Synthesis and Properties of Liquid Polycarbosilanes with Hyperbranched Structures

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ABSTRACT: Liquid polycarbosilanes substituted by unsaturated groups were prepared by a one-pot synthesis with $Cl_2Si(CH_3)CH_2Cl$, Cl_3SiCH_2Cl, and $CH_2=CHCH_2Cl$ (or $HC\equiv CMgBr$) as the starting materials. The as-received polycarbosilanes were characterized by gel permeation chromatography, Fourier transform infrared spectroscopy, and nuclear magnetic resonance and were confirmed to have hyperbranched structures. The polymer yield, Si—H content, side reaction, unsaturated group content, and polymer structure are affected by the amount of the starting materials in feed. The thermal properties of the polycarbosilanes were investigated by thermogarvimetric analysis. The ceramic yield of allyhydridopolycarbosilane is about 60% and that of ethynylhydridopolycarbosilane is over 75%, indicating that the liquid polycarbosilanes have great potential to be promising precursors to SiC. Moreover, the compositions of the polycarbosilanes and the final ceramics can be tailored by controlling the amount of the starting materials. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 1611–1618, 2009

Key words: liquid polycarbosilane; precursor; hyperbranched polymer; SiC

INTRODUCTION

Silicon carbide (SiC) is currently receiving considerable attention for its high strength, low density, resistance to oxidation, corrosion, and thermal degradation at over 1000°C.[1] However, it is difficult to process by conventional forming and machining due to its extreme hardness and nonmelting properties. Preceramic polymeric precursors such as polycarbosilanes afford a potential solution to this problem as they allow the use of conventional processing operations before conversion to ceramic.[2,3] In the past 30 years, polycarbosilane has been studied extensively as a promising precursor to SiC because of its ideal processing and stoichiometry C/Si ratio.[1,4,5]

Yajima inaugurated a new era to synthesize the polymeric precursor of SiC. The Yajima polycarbosilane prepared by Wurtz-Fitting coupling reaction was widely used as a SiC precursor; however, it involves difficult chemistry and gives rise to low ceramic yield.[6] Compared with the Yajima polycarbosilane, liquid hyperbranched hydrodipolycarbosilanes (HBPCSs) can be regarded as excellent effective precursors especially for a matrix source because of their unique structures and favorable properties, such as lower viscosities, more favorable solubilities, and larger amounts of reactive end functional groups. HBPCS was originally synthesized by Greber through Grignard self-addition of Cl—SiR₂—CH₂MgCl, followed by the reduction of the residual chlorine groups with lithium aluminum hydride (LiAlH₄).[7] In an analogous route, Whitmarsh and Interrante[8] and Froehling[9] prepared the HBPCSs with the approximate formula $[SiH_{1.85}Et_{0.15}CH_2]_n$ and $[SiH(CH_3)CH_2]_n$ by Grignard coupling of chloromethyltrichlorosilane (Cl_3SiCH_2Cl) and chloromethylmethyldichlorosilane ($Cl_2Si(CH_3)CH_2Cl$) as the monomers, respectively. In addition, the modification of HBPCS has also been of particular interest. A commercial allyhydridopolycarbosilane (AHPCS), which is partially allyl-subsituted, was widely studied for its excellent properties as an SiC precursor.[10–13] Rushkin et al.[14] reported that AHPCS was obtained by the modification of HBPCS, which was carried out by bromination, and then followed by the reaction with RMgBr regeants to introduce the allyl groups onto the HBPCS chain. In our previous work, we successfully synthesized AHPCS by the one-pot synthesis with Cl_3SiCH_2Cl, $Cl_2Si(CH_3)CH_2Cl$, and allyl chloride ($CH_2=CHCH_2Cl$) as the starting materials.[15] Subsequently, the polymer-to-ceramic conversion of this AHPCS for SiC-based ceramics was further studied.[16] It indicates that the

hydrosilylation, dehydrocoupling, and polymerization crosslinking reactions between Si—H and C=C groups occurred at low temperatures, which mainly accounted for the high ceramic yield. Moreover, our work revealed that the AHPCS structure factors such as the branched structure, side chains, vinyl functionality, and molecular weight had significant influence on its final ceramic yield.[17] To obtain a stoichiometric SiC, we synthesized a novel ethynylhydridopolycarbosilane (EHPCS) and investigated its pyrolytic conversion to SiC including the pyrolysis behavior, structure evolution, and the crystallization behavior.[18]

As mentioned above, although our previous research involves the AHPCS and EHPCS, little work was focused on the synthesis procedure. In this study, a systematic research on the synthesis of liquid polycarbosilanes substituted by unsaturated groups is carried out. The thermal properties of the resultant polycarbosilanes and their compositions are investigated to further study the final ceramics.

