Synthesis of Polycarbosilane/Siloxane Hybrid Polymers and Their Pyrolytic Conversion to Silicon Oxycarbide Ceramics

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Polycarbosilane/siloxane hybrid polymers were synthesized by sol−gel processing of the cyclic organosilicon compound 1,1,3,3-tetraethoxy-1,3-disilacyclobutane (CBS) and the linear polymer poly(diethoxysilylenemethylene) (L-EPCS) derived from CBS by ring-opening polymerization. The structure of these polymers and their pyrolysis to silicon oxycarbide ceramics were investigated by elemental analysis, thermogravimetric analysis, FT-IR, and solid-state NMR spectroscopy. The results obtained indicate that the gel, obtained by hydrolysis/condensation of CBS with acid catalyst, underwent a Si−OH-induced, ring-opening reaction before the organic-to-inorganic conversion took place during pyrolysis, leading to the formation of intermolecular Si−O−Si(Me) linkages. In the case of the linear polycarbosilane (L-EPCS), sol−gel processing under acid catalysis leads to a gel of the type $[SiOCH_2]_x[Si(OR)O_{0.5}CH_2]_y$ (R = H or Et). ^{29}Si SSNMR spectra show that this gel, which has a nearly pure SiC_2O_2 microenvironment at the outset, converts into a silicon oxycarbide that contains a statistical distribution of the five possible $SiC_{4-x}O_x$ environments between 600 and 1000 °C. This rearrangement of the Si environments was attributed to redistribution reactions involving the exchange of Si−O and Si−C bonds during the latter stages of the pyrolysis, likely facilitated by an analogous Si−OH-induced attack on the $Si-CH_2-Si$ linkages. Both SSNMR and elemental analysis indicated that bridging CH_2 groups have the effect of increasing the carbidic carbon content and decreasing the free carbon content in the resulting silicon oxycarbide ceramics relative to polymers with pendent $Si-CH_3$ groups.

Introduction

Due to its excellent mechanical strength and toughness, its high-temperature stability (up to ca. 1500 °C),[1,2] its resistance to oxidation and corrosion, and its amorphous structure, silicon oxycarbide, a ceramic material having the general formula SiO_xC_y, is a good candidate for many applications[3,4] including protective coatings.[5,6] The increased chemical and thermomechanical stability of these glasses compared to silica is apparently due to the incorporation of carbon in place of oxygen in the silica structure, thereby leading to a “tightening” of the network structure.[7] However, due to its intrinsically low solubility, the incorporation of carbon by direct reaction with silica at high temperatures does not provide a very effective route to this ceramic material.

In the past two decades, there has been much interest in the synthesis of ceramics from polymeric precursors.[8,9] This new approach offers many potential advantages over conventional “heat and beat” ceramic synthesis and fabrication methods, such as low processing temperature, control of the ceramic composition and microstructure, high purity, and more facile production of complex shapes, especially fibers and coatings. In the case of SiO_xC_y, cross-linked organosiloxane polymers have been typically used as the precursors, resulting in substantial incorporation of carbidic carbon, invariably along with a considerable amount of free carbon.[10,11] This route to silicon oxycarbide typically involves the hydrolysis/condensation (sol−gel processing) of organically modified alkoxy silanes, having the general formula of $R'_nSi(OR)_{4-n}$, to form cross-linked organic/inorganic hybrid polymers and subsequent pyrolysis of the obtained polymers. This route is attractive as an approach to silicon oxycarbide glasses since it provides a relatively easy way to introduce carbon, as

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Si−C bonded organic substituents, into the gel structure and relatively low temperatures are required to convert these gels into SiO_xC_y glasses; moreover, the use of the sol−gel method offers distinct processability advantages over the ceramic approach.

There have been a number of studies on the synthesis of silicon oxycarbides from polymeric precursors[6,10,11] resulting in an improved understanding of the precursor-to-ceramic conversion process.[12] Zhang and Pantano studied the influence of the R′ group, starting from $R'Si(OR)_3$ precursors and found that only C directly bonded to Si can be retained in the glass structure; the other carbons evolved as hydrocarbon or formed a free carbon phase.[1] Corriu and co-workers used TGA-MS and solid-state NMR spectroscopy to follow the pyrolysis of the $RSiO_{1.5}$ system (R = CH_3, H) to silicon oxycarbides.[13] Thermally induced Si−H/Si−O or Si−C/Si−O redistribution reactions involving four-membered ring species were proposed to explain the structural changes observed by ^{29}Si NMR spectroscopy above ca. 400 °C, as well as the formation of the volatile silanes, hydrogen, and hydrocarbons evidenced by their TGA-MS studies. Similar redistribution mechanisms have been used by other workers to account for the evolution of the various initial polymer structures to the nearly statistical distribution of possible $SiO_{4-n}C_n$ sites typically observed for these silicon oxycarbide ceramics at 1000 °C.[11,14,15]

Babonneau, Sorarù, and co-workers investigated the formation of silicon oxycarbide glasses from sol−gel precursors which contained Si−H in addition to Si−CH_3 bonds. They postulated that, besides the redistribution reactions between the various Si−X bonds (X = H, C, or O), another mechanism is apparently operative above 400 °C, involving the reaction of Si−H bonds either with terminal Si−OH groups present in the gel or with water produced by condensation reactions between these terminal groups. All of these reactions lead to a decrease in the concentration of the terminal groups, Si−OH, Si−H, and eventually Si−CH_3, and thus to a more highly cross-linked network.[14]

