Sol-Gel Synthesis of a Siloxypolycarbosilane Gel and Its Pyrolytic Conversion to Silicon Oxycarbide

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A new ethoxy-substituted polycarbosilane (**I**) has been prepared from a highly branched chloropolycarbosilane $[Si(OEt)_x(Et)_{0.15}Cl_yCH_2]_n$. After hydrolysis, condensation, and drying, a gel having the general formula $[CH_2Si(OH)_a(OEt)_b(Et)_{0.15}O_c]_n$ (**II**) was obtained from **I**. The dried gel was pyrolyzed under argon to give a silicon oxycarbide glass. The gel and its pyrolysis chemistry were characterized by infrared and ^{29}Si, ^{13}C, and ^{1}H magic angle spinning nuclear magnetic resonance (MAS NMR). By 600 °C the gel has developed a fully condensed structure and can be represented by the approximate formula $[CH_2SiO]_n$, but with a distribution of Si microenvironments ranging from X (SiC_4) to Q (SiO_4, minor component). The conversion of the polymeric network into a silicon oxycarbide glass occurs between 600 and 1000 °C. A comparison between the chemical analysis data and the ^{29}Si NMR spectra simulations leads to an estimation of the carbon content and its distribution in the silicon oxycarbide. The results were compared with those obtained from a methylsilsesquioxane gel, $CH_3SiO_{1.5}$ (**III**). These results show that a higher proportion of the carbon in the initial precursor is retained in the oxycarbide product if the carbon atoms are initially bonded to two silicon atoms rather than one. Moreover, the amount of carbon that is incorporated into carbidic sites (CSi_4) in the case of the "CH_2SiO" precursor is found to be approximately twice that obtained by using the $CH_3SiO_{1.5}$ gel.

Introduction

The introduction of nitrogen into silica-based glasses has been used to enhance their mechanical, chemical, and thermal properties.[1] This effect is attributed to the substitution of divalent oxygen atoms by trivalent nitrogen atoms.[2]. On this basis, the introduction of four-coordinated atoms such as carbon atoms would be expected to provide a greater degree of cross-linking of the network, thereby further tighting the structure. A few papers have reported the preparation of oxycarbide glasses by the traditional melting process[3,4] starting from mixtures of silicon carbide and silica; however, it appears to be quite difficult to retain carbon inside the network at the high temperatures involved in melting the silica and a limit in the amount of carbon incorporation was reached at only the 2.5% C level. Nonetheless, even at this level properties such as hardness, density, Young's modulus, and fracture toughness were enhanced to a substantially greater extent than was observed for comparable N additions.

The hydrolysis/condensation of organosilanes (the sol-gel process) has been employed as an alternative route to oxycarbide glasses, taking advantage of the relative ease of introducing carbon, as Si–C bonded organic substituents, into the gel structure, and the relatively low temperatures required to convert these gels into a SiO_xC_y glass. There are a number of studies reported in the literature using organically modified silicon alkoxides or chlorides as precursors and leading to the formation of "black glasses".[5-19] These oxycarbides exhibit very good oxidation resistance properties, and resist crystallization up to ca. 1400–1500 °C.[15,16] They have been used as matrices for C and SiC fiber reinforced composites,[17] as binders/sintering aids for SiC powder,[18] and as a source of ceramic fibers.[19]

The existence of a silicon oxycarbide phase with C atoms covalently bonded to Si atoms has been evidenced in these "black glasses" by ^{29}Si MAS NMR spectroscopy.[6,7,9-14] However, in addition, a free carbon phase always seems

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to be present that usually represents more than 50% of the total carbon.[11] In a prior study, Si-H groups were introduced into methyl-substituted silica gels in an effort to decrease the amount of this free carbon.[13,14] These groups were expected to react during the pyrolysis with CH_3–Si bonds to form Si–CH_2–Si bridges, thus promoting the retention of the C atoms within the oxycarbide phase. Indeed, the NMR results evidenced a decrease in the free carbon content of the pyrolyzed gels relative to that obtained using the $[CH_3SiO_{1.5}]_n$ gel alone.

Rather than depending on the formation of Si–CH_2–Si bonds during the pyrolysis, we have employed here as a SiO_xC_y source a polycarbosilane gel in which the majority of the carbon is initially present in the form of Si–CH_2–Si bridges. The ethoxy-substituted polycarbosilane used to prepare this gel was derived from a highly branched chloropolycarbosilane, $[CH_2SiCl_{1.7}(OEt)_{0.15}(Et)_{0.15}]_n$ (CPCS), used by some of the present authors in the synthesis of a hydridopolycarbosilane precursor for silicon carbide.[20] Treatment of this chloropolycarbosilane with ethanol leads to an ethoxypolycarbosilane of the approximate composition $[CH_2Si(OEt)_{1.85}(Et)_{0.15}]_n$ (**I**) which can be hydrolyzed to form the gel $[CH_2Si(OH)_a(OEt)_b(Et)_{0.15}O_c]_n$ (**II**).[21] The structure of this gel and its pyrolysis to silicon oxycarbide was investigated by infrared and multinuclear MAS NMR (^{29}Si, ^{13}C, and ^{1}H). In addition, the structure and chemical composition of the silicon oxycarbide obtained at 1000 °C was extracted from chemical analysis and ^{29}Si MAS NMR data. A direct comparison is made with an oxycarbide sample derived from a methylsilsesquioxane $[(CH_3)SiO_{1.5}]_n$ (**III**) in order to examine the effect of the precursor structure on the amount and form of the carbon incorporated into the pyrolysis product.