EXPERIMENTAL

Materials

$Cl_2Si(CH_3)CH_2Cl$ and Cl_3SiCH_2Cl are industrial grade and distilled before use. $CH_2=CHCH_2Cl$ (analytical reagent grade) was obtained from Guoyao Shanghai Chemical Regents Center and used as received. Ethynylmagnesium bromide ($HC\equiv CMgBr$, 0.5 mol/L in THF) was obtained from Sigma-Aldrich. Magnesium (Mg, 99% purity) and lithium aluminum hydride ($LiAlH_4$, 99% purity) were stored in inert ambience. THF was distilled from a sodium benzophenone ketyl before use. All other reagents are analytical grade and used as received. All manipulations involving air and/or water sensitive compounds were performed under nitrogen atmosphere using standard Schlenk technology.[19]

Characterization

Gel permeation chromatography (GPC) measurements were performed at 35°C with THF as the eluant (1.0 mL/min) using an Agilent 1100 system. The spectrum was calibrated with narrow polystyrene standards. The Fourier transform infrared spectroscopy (FT-IR) spectra in the range of 4000–400 cm^{-1} were obtained with the KBr plates using Nicolet Avator 360. Nuclear magnetic resonance (NMR) experiments were carried out on a Bruker AV300 MHz spectrometer 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 $CDCl_3$ solution. The ^1H, ^{13}C, and ^{29}Si chemical shifts were all referred to (trime-

thylsilyl)silane. The degree of branching (DB) of the resultant polycarbosilanes can be calculated by means of the ^{29}Si NMR, according to the Holtel's research.[20] For the AB_3-type hyperbranched polymers, each dendritic group results in two new growth directions, each semidendritic group in one new growth direction. Since three linear units can be transformed into one dendritic unit and three semidendritic units can be transformed into two dendritic units.[20] In the case of the polycarbosilanes, they are obviously AB_3-type hyperbranched polymers. For the ^{29}Si NMR spectra of the polycarbosilanes, the $CSiH_3$, C_2SiH_2, C_3SiH, and SiC_4 units are labeled as Si^T, Si^L, Si^{SD}, and Si^D, which also represent "tail," "linear," "semidendritic," and "dentritic" units, respectively. An equation of the DB for the polycarbosilanes is obtained based on the Holtel's research:

$$DB = \frac{3(2A_D + A_{SD})}{2(3A_D + 2A_{SD} + A_L)} \qquad (1)$$

where A_L, A_{SD}, and A_D represent the fractions of Si^L, Si^{SD}, and Si^D obtained from the corresponding signals in the ^{29}Si NMR spectra. Thermal analysis of the cured AHPCS and EHPCS was carried out on a thermal gravimetric analysis (TGA) (Netzsch STA 409EP) in argon gas with a ramping rate of 10°C/min ranging from room temperature to 1200°C. Elemental analysis was carried out by Horiba Carbon/Sulfur Analyzer EMIA-320V for carbon element, Horiba Oxygen Nitrogen Analyzer EMGA-620W for oxygen element and Elemental Analyzer EA/MA1110 for hydrogen element.

Synthesis of AHPCS and EHPCS

A series of experiments of synthesizing liquid polycarbosilanes were designed with different molar ratios of $Cl_2Si(CH_3)CH_2Cl$ to Cl_3SiCH_2Cl as 1/0, 0/1, 1/2, 1/1, and 2/1, and different molar ratios of $CH_2=CHCH_2Cl$ (or $HC\equiv CMgBr$) to the overall amount of the two chlorosilanes as 0.1, 0.2, 0.4, and 0.6.

One typical synthesis of AHPCS was achieved with the following procedure: dry THF (200 mL), $Cl_2Si(CH_3)CH_2Cl$ (31.1 g, 0.19 mol), Cl_3SiCH_2Cl (71.7 g, 0.39 mol), and $CH_2=CHCH_2Cl$ (9.2 g, 0.12 mol) were added to a 2 L, three-neck flask with a reflux condenser, mechanical stirrer, and an argon inlet. Grignard reaction was carried out by adding 22.1 g Mg powder (0.92 mol, 30% excess) to the three-neck flask gradually under stirring in an argon atmosphere. The reaction started almost immediately and was controlled by occasional cooling of the three-neck flask in an ice-water bath. After the addition of magnesium powder was complete, this solution was heated under argon at 60°C for 12 h. The resulting

solution was reduced by 10.4 g LiAlH$_4$ (0.27 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 4M HCl (270 mL) and hexane (250 mL) in an ice bath. The organic phase was then separated and washed with dilute 1 M HCl. Then, the organic layer was dried over powder sodium sulfate under argon atmosphere for 2 h. The solvent was stripped off at 60°C and under vaccum to give a viscous, transparent, pale yellow oil with a yield of 65.3% (21.6 g).

The synthesis procedure of the EHPCS is similar to that of AHPCS, except that the starting materials are HC≡CMgBr, Cl$_3$SiCH$_2$Cl, and Cl$_2$Si(CH$_3$)CH$_2$Cl. One typical feed capacity was as follows: Cl$_2$Si(CH$_3$)CH$_2$Cl (16.4 g, 0.10 mol), Cl$_3$SiCH$_2$Cl (36.8 g, 0.20 mol), HC≡CMgBr /THF (60 mL, 0.03 mol), Mg powder (9.4 g, 0.39 mol, 30% excess), LiAlH$_4$ (5.8 g, 0.15 mol, 30% excess). A viscous, dark yellow oil was obtained 8.7 g about 56.6% in yield.

