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^{29}Si nuclear magnetic resonance study of the structure of silicon oxycarbide glasses derived from organosilicon precursors

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Several silicon oxycarbide glasses with O/Si ratios 1.2 and 1.8 were prepared by pyrolysis below 1000 °C of organosilicon precursors. Their structure was investigated using ^{29}Si magic-angle spinning nuclear magnetic resonance. The spectra obtained are consistent with a purely random distribution of Si–O and Si–C bonds, which depends on the O/Si ratio of the glass only, regardless of the structure of the precursors. This result is interpreted by the occurrence, during the pyrolysis of entropically controlled redistribution reactions involving the exchange of Si–O and Si–C bonds.

1. Introduction

In the SiC/SiO_2 system, the only stable phases at low temperature are crystalline silicon carbide and silica. However, the existence of metastable silicon oxycarbide species, incorporating silicon–oxygen and silicon–carbon bonds, is now well established. Evidence of such species was found at the interface between SiC substrates and the SiO_2 surface layers formed by oxidation [1]. More recently, it was found that the pyrolysis in an inert atmosphere of organosilicon polymers containing Si–O and Si–C bonds, leads to the formation of silicon oxycarbide species in large yields. Thus, Lipowitz *et al.* [2] showed that Nicalon ceramic fibres, obtained by pyrolysis of a polycarbosilane cross-linked by siloxane bridges, consist of β-SiC and graphite crystallites embedded in a continuous phase of glassy silicon oxycarbide. In the same way, black glasses, of general formula SiO_xC_y, obtained by pyrolysis of cross-linked polysiloxanes, consist of an amorphous silicon oxycarbide phase, usually incorporating a residual free carbon phase [3–5]. This last route is quite versatile, and it was shown that the use of polysiloxanes incorporating different structural units and substituents permits control of the composition of the oxycarbide phase [6, 7] and the free carbon content in the glass [7–11].

The characteristic feature of silicon oxycarbide species is the presence of silicon atoms bonded simultaneously to oxygen and carbon atoms in $\underline{Si}O_xC_{4-x}$ tetrahedra. The most powerful tool for investigating the environment of silicon atoms in these compounds is certainly high-resolution solid-state ^{29}Si nuclear magnetic resonance (NMR). This technique has been used by several authors to characterize silicon oxycarbide glasses, or to study the formation and the evolution of the bonding to silicon during the pyrolysis [3–17]. From the spectra reported in the literature, it appears that the environment of silicon atoms in oxycarbide glasses is complex: in all cases, a mixture of at least three of the five possible $\underline{Si}O_xC_{4-x}$ tetrahedral sites is observed. Thus, the environment of the silicon atoms in the oxycarbide glasses and in the precursor are quite different; this behaviour was ascribed to the occurrence during the pyrolysis of redistribution reactions involving the exchange of Si–O with Si–C bonds, which lead to a modification of the environment of silicon atoms above ~ 500 °C [6, 13, 14].

The distribution of $\underline{Si}O_xC_{4-x}$ sites depends on the composition of the glass, and more precisely on its O/Si ratio [6, 7] (the C/Si ratio in the glass is not a relevant parameter as a large fraction of the carbon atoms belong to the excess carbon phase, whereas all the oxygen atoms are bonded to silicon atoms in Si–O–Si bridges [2, 12]). The temperature of pyrolysis also greatly influences this distribution: the relative amount of $\underline{Si}O_4$ and $\underline{Si}C_4$ sites increases with the pyrolysis temperature, and at ~ 1400 °C the silicon oxycarbide phase may rather be described as a mixture of silicon carbide and silica [6, 8, 9, 17].

Up to now, the papers dealing with the structure of silicon oxycarbide glasses actually concerned only one glass composition, arising from one given polysiloxane precursor, with no attempt to describe the variation of the structure of the glass with its composition or with the nature of the precursor. The aim of this work was to establish the relationships between the environment of the silicon atoms in silicon oxycarbide glasses and the O/Si ratio in these glasses, in order to understand the relative importance of the structure of the precursors and of the redistribution reactions in the formation of this environment. For this purpose, we report the ^{29}Si magic angle spinning

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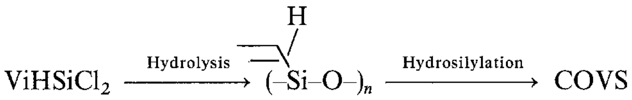
NMR (MAS NMR) of a number of silicon oxycarbide glasses with O/Si ratio ranging from ~ 1.2–1.8. These glasses are derived from different polysiloxane precursors containing various structural units and substituents, by pyrolysis in argon at moderate temperatures (900 or 970 °C), in order to avoid the phase separation to SiC and SiO_2.

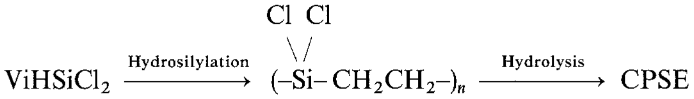
2. Experimental procedure

2.1. Preparation of the precursors

For this study, five polysiloxane precursors containing various structural units and functional groups have been used. These precursors are representative of the precursors described in the literature. The T precursor [6] has been obtained by hydrolysis/condensation (catalysed by tetrabutylammonium fluoride) of methyltrimethoxysilane in acetone. T/D and D/Q precursors have been obtained by hydrolysis/condensation of equimolar amounts of the corresponding chloro-silanes in diethylether, as described elsewhere [14]. Cross-linked oligovinylsiloxane (COVS) and cross-linked polysilethylene (CPSE) precursors [6, 15] have been obtained in two steps from dichlorovinylsilane using hydrolysis/condensation and hydrosilylation (catalyised by hexachloroplatinic acid) according to



$$\mathrm{ViHSiCl_2} \xrightarrow{\text{Hydrolysis}} (\overset{\mathrm{H}\ \ =\!\!\diagdown}{\text{–Si–O–}})_n \xrightarrow{\text{Hydrosilylation}} \mathrm{COVS} \qquad (1)$$



$$\mathrm{ViHSiCl_2} \xrightarrow{\text{Hydrosilylation}} (\overset{\mathrm{Cl}\ \mathrm{Cl}}{\text{–Si–}}\mathrm{CH_2CH_2}\text{–})_n \xrightarrow{\text{Hydrolysis}} \mathrm{CPSE} \qquad (2)$$

