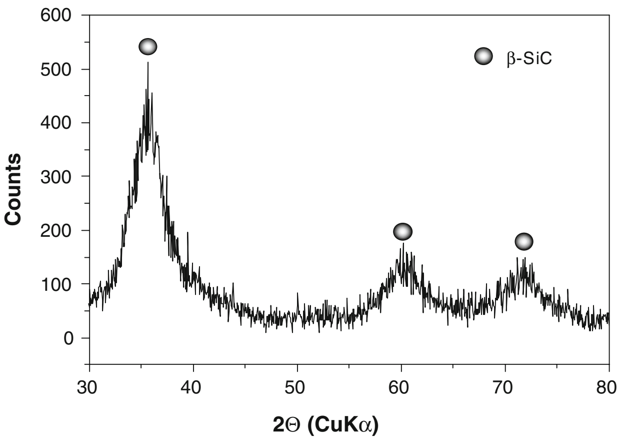

Fig. 10 X-ray diffraction pattern of crushed powder after heat treatment at 1200 °C for 1 h in N_2 atmosphere

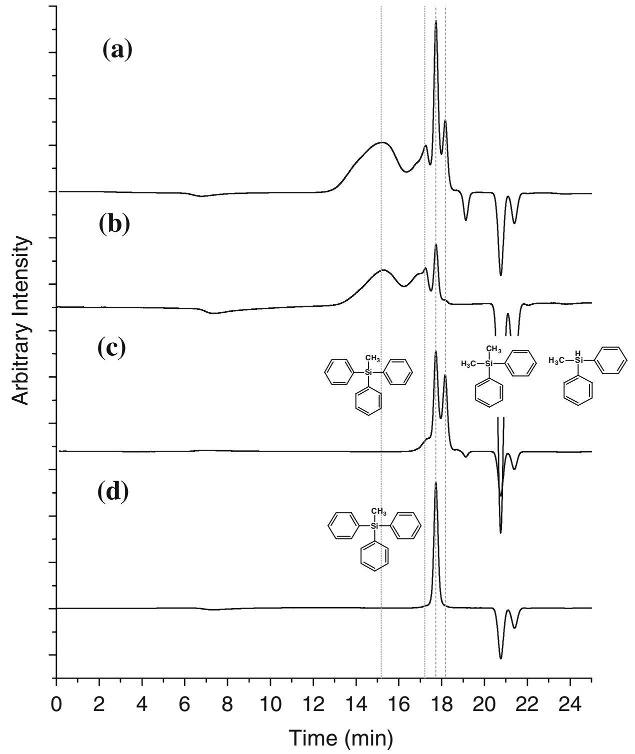

Fig. 11 GPC data of the samples (*a*) as synthesized polyphenylcarbosilane, (*b*) purified polyphenylcarbosilane, (*c*) clear liquid byproduct, and (*d*) triphenylmethylsilane

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