Curing and pyrolysis of polycarbosilanes

Thermal curing of the as-synthesized polycarbosilanes was carried out in a schlenk flash, using 1 g samples, placed in 170°C for 6 h at an argon atmosphere. The liquid AHPCS transformed into a compact pale orange rubbery solid, while the liquid EHPCS transformed into a hard dark brown rubbery solid. These solids were used both for TGA and for a macroscopic pyrolysis. In the macroscopic pyrolysis experiment, the cured sample was put in an alumina pan and heated up to 900°C at a rate of 5°C/min then was kept at this temperature for 60 min, in a glass silica tube under an argon atmosphere. Black, frothy chunks were obtained after the pyrolysis process.

RESULTS AND DISCUSSION

Characterization

Viscous liquid products were obtained via Grignard coupling of Cl$_3$SiCH$_2$Cl, Cl$_2$Si(CH$_3$)CH$_2$Cl, and CH$_2$=CHCH$_2$Cl (or HC≡CMgBr), followed by reduction with LiAlH$_4$. The weight-average molecular weight (M_w) and polydispersity index of the resulting polymers were measured by GPC. The M_w of AHPCS and EHPCS ranges from 800 to 1900 and 1600 to 9600, respectively. The polydispersity index of AHPCS varies from 1.6 to 3.5, while that of EHPCS from 2.7 to 17.8. The results reveal that the polymers have wide molecular distributions.

The reaction sequence of the polycarbosilane is shown in Scheme 1. According to the reported articles,[8,15,18] we suppose that the initial step in the polymerization is the formation of the intermediate R$_3$Si—CH$_2$MgCl (R= CH$_3$, Cl or another CH$_2$SiR$_3$ group) and CH$_2$=CHCH$_2$MgCl. The complicated branched structure is formed by the coupling reaction of the intermediate and CH$_2$=CHCH$_2$MgCl (or HC≡CMgBr) with remaining SiCl groups.

The as-synthesized polymers were characterized by means of FT-IR and NMR. As shown in Figure 1, the functional groups in polycarbosilane including Si—CH$_3$, Si—CH$_2$—Si, Si—H, and CH=CH$_2$ (or C≡CH) were identified by FT-IR, as follows: 3077 cm^{-1} (w, C—H stretch in CH=CH$_2$), 1630 cm^{-1} (w, C=C
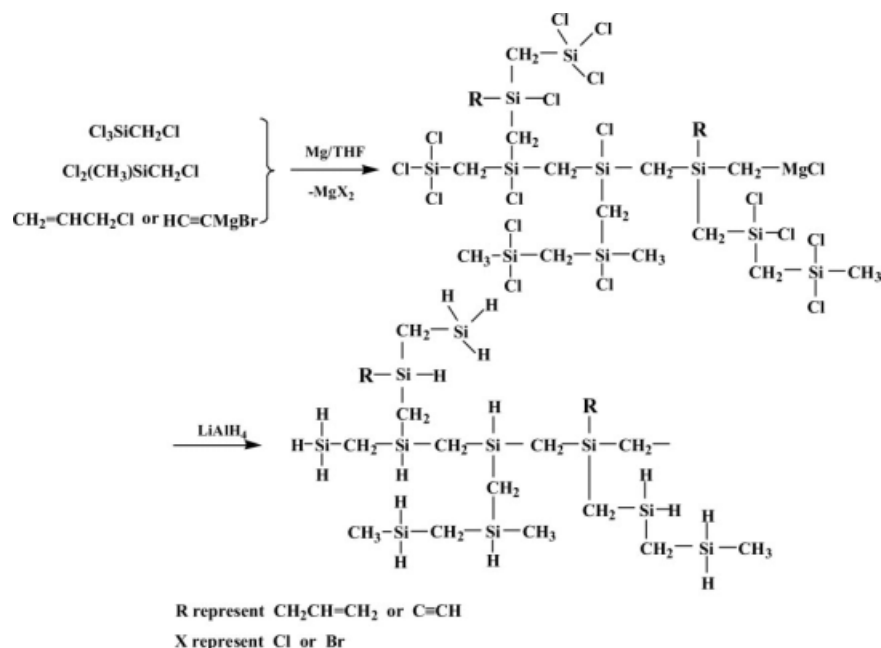
Scheme 1 Reaction sequence of AHPCS and EHPCS.
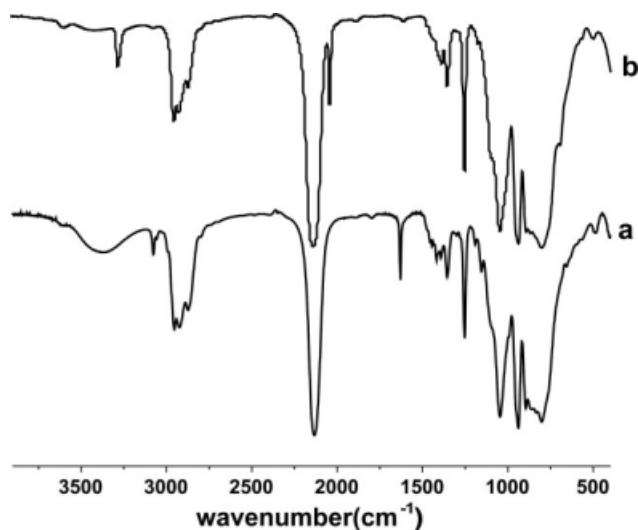
Figure 1 The FT-IR spectra of AHPCS (a) and EHPCS (b).