Experimental Section

Preparation of the Ethoxypolycarbosilane (I). The preparation of CPCS was carried out as described previously from $ClCH_2SiCl_3$ and Mg in diethyl ether.[20] After the reaction, the ether solution was removed to a three-necked flask via a cannula fitted with a fritted glass filter. Dry nitrogen gas was bubbled through the solution and allowed to exit through a condenser. Excess ethanol was added slowly with vigorous stirring at room temperature. After complete addition of the ethanol, the solution was stirred for several hours at room temperature while continuing the flow of N_2 (to remove HCl(g)). Ether was removed at room temperature under vacuum, and then pentane was added. The polymer solution was separated from the $MgCl_2$ present by cannula filtration, and the product (**I**) recovered by evaporation of the pentane under vacuum. The replacement of the Cl groups by ethoxy was quantitative based on ^{1}H NMR integration. ^{1}H NMR (C_6D_6) δ (in ppm from C_6D_6) 0.1–1.0 (m, 2H, $SiCH_2Si$), 1.0–1.5 (m, 3H, OCH_2CH_3), 3.6–4.2 (m, 2H, OCH_2CH_3).

Hydrolysis of I. I was mixed with ethanol and then 64 mL of dilute (2 M) HCl(aq) was added for each mole of carbosilane (this corresponds to a 2:1 molar ratio of H_2O:OEt groups in the polymer). The mixture was stirred on a hot plate at 100 °C for 5 h, and then the ethanol was removed under vacuum. The gel was dried in vacuo at 100 °C for 2 days, after which a white powder (**II**) was obtained. The same procedure was used for the preparation of a dried methylsilsesquioxane gel (formally, $CH_3SiO_{1.5}$) (**III**) for comparison purposes. This was prepared starting from $CH_3Si(OMe)_3$, which was obtained from Hulls America.

The dried gel was pyrolyzed under flowing argon at 10 °C/min. Samples were removed from the furnace at various temperatures for elemental analysis and solid-state NMR and IR studies.

Measurements. Elemental analyses were performed at the Service Central d'Analyse du CNRS, Vernaison, France). TGA experiments were run with a Netzsch STA 409 apparatus under argon flow at 10 °C/min. MAS NMR spectra were recorded on a MSL 400 Bruker spectrometer. Pulse widths of 2.5 μs for ($\theta \approx 30°$) and recycle delays of 60 s were used for ^{29}Si NMR (79.5 MHz). For each ^{29}Si NMR spectrum, 800–1400 transients were accumulated with a spectral width of 50 kHz. Quantitative analysis of ^{29}Si NMR spectra is difficult due to the long ^{29}Si relaxation times. Short pulse widths and relatively long recycle delays were used in this work 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 $(CH_2)SiO$ 1000 °C sample with a longer recycle delay (300 s) and produced no significant difference. It will thus be assumed in this study that the NMR parameters used allow at least a level of quantitative accuracy that is sufficient to obtain an indication of the general trend in the evolution of the Si site distribution versus pyrolysis temperature for the two systems examined. ^{29}Si CP-MAS spectra were recorded with proton decoupling, with contact times of 2 ms. For the ^{1}H NMR spectra (400 MHz), eight transients were recorded with a pulsewith of 6 μs ($\theta \approx 80°$) and a recycle delay of 2 s. The ^{13}C MAS NMR spectra were recorded at 100.6 MHz using cross-polarization techniques (CP) with contact times of 2 μs; 500 transients were accumulated. The samples were spun at 5 kHz in zirconia rotors. Peaks will be labeled with the X, M_n, D_n, T_n, and Q_n notation. X, M, D, T, and Q respectively refer to $SiC_{4-x}O_x$ units with x = 0, 1, 2, 3, or 4, n is the number of bridging O atoms surrounding Si. The spectra were simulated with the program FIT.[22] Infrared spectra were recorded with a Perkin-Elmer 783 spectrometer using KBr pellets.

Results

Characterization of the Dried Gel. The ^{29}Si MAS NMR single pulse excitation (SPE) spectrum of the dried gel (**II**) shows three main peaks at −57.5, −18.0, and 7.2 ppm (Figure 1a). Actually, this last signal can be split into two components at 8.5 and 0 ppm using cross polarization (CP) techniques (Figure 1b). These four peaks can be assigned to $SiCO_3$ units (−57.5 ppm), SiC_2O_2 units (−18 ppm), SiC_4 units (0 ppm), and SiC_3O units (8.5 ppm).[23] The respective chemical shift values for the $SiCO_3$ and the SiC_2O_2 units are intermediate between values for T_2 (−58 ppm) and T_3 (−66 ppm) units, and between values for D_1 (−13 ppm) and D_2 (−22 ppm) units, reported for methyl-substituted silicon alkoxides.[23] This difference could arise from the presence of nonbridging oxygen ligands bonded to Si in the case of the "$[CH_2Si(OEt)_2]_n$"-derived gel.