Most of these previous studies employed polysiloxane precursors with terminal organic substituents on Si. The major problem in this case is the formation of a large percentage of free carbon in the final glass as well as excessive weight losses on pyrolysis (through the volatilization of silanes, siloxanes, and/or hydrocarbons). However, Babonneau and Sorarù have shown that, through reactions involving the elimination of H_2 and the formation of a Si−CH_2−Si bridge, a suitable choice of Si−CH_3 and Si−H functionalized silicon alkoxides can lead to an appreciable decrease in the free carbon content and to an almost pure silicon oxycarbide phase.[14] An alternative approach has employed organic/inorganic hybrid polymers with preformed −CH_2− bridges between silicons.[11,15] For example, a highly branched polycarbosilane of the type $[Cl_3SiCH_2]_x[Cl_2SiCH_2]_y[ClSiCH_2]_z[SiCH_2]_a$ was obtained by Mg-induced coupling of Cl_3SiCH_2Cl. This was initially reduced with $LiAlH_4$ to prepare a high-yield precursor to near-stoichiometric SiC.[16,17] However, it was also found that replacement of the Cl groups by alkoxide can be used to obtain a convenient, high-yield, sol−gel precursor (B-EPCS) to bulk SiO_xC_y ceramics[11,18] and coatings.[6] This highly branched polycarbosilane was found to give a SiO_xC_y product with the maximal carbidic content possible for a precursor that initially contained one oxygen per Si.[11]

An analogous linear polycarbosilane, $[Si(OEt)_2CH_2]_n$ (L-EPCS), was obtained by the ring-opening polymerization of the cyclic carbosilane monomer 1,1,3,3-tetraethoxy-1,3-disilacyclobutane, $[Si(OEt)_2CH_2]_2$ (CBS).[19,20,21] As is the case for the branched polymer (B-EPCS), both L-EPCS and the CBS monomer used to obtain it have the same C/Si ratio as does methylsilsesquioxane (MTES), but in place of the pendent CH_3 groups in methylsilsesquioxane, these potential SiO_xC_y precursors contain their carbon in the form of bridging Si−CH_2−Si groups.

In most of these prior studies of SiO_xC_y precursor systems, the detailed characterization of the polymers and the conversion process were limited by the complexity of the SiO_xC_y precursor system under investigation. Thus, in the case of the branched polycarbosilane B-EPCS,[11] after hydrolysis and condensation to form a "$[Si(O)CH_2]$" gel, we are starting with a system that already has a distribution of M, D, and T Si environments. The current paper now extends these studies of Si−CH_2−Si bridged precursors to include the linear polymer L-EPCS and its cyclic precursor CBS, both of which have only a $(RO)_2Si(CH_2)_2$ (D) silicon environment at the outset.

Experimental Section

Preparation of the Carbosilanes. The linear poly(diethoxysilylenemethylene) (L-EPCS) was synthesized by ring-opening polymerization of 1,1,3,3-tetraethoxy-1,3-disilacyclobutane (CBS) with Karsted's catalyst in a manner similar to that described previously for other poly(silylenemethylenes).[20,21] The preparation of 1,1,3,3-tetraethoxy-1,3-disilacyclobutane has been described in detail elsewhere.[6,20]

Preparation of the Gels. CBS or L-EPCS was converted to an inorganic/organic network polymer by the usual sol−gel method, with an acid(HCl) catalyst. CBS or L-EPCS was dissolved in ethanol (molar ratio of 4 to Si) at ca. 50 °C. Then H_2O (molar ratio of 4 to Si, in the form of 1 M HCl aqueous solution) was introduced. In the case of CBS, the solution gelled in several minutes; the L-EPCS solution gelled in about 10−20 min. The gelled solution was aged overnight (ca. 16 h) at 50−60 °C. The solvents were then stripped off and the gel from CBS was dried either in an oven at ca. 160 °C or under vacuum at ca. 50 °C for at least 6 h. The gel from L-EPCS was dried under vacuum at 50−60 °C for at least 6 h. A white solid was obtained. The hydrolysis/condensation of MTES was conducted under the same conditions for purposes of comparison.

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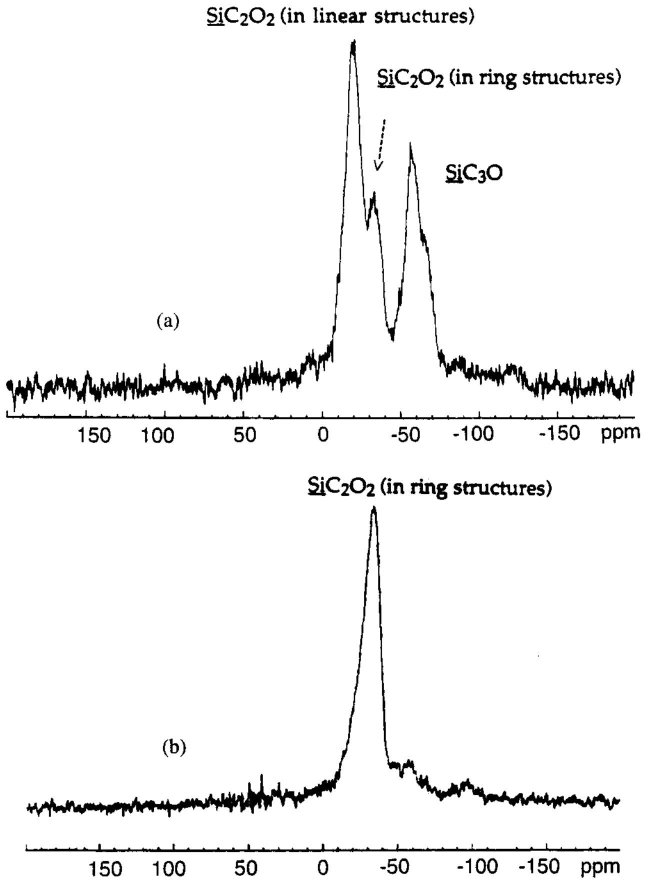


Figure 1. ^{29}Si SSNMR spectra of the CBS gel: (a) dried at 160 °C; (b) vacuum-dried at 50 °C.