stretch in CH=CH$_2$), 3285 cm^{-1} (w, ≡C—H stretch), 2045 cm^{-1} (m, C≡C stretch), 2100 cm^{-1} (vs, Si—H stretch), 940 cm^{-1} (vs, Si—H bending), 2950, 2873 cm^{-1} (s, CH$_3$ stretch), 2920 cm^{-1} (s, CH$_2$ stretch), 1400, 1250 cm^{-1} (Si—CH$_3$ deformation), 1355 cm^{-1} (s, Si—CH$_2$—Si deformation), 1040 cm^{-1} (vs, Si—CH$_2$—Si stretch), 800 cm^{-1} (vs, Si—C stretch).[9,21]

The NMR result was taken to further confirm the structure of the liquid polycarbosilanes. In the ^{1}H NMR spectra (Fig. 2), the groups of signals around 0 ppm are assigned to the various the Si—CH$_3$ and Si—CH$_2$ functionalities.[8,9] The three peaks that ranged from 3.5 to 4.5 ppm are attributed to the proton absorption of Si—H$_x$ (x = 3, 2, or 1) groups. As reported previously,[8,15,22] chlorosilanes underwent a

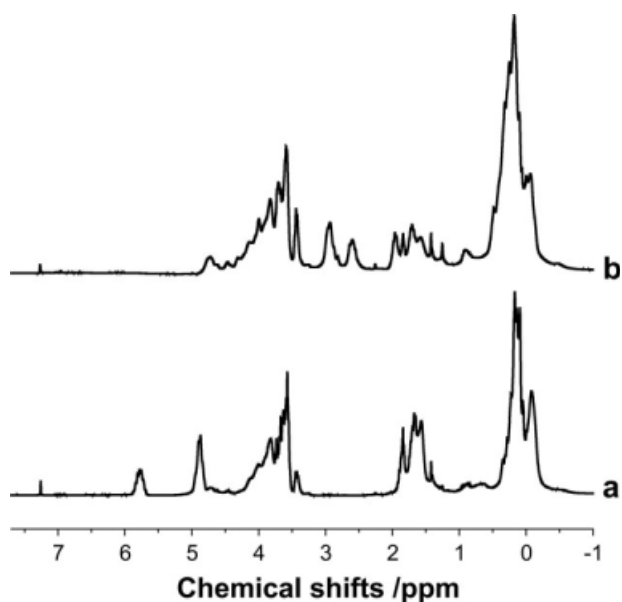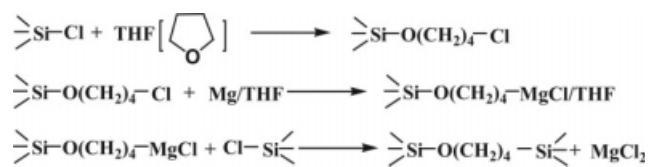**Scheme 2** Side reaction mechanism of THF and chlorosilanes.

side reaction with ether, resulting in the incorporation of methylene from THF into the polymer chain. The side reactions of THF and chlorosilanes are outlined in Scheme 2. It is supposed that Si—O(CH$_2$)$_4$—Si and Si—O(CH$_2$)$_4$—Cl segments were formed due to the side reaction. The multiplet ranged from 1.5 to 2 ppm is assigned to the methylene protons of SiOCH$_2$CH*$_2$CH*$_2$CH$_2$ segments derived from THF. The multiplets at about 1.9 and 3.4 ppm are assigned to the methylene protons of SiCH*$_2$Cl and SiOCH$_2$CH$_2$CH$_2$CH*$_2$Cl group, respectively, because the CH$_2$Cl group does not reduce as easily as SiCl.[8] Buried under Si—H$_x$ peaks, the absorption of methylene proton from SiOCH*$_2$CH$_2$CH$_2$CH$_2$ segments lies about 3.7 ppm. Moreover, the two multiples at 4.9 and 5.8 ppm are assigned to the protons of double bond, indicating that the allyl groups have been introduced to the side chain of the AHPCS. Compared with the AHPCS, the two multiples at 2.6 and 2.9 ppm are due to the proton of ethynyl, indicating that the ethynyl groups are attached to the EHPCS.