The enhancement of the intensities and the relative narrowing of the 8.5 and 0 ppm peaks observed in the ^{29}Si CP spectrum are consistent with a more protonated environment for these two Si sites. Proton decoupling was applied during signal acquisition in this case, which could account for the observed narrowing of the lines corresponding to protonated sites. Along with their chemical shift values, this provides good evidence for their

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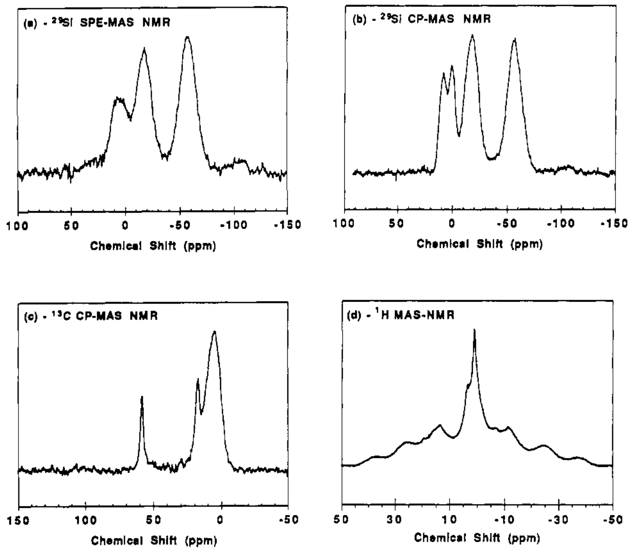

Figure 1. ^{29}Si MAS NMR (a), ^{29}Si CP MAS NMR (b), ^{13}C CP MAS NMR (c), and ^{1}H MAS NMR (d) spectra of the dried gel **II**.

Table 1. Elemental Analysis for the Various $(CH_2)SiO$ (II) Samples[a]

samples	Si (wt %)	C (wt %)	H (wt %)	C/Si	H/Si
gel	36.21	22.65	4.91	1.46	3.80
600 °C	44.07	16.62	3.36	0.88	2.13
800 °C	39.32	13.73	1.90	0.81	1.35
1000 °C	45.41	17.31	0.30	0.88	0.18
1200 °C	46.80	15.70	0.20	0.78	0.12
1400 °C	46.06	15.08	0.12	0.76	0.07
1600 °C	47.71	14.15	0.13	0.69	0.08

[a] Oxygen was not analyzed.

assignment as SiC_3O and SiC_4 units, respectively, where each of the carbon atoms attached to these Si atoms bears two protons. The SPE spectrum was simulated with four components, and the following composition was found: $SiCO_3$, ≈40%; SiC_2O_2, ≈40%; SiC_3O, ≈10% and SiC_4, ≈10%.

The ^{13}C CP MAS NMR spectrum of the gel exhibits a broad peak at 5.1 ppm due the Si–CH_2–Si groups, and two sharper peaks at 17.1 and 58.0 ppm, due to O–CH_2–CH_3 groups[24] (Figure 1c). The latter peaks can be assigned to residual ethoxy groups, that have not been hydrolyzed, or to trapped ethanol. Such groups are also visible in the ^{1}H MAS NMR spectrum which shows two sharp peaks at 1.1 and 3.4 ppm[25] (Figure 1d). The broad component underneath these peaks which is responsible for the spinning sidebands is attributed to the Si–CH_2–Si groups. The presence of the ethoxy groups agrees with the ^{29}Si NMR chemical shift of the $SiCO_3$ units, which suggested the presence of terminal O–R (R = H or ethyl) groups still bonded to Si.

Elemental analyses for the gel are reported in Table 1. The high C/Si ratio (ca. 1.5) strongly supports the conclusion that the dried gel contains residual ethoxy groups.

Conversion of the Dried Gel into Silicon Oxycarbide.

Chemical Analysis. Elemental analyses were performed on samples of **II** after firing under argon at 600, 800, and 1000 °C (Table 1). The evolution of the C/Si and H/Si molar ratios are reported in Figure 2. From room temperature to 600 °C, both the C/Si and H/Si ratios decrease to reach the following values: 0.9 and 2.1. From 600 to 1000 °C, the C/Si ratio is almost stable, 0.85 ± 0.05, while the proton content continues to decrease. The H/Si ratio is less than 0.2 at 1000 °C.

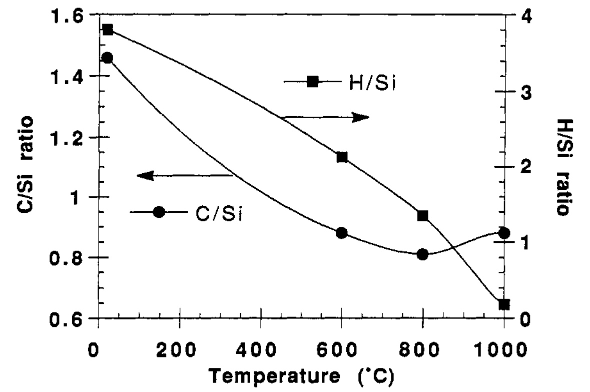

Figure 2. C/Si and H/Si ratios from chemical analysis on pyrolyzed samples of **II**.