For example, in the L-EPCS case, 1.261 g of polymer (9.55×10^{-3} mol) was dissolved in 1.76 g ethanol (0.038 mol) and stirred at ca. 50 °C for ca. 30 min, and then 0.68 g of water (0.038 mol, in the form of 1 M HCl aqueous solution) was introduced. The gelled solution was aged overnight and was dried under vacuum at 50–60 °C for at least 6 h. About 0.5 g of white solid was obtained. The gel yield is ca. 90%.

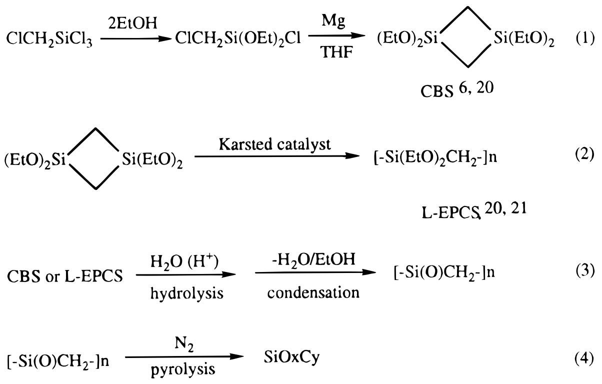
Pyrolyses were conducted in a temperature-programmed CM high-temperature furnace under nitrogen at atmosphere pressure with a N_2 flow rate of ca. 25 cm^3/min and a heating rate of 5 °C/min. The sample was placed in a molybdenum boat and was transferred into an airtight high-temperature furnace tube. The sample was flushed with N_2 for ca. 20 min before the heating was started. At various temperatures the furnace tube was taken out and air cooled to room temperature while the sample was still under N_2 flow. A certain amount of sample was taken out for elemental analysis and solid-state NMR and IR studies. The remaining sample was put back into the furnace tube and flushed with N_2 for 20 min before being put back into the furnace and heated to the next temperature stage.

Measurements. Elemental analyses were performed by either Galbraith Laboratories Inc. or Leco Corp. TGA studies were carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 5 °C/min under N_2. IR spectra were obtained by using a Perkin-Elmer 1800 Fourier transform infrared spectrometer. The solid samples were first ground to a fine powder (in air) by using a mortar and pestle, followed by mixing with KBr, and then pressed into pellets for IR transmission studies. Solid-state NMR spectra were recorded on a Chemagnetics CMX-360 SSNMR spectrometer for the L-EPCS samples and a MSL300 Bruker spectrometer for the CBS samples. The cross-polarization magic angle spinning technique (CP-MAS) was used to record ^{13}C NMR spectra with a contact time of 2 or 3 ms, pulse delay of 6 s, spinning speed of 4 kHz. Single-pulse experiments were used for ^{29}Si NMR spectra with pulse widths of 2 μs ($\theta = 30°$), pulse delays of 60 s, and 200–1000 acquisitions. Peaks are labeled with the usual C, M_n, D_n, T_n, and Q_n notation.[11] C, M, D, T, and Q respectively refer to $SiC_{4-x}O_x$ units with $x = 0$, 1, 2, 3, or 4, and n is the number of bridging O atoms surrounding Si. Quantitative analysis of ^{29}Si NMR spectra is difficult due to the long relaxation times. Short pulse widths and relatively long recycle delays were used to try to overcome this problem. Due to the high number of scans necessary to get good signal/noise ratios, it was not possible to measure T_1 relaxation times in a reasonable time period. One experiment was run on the gel obtained by hydrolysis/condensation of a highly branched methoxy-substituted polycarbosilane (B-MPCS), with a recycle delay of 120 s and produced no significant differences. As is generally done in this field,[11] it was assumed in this study that the NMR parameters used allow a level of quantitative accuracy sufficient to indicate the general trend in the evolution of the Si sites during pyrolysis.

X-ray diffraction of solid samples were obtained on a Philips PW 1710 automated powder diffraction instrument with Cu Kα radiation equipped with a monochromator in the exit beam. Usually, the scanning angle employed was from 10° to 80° 2θ. The peak data were collected with an IBM-PC interfaced to the XRD spectrometer and plotted later.

Results and Discussion

The reactions involved in the synthesis of the hybrid carbosilane/siloxane gels derived from the cyclic carbosilane (CBS) and their pyrolytic conversion to SiO_xC_y are as follows:



Two rather different $[Si(O)CH_2]_n$ gels and SiO_xC_y products were obtained from reaction 3, depending whether ring-opening polymerization is conducted prior to sol–gel processing, which leads to a linear polymer with pendent (hydrolyzable) alkoxy groups (L-EPCS), or if the cyclic carbosilane is used directly as the sol–gel precursor (CBS).