On the other hand, the molecular structure of the polymer was also characterized by ^{13}C NMR as presented in Figure 3. The complex multiplets from −15 to 8 ppm are assigned to Si—CH$_2$—Si chain due to the numerous environments around silicon element. The signal centered at 27 ppm is attributed to residual CH$_2$Cl end group that is not completely reduced by the LiAlH$_4$.[8] Groups of signals from 30 to 70 ppm are attributed to the methylene carbons
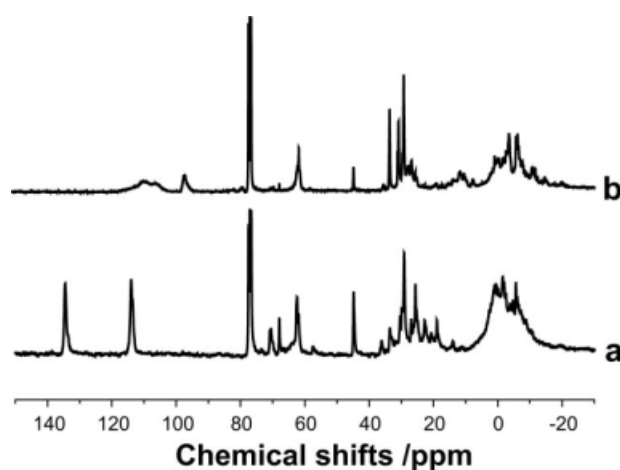

Figure 2 ^{1}H NMR spectra (CDCl$_3$) of AHPCS (a) and EHPCS (b).

Figure 3 ^{13}C NMR spectra (CDCl$_3$) of AHPCS (a) and EHPCS (b).

derived from THF.[15,22] In the ^{13}C NMR spectrum of AHPCS, the peaks at 114 and 134 ppm are attributed to double bond groups introduced into the polymer. And in that of EHPCS, signals at 97 and 110 ppm attributed to carbons from C≡C*H and *C≡CH, respectively, which proves the existence of the ethynyl groups.

The ^{29}Si NMR spectra of the two polycarbosilanes are shown in Figure 4. The signal at around −110 ppm is due to the silicon of sample tube. The multiplets from −55 to −65 ppm are assigned to the CSiH$_3$ groups. The peaks from −28 to −38 ppm are attributed to C$_2$SiH$_2$ units in the polymer main chain, whereas the peaks between −8 and −15 ppm presumably come from the C$_3$SiH units. The signal at about 5 ppm is due to the SiC$_4$ units. These tetracarbosilicon units, tricarbosilicon units, and monocarbosilicon are the further evidence of a branched structure.[8,14] In conclusion, the resultant polymers were confirmed as AHPCS and EHPCS by FT-IR and NMR, bearing active Si—H groups and unsaturated groups.

Synthesis

A series of hyperbranched polycarbosilanes substituted by allyl or ethynyl groups were synthesized. In our study, the influences of feed molar ratio on the polymer yield, Si—H content, side reaction, unsaturated group content, and polymer structure were investigated.

To investigate the influence of molar ratio of Cl$_2$Si(CH$_3$)CH$_2$Cl to Cl$_3$SiCH$_2$Cl on the polymer yield (Table I), the predetermined experiments were designed with different molar ratios of Cl$_2$Si(CH$_3$)CH$_2$Cl to Cl$_3$SiCH$_2$Cl as 1/0, 0/1, 1/2, 1/1, and 2/1, while keeping the molar ratios of CH$_2$=CHCH$_2$Cl (or HC≡CMgBr) to the overall amount of the two chloro-

TABLE I
Yields of AHPCS and EHPCS with Various Feed Molar Ratios of Cl$_2$Si(CH$_3$)CH$_2$Cl to Cl$_3$SiCH$_2$Cl

Molar ratio in feed (Cl$_2$Si(CH$_3$)CH$_2$Cl/ Cl$_3$SiCH$_2$Cl)	Polymer	Yield (%)	Polymer	Yield (%)
1/0	AHPCS-1	45.3	EHPCS-1	47.2
0/1	AHPCS-2	42.6	EHPCS-2	41.7
1/2	AHPCS-3	65.3	EHPCS-3	56.6
1/1	AHPCS-4	47.3	EHPCS-4	47.9
2/1	AHPCS-5	63.7	EHPCS-5	54.3

silanes as constant. Generally speaking, it would give a low yield with the starting chlorosilanes of Cl$_2$Si(CH$_3$)CH$_2$Cl or Cl$_3$SiCH$_2$Cl only. It is suggested that the copolymerization of Cl$_2$Si(CH$_3$)CH$_2$Cl, Cl$_3$SiCH$_2$Cl, and CH$_2$=CHCH$_2$Cl (or HC≡CMgBr) results in higher yield than that of Cl$_2$Si(CH$_3$)CH$_2$Cl (or Cl$_3$SiCH$_2$Cl) only and CH$_2$=CHCH$_2$Cl (or HC≡CMgBr) does. For both AHPCS and EHPCS, the yield reaches the highest with the ratio of Cl$_2$Si(CH$_3$)CH$_2$Cl to Cl$_3$SiCH$_2$Cl of 1/2.