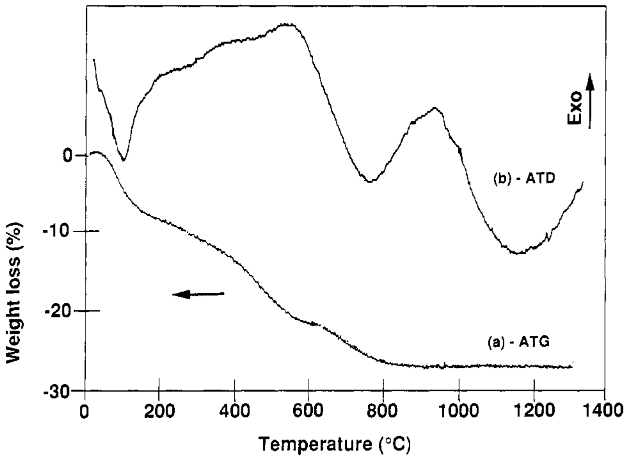

Figure 3. TGA (a) and DTA (b) curves of the dried gel **II** (argon flow; 10 °C/min).

TGA. The TGA curve of the dried gel under flowing nitrogen is shown in Figure 3. Three regions of weight loss can be distinguished, from room temperature to 200 °C (≈9%), from 200 to 520 °C (13.5%) and then from 600 to 750 °C (6.5%). The first weight loss, associated with an endothermic process, is assigned to a loss of solvent and water, either adsorbed by the gel or coming from the ongoing condensation process. The two other steps, which correspond to a loss of carbon and hydrogen according to chemical analysis, are attributed to the completion of the condensation process and the decomposition of the bridging CH_2 groups, respectively.

^{29}Si MAS NMR Spectra. The spectra of the pyrolyzed samples are shown in Figure 4, along with their simulations. At 600 °C, the spectrum is quite similar to that of the gel, except that most of the peaks have shifted upfield: −62.0, −20.0, −3.0, and 7.0 ppm respectively for $SiCO_3$, SiC_2O_2, SiC_4, and SiC_3O units. At 800 °C, the peaks broaden significantly, and the peak at −101 ppm, due to SiO_4 units,[23] which is barely noticeable in the dried gel, becomes more substantial. The same components are seen for the sample pyrolyzed to 1000 °C.

The percentages of each site versus pyrolysis temperature, extracted from the simulations, are shown in Figure

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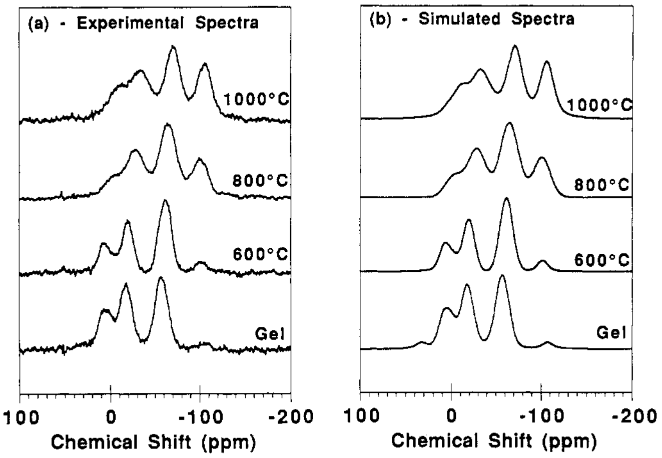

Figure 4. Experimental (a) and simulated (b) ^{29}Si MAS NMR spectra of samples pyrolyzed below 1000 °C.

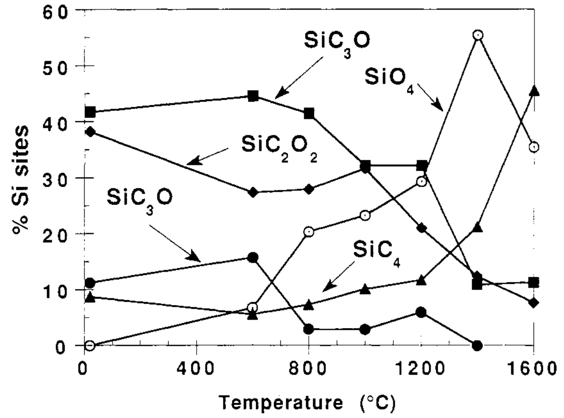

Figure 5. Evolution of the percentages of $SiC_{4-x}O_x$ units in the pyrolyzed samples.

5. This semiquantitative analysis of the Si site distribution was carried out according to the assumptions mentioned in the Experimental Section. Up to 600 °C, the main changes are a slight decrease in the SiC_2O_2 unit content and an increase in the SiO_4 unit content. This phenomenon has already been reported for methylsilsesquioxane[26,27] and assigned to redistribution between Si–C and Si–O bonds, which occurs in that case with loss of siloxane species. From 600 to 1000 °C, the SiO_4 unit content strongly increases, while a smaller increase in the SiC_4 units can also be observed. The average number of Si–C bonds per Si site have been calculated from the NMR simulations (Figure 6). It shows a decrease in the Si–C bonding between 600 and 800 °C. At 1000 °C, ca. 1.5 Si–C bonds are still present per Si site.

The variation of the chemical shift values versus pyrolysis temperature for the various sites is presented in Figure 7. Up to 600 °C, the chemical shift values do not change, except for the $SiCO_3$ units where a 5 ppm upfield shift is observed from −57.5 to −62 ppm. This indicates that the local environments of the Si atoms are relatively stable over this temperature range. The change for the $SiCO_3$ units are presumably related to the disappearance of the terminal groups, and the presence at 600 °C of only fully condensed sites. From 600 to 1000 °C, an upfield shift is observed for all the sites. A similar observation has been reported in the study of the conversion process for Yajima's polycarbosilane to SiC[28] and assigned to a change in the carbon environments, which become increasingly less protonated.