CBS System. *1. Characterization of the CBS Gel.* The hydrolysis/condensation of CBS was found to proceed quite rapidly in comparison with that of the linear polymer, L-EPCS, and also relative to methylsilsesquioxysiloxane (MTES). Whereas the CBS sample usually gelled within minutes, the gelation of L-EPCS took a little longer—about 10~20 min—and MTES was found to take at least several hours when the same conditions were employed for the hydrolysis and condensation (acid hydrolysis, excess H_2O, same temperature range). This could be due to the expected slower diffusion of the polymer species in solution, thereby decreasing the rate of condensation relative to the CBS species. Also, although CBS is monomeric like MTES, it has two silicon centers per molecule vs one for MTES. Since the rates of hydrolysis and condensation should depend on the effective concentration of Si centers, an enhancement of these rates for CBS, relative to MTES, would

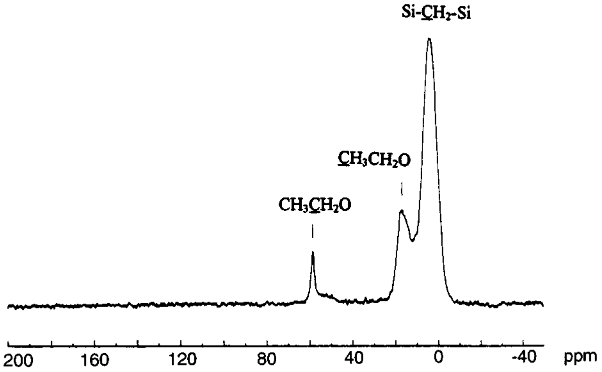


Figure 2. ^{13}C SSNMR spectrum of the CBS gel dried at 160 °C.

also be expected. Moreover, in the CBS compound, the silicon in the ring may be more susceptible to hydrolysis, because rehybridization may make it more susceptible to an S_N2 hydrolysis mechanism or because pentacoordination may actually relieve ring strain. The ring strain of the disilacyclobutane ring causes the Si atoms to be more electropositive than the Si atoms in MTES. This was indicated by the chemical shifts of the Si atoms in the ^{29}Si NMR spectra. The chemical shift of −20.4 ppm for the Si in CBS is much higher than the −45.0 ppm for the Si in MTES. The more electropositive silicon atoms would also be expected to lead to higher hydrolysis and condensation rates.[22]

The SSNMR characterization of the gel from CBS obtained by hydrolysis/condensation indicated that the four-membered rings have partially opened after the gel was dried at 160 °C. In the ^{29}Si NMR spectrum of the dried gel shown in Figure 1a, besides the expected D units (−35 ppm) arising from Si in a strained ring structure, there were significant amounts of T units (−60 ppm) and D units (−22 ppm) in linear $Si-CH_2-Si$ structures.[23,24] The ^{13}C SSNMR spectrum (Figure 2) confirmed these changes: there is one major peak that is attributed to bridging CH_2 (3 ppm) with a shoulder at lower field that is attributed to terminal CH_3. In addition, there are peaks attributable to residual $-OCH_2CH_3$ groups, as indicated by the peak at ca. 59 ppm, which is assigned to OCH_2CH_3.[24]

To compare these results with that of the CBS gel prior to being thermally dried, another sol−gel processing experiment was carried out. Instead of being dried in air at 160 °C, the gel was dried in vacuum at 50 °C for 6 h. The ^{29}Si NMR spectrum of this gel (Figure 1b) indicates that some ring opening occurred during the sol−gel process by the small amount of T units (−60 ppm) and linear D units (the shoulder at −22 ppm) observed. However, the major proportion of the CBS rings have not opened under these reaction conditions.

It is believed that the silanol groups that formed during the sol−gel process played an important role in the ring opening reaction. The proposed mechanism is shown in Scheme 1. During the ring-opening process, the two D units in the ring are converted into linear D and T units.

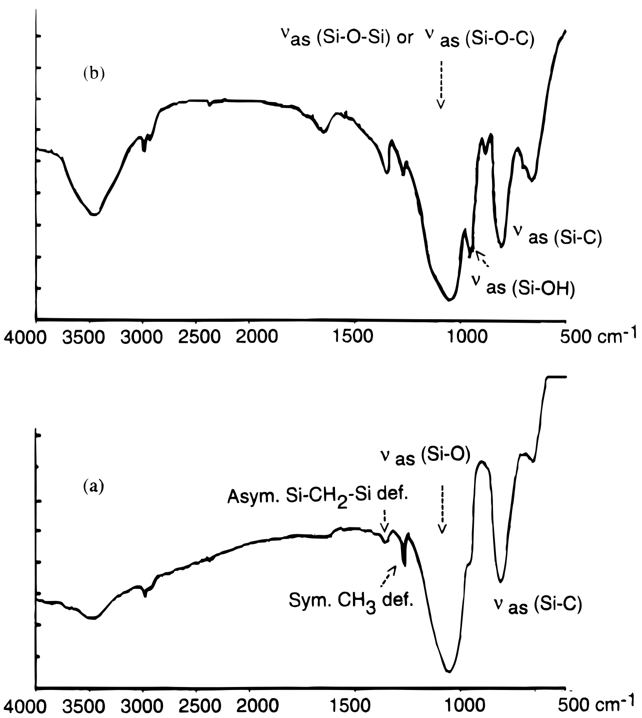
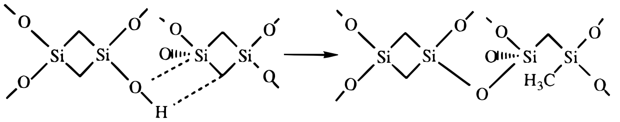


Figure 3. FTIR spectra of the CBS gel: (a) dried at 160 °C; (b) vacuum-dried at 50 °C.