It is revealed that the Si—H bond plays a key role to form a polymeric network through the hydrosilylation with the active groups such as Si—CH$_2$—CH=CH$_2$.[17,23] Therefore, the contents of Si—H in the AHPCS and EHPCS were investigated. As shown in Figure 5, the A (Si—H) represents the relative area integral of peaks assigned to Si—H$_x$ groups in ^{1}H NMR. Obviously, the A (Si—H) decreases with the increase in the amount of Cl$_2$Si(CH$_3$)CH$_2$Cl. According to the reaction sequence of AHPCS and EHPCS, the Si—H bonds were introduced by reduction of the Si—Cl bonds with LiAlH$_4$. Moreover, the content of the Si—Cl bonds in Cl$_2$Si(CH$_3$)CH$_2$Cl is lower than that in

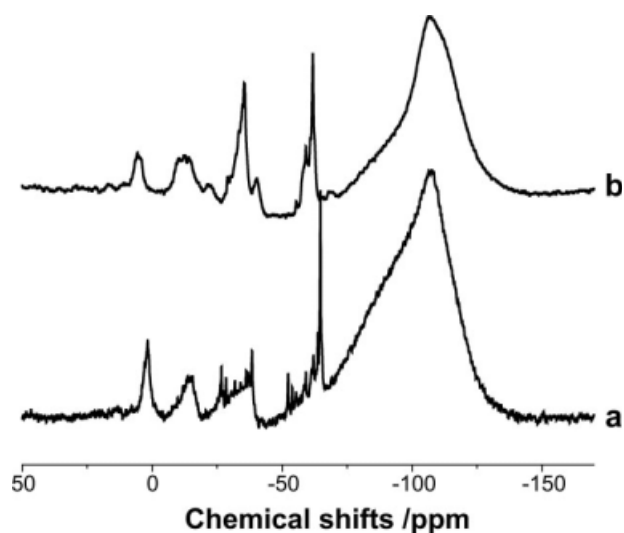**Figure 4** ^{29}Si NMR spectra (CDCl$_3$) of AHPCS (a) and EHPCS (b).
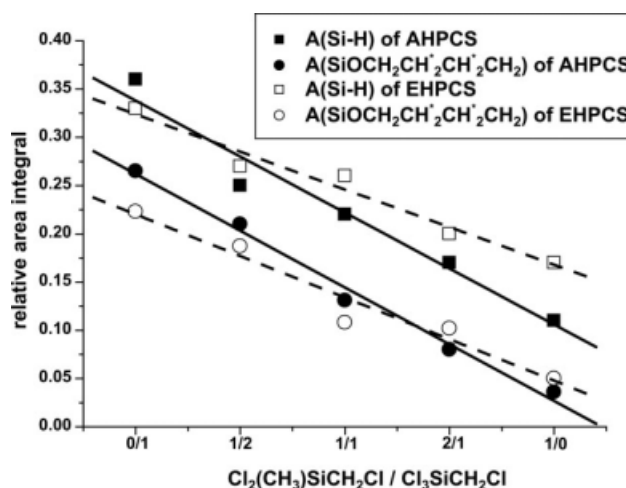
Figure 5 Relative area integrals of Si—H and SiOCH$_2$CH*$_2$CH*$_2$CH$_2$ in AHPCS and EHPCS with various feed molar ratios of Cl$_2$Si(CH$_3$)CH$_2$Cl to Cl$_3$SiCH$_2$Cl.
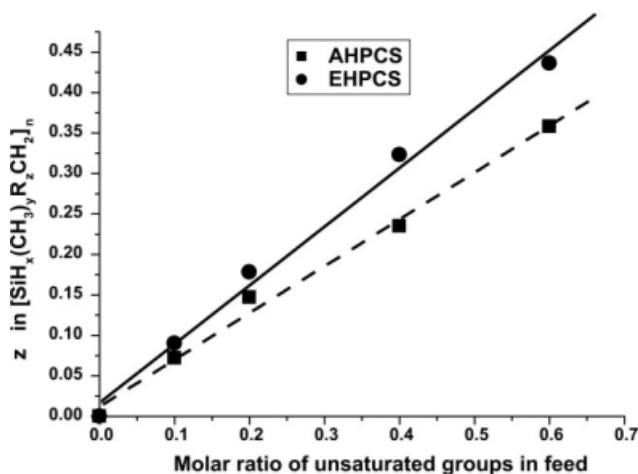
Figure 6 Value of Z in AHPCS and EHPCS with different feed molar ratios of unsaturated groups (Cl$_2$Si(CH$_3$)CH$_2$Cl/ Cl$_3$SiCH$_2$Cl = 1/2).

Cl$_3$SiCH$_2$Cl, which is responsible for the lower Si—H content with higher Cl$_2$Si(CH$_3$)CH$_2$Cl ratio in feed.