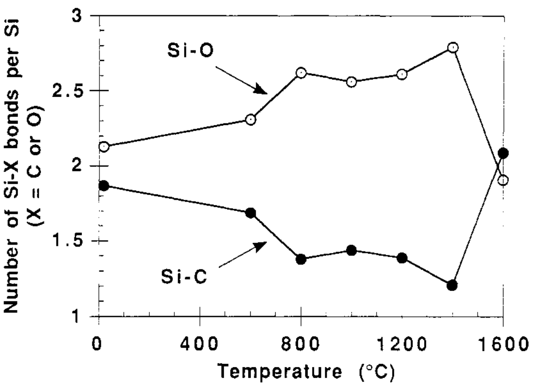

Figure 6. Evolution of the average number of Si–C bonds per Si sites in the pyrolyzed samples.

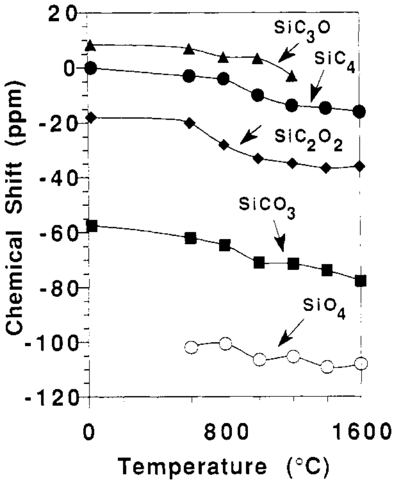

Figure 7. Variation of the chemical shift values of the various $SiC_{4-x}O_x$ units in the pyrolyzed samples.

The following composition is derived from the spectral simulations for the Si-containing phase in the sample pyrolyzed at 1000 °C: 23% SiO_4 units, 32% $SiCO_3$ units, 32% SiC_2O_2 units, 3% SiC_3O units, and 10% SiC_4 units. Assuming that the carbon atoms are bonded to four silicons, the C/Si ratio is found to be 0.36 in this phase. This value can be underestimated since some residual hydrogen could still be bonded to carbon atoms. Chemical analysis of this sample gave a total C/Si ratio of 0.88. The deficit in the C/Si ratio, comparing ^{29}Si NMR data and chemical analysis, strongly suggests the presence of a free carbon phase, amounting to ≈65 mol % of the total carbon content.

^{13}C CP MAS NMR and ^{1}H MAS NMR Spectra. The ^{13}C CP MAS NMR spectra of the pyrolyzed samples are presented in Figure 8a. Relative to that of the dried gel, the spectrum for the sample heated to 400 °C shows just a slight decrease in the relative intensities of the peaks due to O–CH_2–CH_3 groups. By 600 °C, these peaks have totally disappeared, and a single peak at 5 ppm similar to that present in the gel remains due to Si–CH_2–Si groups. At 800 °C, the quality of the spectrum changes indicating a strong modification in the carbon environment. The

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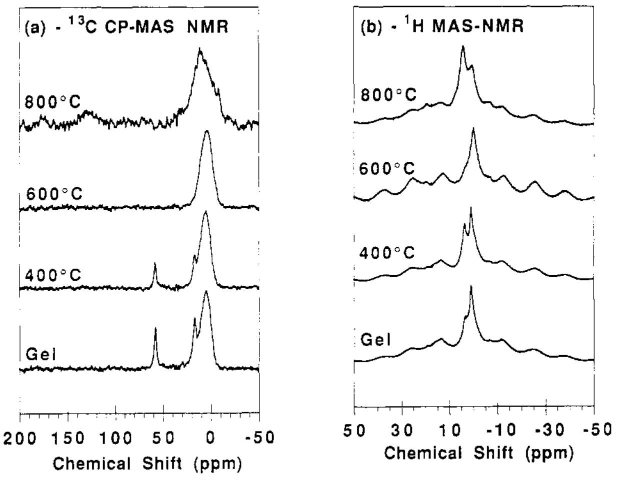

Figure 8. ^{13}C CP MAS NMR (a) and ^{1}H MAS NMR (b) spectra of pyrolyzed samples.

peak due to aliphatic carbon sites broadens, presumably due to the presence of a distribution of sites, and is shifted to lower field ($\delta = 10$ ppm) indicating that fewer protons are bonded to these carbons. At this temperature, a new signal appears at 130 ppm along with its spinning side bands, revealing a chemical shift anisotropy. This signal is attributed to aromatic carbon atoms[29] and is presumably related to the formation of a free carbon phase. The shape of the static spectrum, which can be extracted from the envelope of the spinning sidebands, is characteristic of the degree of condensation of the aromatic species. The present signal, despite a low signal/noise ratio, seems to correspond to a relatively small degree of condensation.