Scheme 1. Proposed Si−OH-Induced Si−C Cleavage Process for the CBS Gel



The FTIR spectrum of the vacuum-dried (at 50 °C) CBS gel (Figure 3b) showed an intense absorption band at about 900 cm^{-1}, attributable to Si-OH stretching. This peak was considerably reduced in intensity in the IR spectrum of the thermally (160 °C) dried gel (Figure 3a). The loss of these groups could be caused by the ring-opening process shown above or by condensation between silanol groups:

$$-\text{Si}-\text{OH} + \text{HO}-\text{Si}- \rightarrow -\text{Si}-\text{O}-\text{Si}- + H_2O$$

2. Conversion from the CBS Gel to Silicon Oxycarbide. In the TGA trace of the CBS gel under N_2 up to 1000 °C, three regions of weight loss can be distinguished. The first weight loss at around 200 °C is attributed to the loss of solvent and water. The other two stages are attributed to the completion of the condensation process and the decomposition process, respectively.[11] Overall, the polymer gave a ca. 91% ceramic yield. This is significantly higher than what is exhibited by MTES (ca. 80%).[6]

A ^{29}Si SSNMR study of the pyrolysis process (Figure 4) shows that the CBS ring-opening process is completed by ca. 600 °C. At this point, the ^{29}Si SSNMR spectrum consists of only two peaks assigned to D (−23 ppm) and T (−66 ppm) units. Between 600 and 1000 °C, dramatic structural changes occur, and the ceramic obtained at 1000 °C contains at least four of the five possible Si

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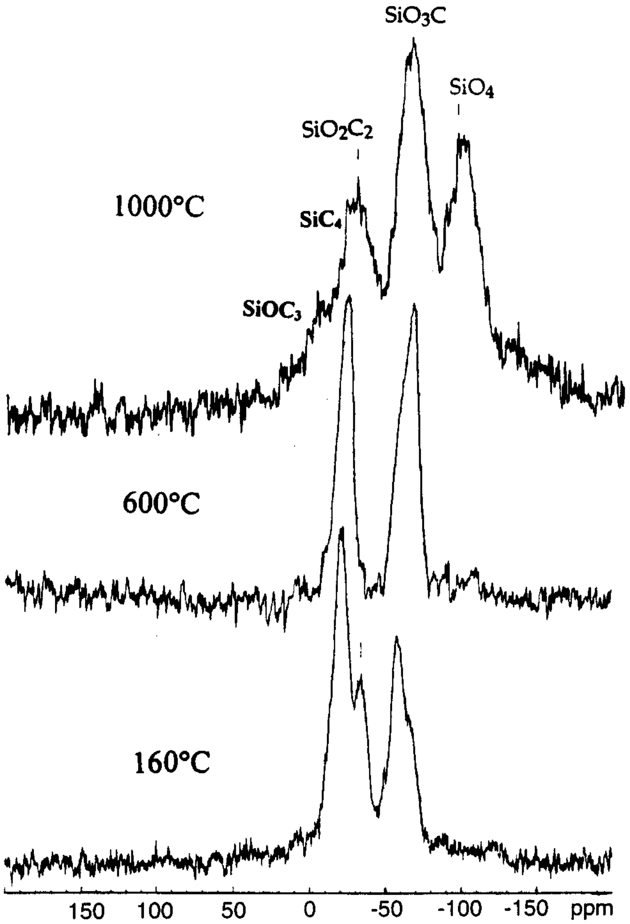

Figure 4. ^{29}Si SSNMR spectra of the CBS gel after being pyrolyzed to different temperatures.

structural units, C, M, D, T, and Q. The reformation of the environments of the silicon atoms may be accounted for by the occurrence of redistribution reactions involving the Si–O and Si–C bonds, which typically starts at ~500 °C and reaches a metastable equilibrium state at ca. 900 °C.[15]

Figure 5 shows the changes in the FTIR spectra during the pyrolysis. There was no major change when the gel was heated to 600 °C, although the ring-opening reaction is completed in this temperature range. From 600 to 1000 °C, the conversion from an organic/inorganic hybrid structure to an inorganic ceramic occurs. Thus, the organic group absorptions have totally disappeared by 1000 °C. The spectrum showed two major peaks due to the inorganic structure: one at 1100 cm^{-1} attributed to Si–O–Si, another at 800 cm^{-1} assigned to Si–C. The peak at 1920 cm^{-1} has been reported as being due to free carbon and the other peaks at 1610 and 3500 cm^{-1} may be due to absorbed water or the result of partial carbothermal reduction of the Si–O bond, coincident with the formation of Si–OH and Si–H bonds, at >800 °C.[25] The evidence for this includes the appearance of a weak Si–H stretching band at 2100 cm^{-1} and the reappearance of the nonbridging Si–OH stretch at ~900 cm^{-1} in the 1000 °C spectrum, which is not seen at 800 °C.

3. Structure of the Ceramic Obtained from CBS Gel. The structure of the ceramic obtained at 1000 °C was analyzed by SSNMR spectroscopy and elemental analysis. From the ^{29}Si SSNMR spectrum, we can obtain the percentages of C, M, D, T, Q units by deconvolution and integration. The results are listed in Table 1. In this table, we also include the results for the B-EPCS, MTES, and L-EPCS systems from previous reports for comparison.