As mentioned above, the side reactions of THF and chlorosilanes occurred during the Grignard coupling, and the resultant Si—O(CH$_2$)$_4$—Si and Si—O(CH$_2$)$_4$ —Cl segments increase the content of oxygen in the final polycarbosilanes precursor, which is unexpected to obtain the high performance SiC ceramic with low oxygen. The contents of Si—O(CH$_2$)$_4$ units in the polymers were also determined by ^{1}H NMR (Fig. 5). Similarly, the A (SiOCH$_2$CH*$_2$CH*$_2$CH$_2$) represents the relative area integral of peaks assigned to the protons derived from SiOCH$_2$CH*$_2$CH*$_2$CH$_2$ units. The A (SiOCH$_2$CH*$_2$CH*$_2$CH$_2$) reduces with increase in the amount of Cl$_2$Si(CH$_3$)CH$_2$Cl, indicating that the side reaction can be significantly suppressed. It might be due to the reported experimental results that the side reaction of Cl$_3$SiCH$_2$Cl and ether took place while that of Cl$_2$Si(CH$_3$)CH$_2$Cl and THF was hardly observed.[8,9]

The content of unsaturated groups greatly influenced the crosslinking property and the ceramic yield of polycarbosilanes.[17] The influence of the amount of CH$_2$=CHCH$_2$Cl (or HC≡CMgBr), on the factual content of allyl or ethynyl groups, could not be neglected. The theoretical average formula of the as-synthesized polycarbosilane is taken as [SiH$_x$(CH$_3$)$_y$R$_z$CH$_2$]$_n$, where R represents the allyl or ethynyl group. The value of Z was calculated from ^{1}H NMR spectra of AHPCS and EHPCS, as shown in Figure 6. In the present study, the molar ratio of Cl$_2$Si(CH$_3$)CH$_2$Cl to Cl$_3$SiCH$_2$Cl was kept constant as 1/2 based on the finding that the yield reaches the highest with this ratio, and the molar ratio of unsaturated groups is for the molar ratio of unsaturated groups to the sum amount of the two chlorosilanes. The value of Z in the formula increases as the molar ratio of the unsatu-

TABLE II
Db of Polycarbosilanes with Various Molar Ratios of Starting Materials

Polymer	Molar ratio in feed (Cl$_2$Si(CH$_3$)CH$_2$Cl/ Cl$_3$SiCH$_2$Cl/CH$_2$=CHCH$_2$Cl)	DB
AHPCS-3	1/2/0.6	0.70
AHPCS-4	1/1/0.4	0.75
AHPCS-5	2/1/0.6	0.80
AHPCS-6	1/2/1.8	0.74
AHPCS-7	1/2/1.2	0.73
AHPCS-8	1/2/0.3	0.68

rated groups increases. Moreover, an approximately linear relationship is found between the Z and the molar ratio of the unsaturated groups in feed. Thus, the content of unsaturated groups could be readily controlled by varying the amount of CH$_2$=CHCH$_2$Cl (or HC≡CMgBr) in feed.

It was reported that the highly branched structure is criticial to a high final ceramic yield in our previous work.[16,17] As well known, the DB is an important parameter for a branched polymer. Therefore, the DB was determined by means of ^{29}Si NMR spectra, as mentioned in the Experimental section. In the ^{29}Si NMR spectra of the polycarbosilanes (Fig. 4), the CSiH$_3$, C$_2$SiH$_2$, C$_3$SiH, and SiC$_4$ units are labeled as Si^T, Si^L, Si^{SD}, and Si^D, which also represent "tail," "linear," "semidendritic," and "dentritic" units, respectively. The DB was calculated via the corresponding fractions of Si^L, Si^{SD}, and Si^D in the ^{29}Si NMR spectra, according to eq. (1). As exemplified in the AHPCS, the DBs are given in Table II. The DBs are 0.70, 0.75, and 0.80 for AHPCS-3, AHPCS-4, and AHPCS-5, respectively. It seems that the DB increases with the amount of Cl$_2$Si(CH$_3$)CH$_2$Cl increasing if the molar ratio of CH$_2$=CHCH$_2$Cl to the sum amount of the two chlorosilanes is kept constant. With the molar
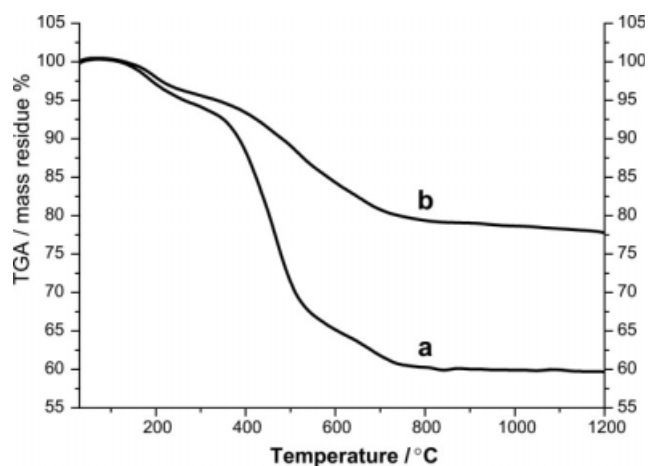

Figure 7 TGA curves of cured AHPCS-3 (a) and EHPCS-3 (b) at 170°C for 6 h.