^{1}H MAS NMR spectra were also recorded on the same samples (Figure 8b). Peaks due to O–CH_2–CH_3 groups at 3.8 and 1.1 ppm are still present at 400 °C and disappear at 600 °C. At this latter temperature, the spectrum is dominated by one signal at 0 ppm due to Si–CH_2–Si groups. At 800 °C, this signal is still present, together with a new one at 4.2 ppm. Such a chemical shift can correspond to Si–H, Si–OH, or H_2O.[30,31] According to the infrared data presented below, the amount of Si–H is low and cannot account for the high intensity of the NMR signal, which thus should be assigned to O*H*, either in Si–OH groups or H_2O. An identical behavior in the evolution of the ^{1}H MAS NMR spectra has been previously observed for sol–gel-derived Si–C–O systems.[11]

Infrared Spectra. The infrared spectra of the gel and pyrolyzed samples are presented in Figure 9. Water and perhaps ethanol are present in the gel ($\nu_{OH} \approx 3400$ cm^{-1}; $\delta_{HOH} \approx 1630$ cm^{-1}). The two bands at 1265 and 1360 cm^{-1} are due to vibrations of the CH_2 groups in Si–CH_2–CH_3 and Si–CH_2–Si groups.[32] The presence of Si–CH_2–CH_3 groups was previously evidenced in the chlorocarbosilane precursor (CPCS) and attributed to a reaction involving the diethyl ether used as the solvent for its synthesis.[20] The broad bands at $\approx$1000 and 800 cm^{-1} are due to stretching vibrations of Si–O and Si–C bonds, respectively.

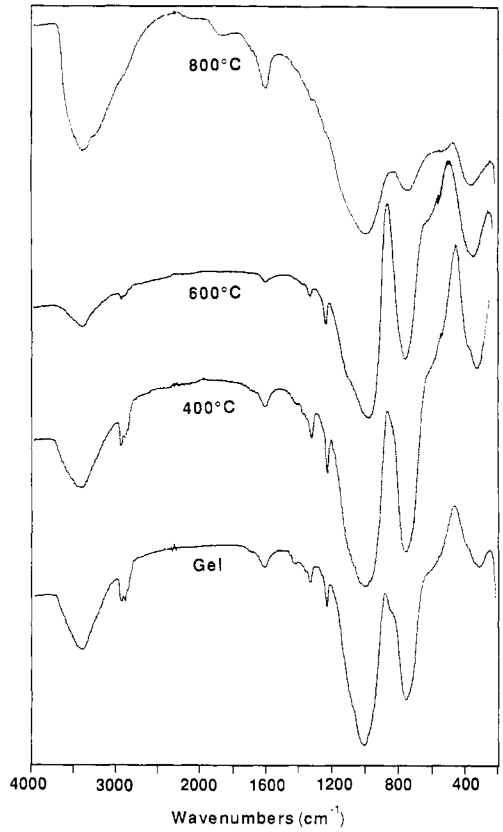

Figure 9. Infrared spectra of the pyrolyzed samples.

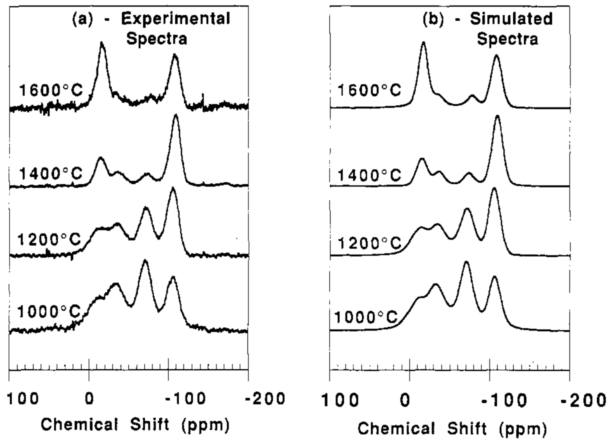

Figure 10. Experimental (a) and simulated (b) ^{29}Si MAS NMR spectra of samples pyrolyzed above 1000 °C.

Up to 600 °C, the spectra do not really change. A decrease in the water content can only be observed. On the contrary, the spectrum of the sample pyrolyzed at 800 °C is strongly modified with intense bands due to the presence of water and/or OH groups. The bands due to Si–CH_2–CH_3 and Si–CH_2–Si have almost disappeared, while new broad bands have appeared at around $\approx$2100–2200 and $\approx$1900 cm^{-1} that can be assigned to Si–H groups and unsaturated carbon species in an amorphous carbon phase, respectively.[33,34]

Thermal Behavior of the Oxycarbide Samples above 1000 °C. The ^{29}Si MAS NMR spectra of samples pyrolyzed at 1000, 1200, 1400, and 1600 °C are presented in Figure 10 along with the simulated spectra. From 1000 to 1400 °C, the general trend is toward a decrease in the mixed species content and an increase in the SiO_4 and

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SiC_4 units content. This trend is amplified above 1200 °C. The number of Si–C bonds per Si remains roughly constant, 1.3 ± 0.1 (Figure 6), as well as the percentage of free carbon (≈60 ± 5%). This shows that redistribution reactions between Si–O and Si–C occur in this temperature range, leading to an enrichment in silica-type and silicon carbide-type units.[18]

Between 1400 and 1600 °C, a decrease in the sites containing Si–O bonds, which is more obvious for the SiO_4 sites than for the mixed species, can be observed (Figure 5). At 1600 °C, the SiC_4 peak is the major component (45%) with a somewhat smaller SiO_4 peak (35%). The mixed species represent 20% of the Si sites at this temperature. The average number of Si–C bonds per Si unit greatly increases, up to 2.1 (Figure 6), while the free carbon content drops to 25%. These data reveal that at 1600 °C, carbothermal reduction occured between the Si–O bonds and free carbon to form silicon carbide.[35]