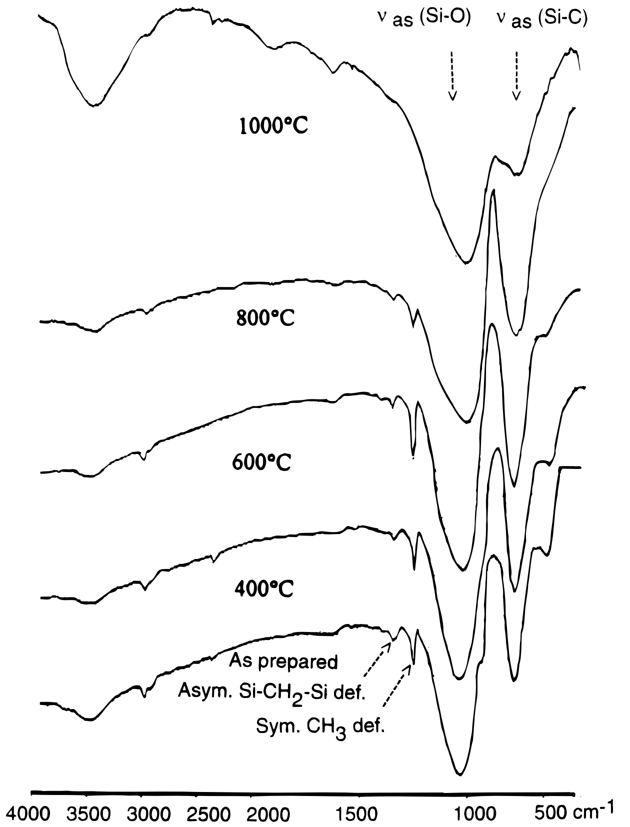

Figure 5. FTIR spectra of the CBS gel after being pyrolyzed to different temperatures.

The ratio of Si–C bonds/Si atoms reflects the amount of carbidic carbon content in the ceramic. For the CBS gel, during pyrolysis, ring-opening reactions, presumably initiated by nearby Si–OH groups, were evidenced, leading to the formation of dangling CH_3 groups and an average "$SiCH_2Si(O)CH_3$" formula. This is presumably the origin of the higher O/Si ratio and lower Si–C bonds/Si ratio observed in this case relative to that of the B-EPCS polymer. Thus, the Si–C bonds/Si ratio observed in this case is less than that obtained from the B-EPCS polymer but is higher than that obtained from MTES which has all of its CH_3 groups as pendent groups.

4. Properties of the Silicon Oxycarbide Ceramic Obtained from the CBS Gel. The resulting oxycarbide ceramic shows no significant weight loss in air up to at least 1000 °C. An examination of the TGA curve in detail shows that there is a weight gain at ca. 400–500 °C which is presumably due to surface oxidation, and a slight weight loss between 500 and 700 °C which is attributed to the loss of excess carbon near the surface. The early surface oxidation of the ceramic presumably prevents the further access of air to the free carbon inside the ceramic.

The 1000 °C product has an amorphous structure. When the temperature was raised to 1800 °C, the silicon oxycarbide structure changed to a SiC crystalline struc-

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Table 1. Chemical Analysis and ^{29}Si NMR Data of Ceramics from Different Gels

		MTES[11]	B-EPCS[11]	CBS	L-EPCS[25]
chemical analysis	Si, %	44.29	45.41	51.9	49.42
	C, %	11.74	17.31	17.4	15.25
	formula	$SiO^{a}_{1.74}C_{0.62}$	$SiO^{a}_{1.44}C_{0.89}$	$Si^{a}O_{1.04}C_{0.78}$	$SiO^{a}_{1.25}C_{0.72}$
	free carbon, %		68.5	38.5	47.9
NMR data	%Q units	39.1	23.4	29.0	14.36
	%T units	37.6	32.2	41.0	39.65
	%D units	18.4	31.6	23.0	36.63
	%M units		2.8		5.88
	%C units	5.0	10.1	7.0	3.49
	O/Si ratio	1.44	1.28	1.42	1.28
	Si−C bonds/Si	0.94	1.44	1.15	1.44

[a] Calculated by difference,

ture, as shown by the XRD data. As is noted previously,[26] the free carbon in the oxycarbide ceramic tends to combine with the oxide at high temperature (1300 °C and above). This carbothermal reduction reaction converts the silicon oxycarbide to silicon carbide.

L-EPCS System. Analogous experiments were carried out on the L-EPCS system. The results and a comparison with the CBS and B-EPCS systems have been previously reported.[27] The dried L-EPCS gel gave a ca. 84% ceramic yield on pyrolysis to 1000 °C. This is lower than the ceramic yield of the CBS system but higher than that of the highly branched B-EPCS system (ca. 72%).[11] The difference between the CBS case and the linear polymer may be due to the fact that CBS is a small molecule and would be expected to be more completely hydrolyzed and more extensively cross-linked than the polymeric form; this is, in fact, evidenced by the relatively small $-OCH_2CH_3$ peaks in the ^{13}C NMR spectrum of the CBS gel. On the other hand, B-EPCS is highly branched, which should lead to a further increase in the steric hindrance toward hydrolysis and condensation relative to the linear polymer, thereby giving a higher initial weight and a higher overall weight loss during pyrolysis. The conversion of the $[SiOCH_2]_n$ network, which has a nearly pure SiC_2O_2 microenvironment at the outset, into a silicon oxycarbide that contains a full distribution of the five possible $SiC_{4-x}O_x$ environments occurs between 600 and 1000 °C signaling the onset of the Si−O/Si−C redistribution process.

One important observation that was common to all of these systems is that the sol−gel process is not 100% complete. Besides the basic parameters that affect the hydrolysis and condensation of the Si−OEt groups, such as the solvent, the ratio of solvent/Si, the ratio of H_2O/Si, steric and inductive effects, the temperature and pH of the system, etc., the distribution of various functional groups, (OR), (OH), and (OSi), on the silicon atoms also affect the process, based on the ideas proposed by Kay and Assink.[28] In our investigation, the residual ethoxy content was found to vary under different hydrolysis conditions, but these groups could be eliminated entirely only after the hydrolysis was carried out a second time on the initially obtained hydrolysis product.