TABLE III
Elemental Analysis for Polymers and Final Ceramics

Polymer	Molar ratio in feed[a]	Polymer composition		Ceramic composition	
		C/Si	Average formula	C/Si	Average formula
AHPCS-1	1/0/0.2	2.20	$SiC_{2.20}O_{0.16}H_{5.50}$	1.56	$SiC_{1.56}O_{0.23}H_{0.75}$
AHPCS-2	0/1/0.2	1.58	$SiC_{1.58}O_{0.18}H_{4.06}$	1.21	$SiC_{1.21}O_{0.27}H_{0.78}$
AHPCS-3	1/2/0.6	1.92	$SiC_{1.92}O_{0.16}H_{4.78}$	1.49	$SiC_{1.49}O_{0.24}H_{0.76}$
AHPCS-6	1/2/1.8	2.04	$SiC_{2.04}O_{0.18}H_{5.08}$	1.56	$SiC_{1.56}O_{0.27}H_{0.81}$
EHPCS-1	1/0/0.1	1.78	$SiC_{1.78}O_{0.14}H_{3.06}$	1.20	$SiC_{1.20}O_{0.24}H_{0.72}$
EHPCS-2	0/1/0.1	1.40	$SiC_{1.40}O_{0.21}H_{3.61}$	0.91	$SiC_{0.91}O_{0.21}H_{0.60}$
EHPCS-3	1/2/0.3	1.48	$SiC_{1.48}O_{0.15}H_{3.39}$	1.04	$SiC_{1.04}O_{0.18}H_{0.63}$
EHPCS-6	1/2/1.8	1.62	$SiC_{1.62}O_{0.21}H_{3.71}$	1.11	$SiC_{1.11}O_{0.19}H_{0.62}$

[a] Molar ratio denotes $Cl_2Si(CH_3)CH_2Cl/Cl_3SiCH_2Cl/CH_2=CHCH_2Cl$ for AHPCS and $Cl_2Si(CH_3)CH_2Cl/Cl_3SiCH_2Cl/HC\equiv CMgBr$ for EHPCS, respectively.

ratio of $Cl_2Si(CH_3)CH_2Cl$ to Cl_3SiCH_2Cl of 1/2, the DB is higher with more $CH_2=CHCH_2Cl$ used. In summary, the DB is relatively high for the AHPCS system. The results indicate that the as-synthesized polycarbosilanes are highly branched.

Thermal property

TGA was used to study thermal behavior of the two polycarbosilanes. It was reported by Froehling[9] that a previous crosslinking treatment before pyrolysis could improve the final ceramic yield of a branched polycarbosilane. The liquid AHPCS and EHPCS were both cured at 170°C for 6 h under argon atmosphere to gain compact yellow solids, and then the solids were used for TGA. According to the TGA curves (Fig. 7), the cured AHPCS lost 6 wt % weight while the cured EHPCS lost 4 wt % below 300°C, attributed to the vaporization of low molecular weight oligomers. From 300 to 800°C, the main weight losses are 34 and 16 wt % for the AHPCS and the EHPCS, respectively, indicating that the AHPCS undergoes weight loss more rapidly than the EHPCS does. It is suggested that the main weight losses might be due to the release of gaseous products such as methane and hydrogen during the polymer-to-ceramic conversion.[23] No obvious weight loss is observed in the range of 800–1200°C. It is considered that the polymer-to-ceramic conversion completes in this stage. In conclusion, the ceramic yield of AHPCS is about 60% and that of EHPCS is over 75%, suggesting that the liquid polycarbosilanes have great potential to be promising precursors to SiC.

Composition of polycarbosilanes and ceramics

To investigate the influence of reaction conditions on the composition of the two polycarbosilanes and their final ceramics, elemental analysis was performed and the results are given in Table III. A series of polycarbosilanes with different C/Si ratios ranging from 1.40 to 2.20 were synthesized through varying the amount of the starting materials. Subsequently, SiC ceramics were obtained after the cured AHPCS and EHPCS were heated at 5°C /min to 900°C and kept at this temperature for 60 min. The C/Si ratios of the final ceramics derived from AHPCS and EHPCS are in the range of 0.91 to 1.56. For the same AHPCS or EHPCS system, it is expected that the C/Si ratios of ceramics increase with the increase in those of polycarbosilanes. As a result, the compositions of final ceramics can be tailored by controlling the compositions of polycarbosilane precursors. It is generally accepted that SiC has quite different properties with different C/Si ratio. For example, Michio et al.[24] reported that the near stoichiometric SiC fiber had the highest density and highest elastic modulus among the fibers with C/Si ratios from 0.84 to 1.68. In this work, the C/Si ratios of ceramics derived from EHPCS are lower than those from AHPCS, because of less carbon contents introduced via the substitution of ethynyl groups than that of allyl groups. Therefore, it can be convenient to get near stoichiometric ceramics from the EHPCS through controlling feed ratios of the starting materials.

CONCLUSIONS

In this work, liquid polycarbosilanes substituted by unsaturated groups were prepared by the one-pot synthesis. The resultant polycarbosilanes were characterized by GPC, FT-IR, and NMR. The polymer yield, Si—H content, side reaction, unsaturated group content, and polymer structure are affected by the amount of the starting materials in feed. Moreover, the thermal properties of the polycarbosilanes were investigated by TGA. The compositions of polycarbosilanes and the final ceramics can be tailored by controlling the amount of the starting materials.

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