Discussion

Our prior work on the synthesis and characterization of the polymer $[CH_2SiCl_{1.7}(OEt)_{0.15}(Et)_{0.15}]_n$ (CPCS) and its reduced derivative, $[CH_2SiH_{1.85}(Et)_{0.15}]_n$ (HPCS), indicated a highly branched structure which contains a distribution of Si environments from $SiCX_3$ to SiC_4.[20] The molecular weight distribution indicated by GPC was quite large ($M_w/M_n = 6.95$), with an average degree of polymerization (n) of around 15. This polymer was prepared from (chloromethyl)trichlorosilane ($ClCH_2SiCl_3$) by Mg-induced coupling in diethyl ether. The reaction proceeds by head-to-tail coupling of the initially obtained Grignard reagent, leading to branching at Si due to its trifunctional nature, but with little or no cross-linking due the virtual absence of C–C or Si–Si coupling. The incorporation of ethyl groups from the diethylether solvent was evidenced by labling studies carried out in perdeuteriodiethyl ether. The chloro groups of the CPCS intermediate were replaced by ethoxy on addition of excess ethanol to an ether solution of the polymer. This "ethoxypolycarbosilane" (**I**) was then treated in the usual manner for the sol–gel synthesis of polysiloxanes from alkoxysilanes (with HCl/H_2O in ethanol) to produce a gel.

From the solid-state NMR characterization reported herein on the dried gel (**II**), a rather detailed description of its composition and structure can be given. The structure is based on a distribution of $SiC_{4-x}O_x$ units, with $x \neq 0$. The major components are the $SiCO_3$ (T, ≈40%) and SiC_2O_2 (D, ≈40%) units, but SiC_3O (M) and SiC_4 (X) units are also present to a lesser extent, ≈10% each. A very small peak was also observed in the expected position for SiO_4; however, this amounts to <1% of the total Si sites. Assuming that the carbons bonded to Si are bridging CH_2 groups, the CH_2/Si ratio per Si sites is 0.93 from the NMR data, close to the value of 1 in the starting precursor.

The actual structure is thus more complex than would be suggested by the "average" approximate formula, $[CH_2SiO_{2/2}]_n$, which would contain only SiC_2O_2 units. Instead, due to the initially branched structure of the starting polymer, which involves one to four methylene bridges at Si as well as the new Si–O–Si bridges formed by hydrolysis and condensation, a variety of other microenvironments for Si are possible. Moreover, due to the presence of a small amount of residual Si–Et functionality and the lack of complete hydrolysis and condensation noted below, the true structure of the initially obtained, dried gel is quite complex. However, the gel will be called CH_2SiO hereafter for simplicity.

Both ^{13}C and ^1H NMR show the presence of residual ethoxy groups in this dried gel, and the chemical shift of the $SiCO_3$ units peak in the ^{29}Si MAS NMR spectrum suggests that these groups are terminal groups bonded to such Si sites. The high C and H content in the elemental analysis is also consistent with the presence of such groups. This shows that the hydrolysis process was not complete. This is not too surprising, considering that the starting polymer is highly branched and that steric hindrance could inhibit the reaction of these ethoxy groups with water.

The thermal analysis data obtained for the dried gel reveals three weight losses during the pyrolysis. The first weight loss below 200 °C is attributed to the loss of residual water and ethanol trapped in the gel. The second weight loss corresponds to a decrease in the C/Si and H/Si ratios. At 600 °C, all the NMR spectra for the various nuclei do not show line broadening. The local order around Si atoms is conserved. The infrared spectra do not show any great changes, suggesting that the bridging $Si–CH_2–Si$ groups are intact. The main difference at this temperature is in both the ^{13}C and ^1H MAS NMR spectra, which show the total disappearance of the signals due to residual ethoxy groups. The ^{29}Si NMR spectrum of the same sample exhibits a chemical shift value for the $SiCO_3$ units which corresponds now to fully condensed species. Indeed, the C/Si ratio found from elemental analysis at 600 °C (0.88, Table 1) is very close to what is expected for a fully condensed network, 0.84, on the basis of the composition extracted from the NMR simulation. It is thus reasonable to assign this next weight loss mainly to the removal of nonhydrolyzed ethoxy groups, and to consider that at 600 °C, the $Si–CH_2–Si$ bridges are largely intact and the siloxane network is now fully condensed.

The third weight loss from 600 and 750 °C is related to a decrease of the H/Si ratio, while the C/Si ratio remains almost constant. The ^{13}C and ^{29}Si NMR peaks broaden and shift, indicating a deprotonation of the C sites. In this temperature range, the number of Si–C bonds decreases, and this is certainly related to the formation of a free carbon phase, as revealed by the presence of an aromatic C signal in the ^{13}C NMR spectrum and the comparison between the ^{29}Si NMR and chemical analysis data. This stage corresponds to the transformation of the polymeric structure into a purely inorganic material, mainly by dehydrogenation reactions. The O*H* peak in the ^1H MAS NMR spectrum of the gel fired at 800 °C suggests the presence of Si–OH and/or adsorbed water in the sample. This phenomenon was already mentioned for methylsiloxane-derived samples and related to the large surface areas.[11,32] According to Kamyia et al.,[34] some Si–O–Si bonds can be cleaved during this conversion process leading to the formation of Si–OH sites, on which water vapor encountered during handling of the samples in air can be absorbed.