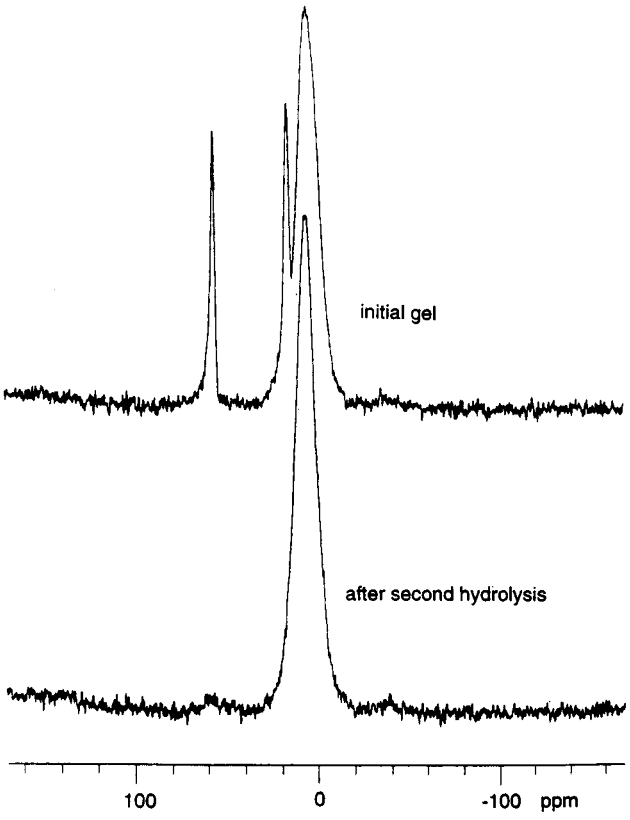

Figure 6. ^{13}C SSNMR spectra of gels obtained from L-EPCS after one and two hydrolysis treatments.

A gel was prepared in this manner by suspending the gel powder, obtained after drying the product obtained from the initial L-EPCS sol−gel treatment, in THF and then carrying out the sol−gel process a second time. The ^{13}C CP-MAS NMR spectrum (Figure 6) of this gel shows no residual ethoxy peaks. The ^{29}Si NMR spectrum of this gel shows a slightly upfield shift of the major D unit peak (−20.6 ppm) compared with the −17.4 ppm position observed for the original gel.[27] The relatively high concentration of Si−OH is evidenced by the FTIR spectrum of this product. These results suggest that this gel is completely hydrolyzed but not completely condensed. We therefore assign it the approximate formula $[Si(O)CH_2]_n[Si(O)(OH)CH_2]_m$. The elemental analysis results for this gel shows a lower C and H content compared to that for the initially obtained gel (Table 2), which is consistent with the conclusion that it is completely hydrolyzed.

The ^{29}Si SSNMR spectrum of the 1000 °C ceramic obtained from this gel (Figure 7) shows no M or C units but a much higher content of Q units compared to the

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(26) Burns, G. T.; Taylor, R. B.; Xu, Y.; Zangvil, A.; Zank, G. A. *Chem. Mater.* **1992**, *4*, 1313.

(27) Liu, Q.; Apple, T.; Zheng, Z.; Interrante, L. V. *Mater. Res. Soc. Symp. Proc.* **1996**, *435*, 513.

(28) Assink, R. A.; Kay, B. D. *J. Non-Cryst. Solids* **1988**, *99*, 359; **1988**, *107*, 35. *Better Ceramics Through Chemistry*; Brinker, C. J., Clark, D. E., Ulrich, D. R., Eds.; 301−306 North-Holland: New York, 1984; pp 301−306.

Table 2. Compositions of Products from Elemental Analysis

	ordinary sol–gel product		sol–gel twice product	
	gel	ceramic	gel	ceramic
Si, %	45.77	49.42	47.41	47.25
C, %	18.90	15.25	16.78	14.23
H, %	5.13		4.28	
O,[a] %	30.20	35.33	31.53	38.52
formula	$SiC_{0.96}H_{3.14}O^{a}_{1.15}$	$SiC_{0.72}O^{a}_{1.25}$	$SiC_{0.83}H_{2.52}O^{a}_{1.17}$	$SiC_{0.71}O^{a}_{1.43}$
free carbon		47.9 %		59.7 %

[a] Calculated by difference.

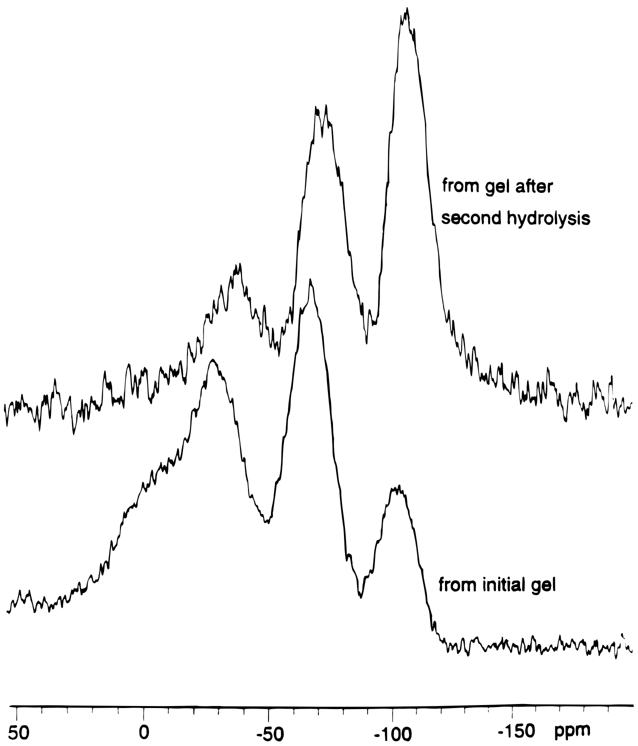
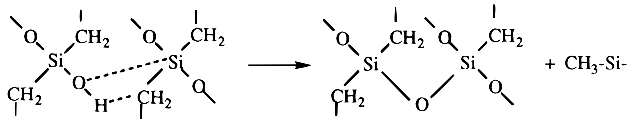


Figure 7. ^{29}Si SSNMR (1pda-MAS) spectra of the ceramics (1000 °C) obtained from L-EPCS after one and two hydrolysis treatments.

Scheme 2. Si–OH-Induced Si–C Bond Cleavage in L-EPCS



product obtained from the incompletely hydrolyzed gel. Also, the elemental analysis of this ceramic indicates a higher O/Si ratio and the free carbon content calculated from the elemental analysis results is higher too (Table 2).

These changes relative to the gel that was formed from the incompletely hydrolyzed L-EPCS can be ascribed to the occurrence of redistribution reactions involving the shift of H and the exchange of Si–O with Si–C bonds at ca. 500 °C, analogous to those proposed for the CBS gel (Scheme 2).

Additional evidence for this reaction is provided by the increase in $Si-CH_3$, and consequent reduction in Si–OH, groups evidenced by IR spectroscopy between 200 and 600 °C for the L-EPCS gel.[27] Given that most organosiloxane gels contain both Si–OH and $Si-CH_x$ groups, it seems likely that a similar process occurs in these cases on pyrolysis. This would facilitate Si–C/Si–O redistribution and, particularly in the case of terminal organic substituents, lead to loss of carbon from the SiO_xC_y network as either free carbon or volatile hydrocarbon products. Indeed, in cases such as MTES, where the Si–C carbon is initially present as a methyl group, this process could be an important contributor to the hydrocarbon (methane) loss observed on pyrolysis. Of course, the importance of this mechanism, which has been suggested previously by several investigators,[10b,13,14,29] will depend on the concentration of Si–OH groups and the temperatures required to effect appreciable rates of reaction. In the case of the cyclic carbosilane precursor, CBS, this $Si-OH + Si-CH_2-Si \rightarrow Si-O-Si + H_3C-Si$ reaction seems to be particularly facilitated, perhaps by the ring strain present in the four-membered $[SiC]_2$ ring. The release of this ring strain may lower the activation energy for the reaction, allowing an appreciable reaction rate at a relatively low temperature where the concentration of Si–OH groups has not been greatly depleted by condensation reactions. On the other hand, even in the case of the L-EPCS system, which lacks the additional driving force of ring strain, the gel that was subjected to a second hydrolysis treatment clearly experienced a significant increase in its O/Si ratio and free carbon content on pyrolysis, relative to the gel that contained an initially lower Si–OH concentration. This suggests that even under the usual conditions of pyrolysis of organosiloxane gels to SiO_xC_y, the presence of these Si–OH groups in the initial gel can be an important factor in determining the carbidic carbon content of the final ceramic material.

Conclusions

The sol–gel processing of the cyclic carbosilane, CBS, was found to proceed much faster than that of both the linear polymer (L-EPCS) and methylsilsesquioxane (MTES), probably due to the more electropositive nature of the Si atoms in CBS.

For the CBS system, ring-opening reactions that are apparently facilitated by the presence of uncondensed Si–OH groups occurred early in the pyrolysis process (even on drying of the gel at ca. 160 °C), creating both D and T units in the polymer. A similar Si–OH-initiated Si–C/Si–O redistribution reaction seems to occur in case of the linear L-EPCS gel, especially when the initial concentration of Si–OH in the gel is enhanced by a further hydrolysis treatment, leading to an increase of the O/Si ratio and free carbon content and a reduction in the carbidic carbon content for the final SiO_xC_y ceramic product obtained on pyrolysis.

Chemical analysis of the ceramics obtained from pyrolysis of these $Si-CH_2-Si$ bridged gels indicates that

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(29) Bois, L.; Maquet, J.; Babonneau, F.; Mutin, H.; Bahloul, D. *Chem. Mater.* **1994**, *6*, 796.

the strategy of adding bridging CH_2 groups in the hybrid polymers is effective in increasing the carbidic carbon content in the resulting SiO_xC_y ceramics. In general, this results in a lower initial O/Si ratio for the initial gel compared to the case where the carbon is bound as a terminal group (such as the $Si-CH_3$ in MTES), leading to a higher incorporation of carbon in the oxycarbide framework.

The detailed studies of these structurally less complex $[Si(O)CH_2]_n[Si(O)(OH)CH_2]_m$ gels (compared to most of the previously studied SiO_xC_y precursors) not only have provided a better understanding of the structural evolution during the polymer-to-ceramic conversion process but also have given a unique perspective on the role of oxygen and OH groups attached to Si in the initial polymer in determining the pyrolysis chemistry and thereby the composition of the ceramic end product. It seems quite clear from these results that the thermodynamic stability of the Si−O bond, coupled with the availability of relatively facile Si−O/Si−C redistribution reactions, leads to the effective retention of essentially all of the initial siloxy oxygen functionality and elimination of any excess carbon present from the final $SiO_{2-x}C_{x/2}$ network as volatile hydrocarbon byproducts or free carbon. This process is enhanced in the presence of uncondensed Si−OH groups which apparently facilitate the conversion of bridging methylene to terminal methyl groups while adding bridging oxygen to the oxycarbide network structure.

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Supporting Information Available: TGA trace of the CBS gel under N_2, TGA trace in air of silicon oxycarbide ceramic obtained from CBS, XRD patterns of silicon oxycarbide ceramics obtained from CBS after being heated to different temperatures, and FTIR spectrum of the gel after a second hydrolysis treatment (6 pages). Ordering information is given on any current masthead page.

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