At 1000 °C, the silicon oxycarbide phase shows a high proportion of carbidic C atoms, with a C/Si ratio of 0.36, according to the NMR simulations. A methylsilsequioxane gel (**III**) prepared from hydrolysis of methyltriethoxysilane was pyrolyzed at 1000 °C for comparison purposes. Formally the C/Si ratio for both systems is equal to 1, but the C atoms are bridging in one case and terminal in the

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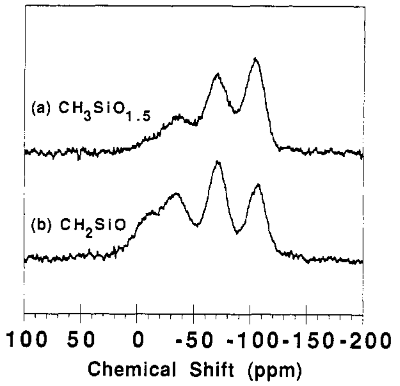

Figure 11. ^{29}Si MAS NMR spectra of (a) the $(CH_2)SiO$ gel (**II**) pyrolyzed at 1000 °C and (b) the $(CH_3)SiO_{1.5}$ gel (**III**) pyrolyzed to 1000 °C.

Table 2. Chemical Analysis and ^{29}Si MAS NMR Data for the $(CH_2)SiO$ (II) and $(CH_3)SiO_{1.5}$ (III) Gels Pyrolyzed to 1000 °C

	$(CH_2)SiO$	$CH_3SiO_{1.5}$
chemical analysis		
Si (wt %)	45.41	44.29
C (wt %)	17.31	11.74
C/Si mol ratio	0.88	0.62
NMR data		
% SiO_4 units	23.4	39.1
% $SiCO_3$ units	32.2	37.6
% SiC_2O_2 units	31.6	18.4
% SiC_3O units	2.8	
% SiC_4 units	10.1	5.0
Si–C bonds per Si	1.44	0.94
C/Si mol ratio	0.36	0.24
% free C/total C	64	62

other case. The average number of Si–C bonds per Si site should be theoretically 1 for the methylsilsesquioxane-derived gel and 2 for the ethoxy-substituted polycarbosilane-derived gel.

The ^{29}Si MAS NMR spectra of the two samples pyrolyzed at 1000 °C are compared in Figure 11. Their chemical compositions, extracted from chemical analysis and NMR data, are presented in Table 2. These data show clearly that the silicon-containing phase of the pyrolyzed $(CH_2)SiO$ gel is richer in carbidic carbon, since the average number of Si–C bonds per Si unit is 1.44 instead of only 0.94 for the pyrolyzed $(CH_3)SiO_{1.5}$ gel. The C/Si ratio calculated from chemical analysis data is also higher for the pyrolyzed $(CH_2)SiO$ gel (0.88) than for the pyrolyzed $(CH_3)SiO_{1.5}$ gel (0.62). The loss of C during the pyrolysis of this last sample is essentially due to redistribution reactions and loss of siloxanes.[13] Such reactions seem to be quite limited for the $(CH_2)SiO$ system. Thus the free carbon content is about the same in both samples, reaching ≈60–65% of the total amount of carbon.

As was previously pointed out in the literature,[36] in these oxycarbide systems derived from organosilanes the amount of carbidic carbon seems to be closely related to the O/Si ratio in the polymeric precursor. Assuming that this ratio is unchanged during the pyrolysis, the use of a trifunctional silane, $RSiO_{1.5}$, should lead to the formation of an oxycarbide phase of the composition, $C_{0.25}SiO_{1.5}$, assuming that the usual valences of C, Si, and O are maintained. Therefore, a large amount of carbon should be either transformed into volatile species and/or converted into free carbon. For the pyrolyzed $(CH_3)SiO_{1.5}$ gel, the C/Si ratio derived from the NMR simulations for the oxycarbide phase is 0.24, very close to the theoretical one, 0.25. In this case, based on elemental analysis of the product, ≈40% of the carbon is transformed into volatile species and ≈40% is converted into a free carbon phase. Several other trifunctional systems have been studied, and the composition of the final oxycarbide phase always seems to lead to a C/Si ratio that is near, or slightly below, 0.23 (0.15–0.20).[33]

For the $(CH_2)SiO$ system, which has a lower initial O/Si ratio, the expected composition for the oxycarbide phase should be $C_{0.5}SiO$, still assuming that the O/Si ratio does not change during pyrolysis. 50% of the carbon should be lost or converted into free carbon. These predictions are in agreement with the experimental data reported in this paper. The C/Si ratio in the oxycarbide phase is 0.36, showing clearly a substantial increase compared to the methylsilsesquioxane derived system, and 65% of the carbon is in a free carbon phase.

We have been using the ethoxycarbosilane **I** as a source of sol–gel and silicon oxycarbide film for surface coating and have found that uniform, adherent, thin films can be deposited on glass and various other substrates by solution coating methods, either before or after hydrolysis of **I**.[37] The results of these efforts and our current studies of the effect of the increased carbidic carbon content of the silicon oxycarbide obtained from this precursor on its mechanical properties will be reported subsequently.

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