All these precursors have been characterized using ^{29}Si CP-MAS NMR and elemental analysis. The main structural units present in these precursors (according to ^{29}Si MAS NMR) and their atomic composition are given in Table I.

2.2. Preparation of the glasses

The pyrolysis of silicon oxycarbide glasses was performed in a STA409 Netzsch thermobalance under argon flow. Typically, ~ 800 mg of the precursor in an alumina crucible were heated at a rate of 10 °C min^{-1} to 900 or 970 °C depending on the samples and then annealed for 30 min at this temperature. The composition of the glasses, derived from elemental analysis, is reported in Table II, together with the rule-of-mixtures composition [18]. All these glasses incorporate significant amounts of excess carbon, as can be seen from the rule-of-mixtures composition, which corresponds to the composition of the glasses if they were composed of the stable phases SiO_2, SiC and C, as expected if the high-temperature phase separation was complete.

2.3. NMR spectroscopy

Solid-state ^{29}Si NMR spectra were obtained on a Brucker FT-AM 300 spectrometer at 59.62 MHz resonance frequency for ^{29}Si, using magic angle spinning (MAS) (spinning frequency 4.1 kHz). The spectra of the polysiloxane precursors were recorded with cross-polarization (CP) using a pulse angle of 90 °,

TABLE I Characterization of the precursors

Precursor	Main structural units (^{29}Si chemical shifts)[a]	Atomic composition[b]
COVS	$SiVi(CH_2CH_2-)(O-)_2$ (– 33 p.p.m.) $SiH(CH_2CH_2-)(O-)_2$ (– 33 p.p.m.) $Si(CH_2CH_2-)_2(O-)_2$ (– 19.5 p.p.m.)	$SiO_{0.99}C_{2.13}H_{4.24}$
CPSE	$Si(CH_2CH_2)_2(OH)(O-)$ (– 12 p.p.m.) $Si(CH_2CH_2-)(O-)_2$ (– 19.5 p.p.m.)	$SiO_{1.24}C_{2.01}H_{4.26}$
T/D	$Si(Me)(O-)_3$ (– 65 p.p.m.) $Si(Me)_2(O-)_2$ (– 20 p.p.m.)	$SiO_{1.32}C_{1.37}H_{3.94}$
T	$Si(Me)(O-)_3$ (– 65 p.p.m.)	$SiO_{1.65}C_{1.02}H_{3.14}$
D/Q	$Si(Me)_2(O-)_2$ (– 20 p.p.m.) $Si(O-)_4$ (– 109 p.p.m.)	$SiO_{1.93}C_{1.19}H_{3.15}$

[a] CP/MAS ^{29}Si NMR.
[b] Oxygen determined by difference.

TABLE II Composition of the glasses

Precursor	Pyrolysis temperature (°C)	Atomic composition[a]	Rule-of-mixtures composition[b]
COVS	900	$SiO_{1.14}C_{1.74}$	0.57 SiO_2 + 0.43 SiC + 1.31 C
CPSE	900	$SiO_{1.29}C_{1.42}$	0.65 SiO_2 + 0.35 SiC + 1.07 C
T/D	970	$SiO_{1.57}C_{0.66}$	0.79 SiO_2 + 0.21 SiC + 0.45 C
T	900	$SiO_{1.69}C_{0.80}$	0.85 SiO_2 + 0.15 SiC + 0.65 C
D/Q	970	$SiO_{1.75}C_{0.37}$	0.88 SiO_2 + 0.12 SiC + 0.25 C

[a] Oxygen determined by difference, hydrogen (usually ≤ 0.5%) neglected.
[b] Moles relative to silicon.

a contact time of 2 ms and a recycling delay of 10 s. The spectra of the glasses were recorded without cross-polarization; 1000–2000 transients were recorded, using a pulse angle of 30° and a recycling delay of 60 s. Considering the high number of scans necessary to obtain an acceptable signal to noise ratio, the number of different sites (5) and their concentration, it was not possible to determine the spin lattice relaxation times. However, preliminary experiments performed with pulse angles ranging from 30°–90° and recycling delays ranging from 10–300 s showed that the above conditions afforded reasonably quantitative spectra, in acceptable accumulation times. Indeed, the O/Si ratios determined by integration of the spectra are in good agreement with the ratios derived from the elemental analysis. All spectra were referenced to an external TMS standard.

2.4. Elemental analysis

Elemental analyses were performed by the "Service Central d'Analyses" of CNRS (Vernaison, France).

3. Results

The ^{29}Si MAS NMR spectra of the five glass samples are displayed in Fig. 1. In all cases, a distribution of $\underline{Si}O_xC_{4-x}$ tetrahedral sites is observed. This distribution depends on the composition of the glass: the relative amount of "Si–C rich" tetrahedra increases when the O/Si ratio decreases. The chemical shifts and the widths of the corresponding peaks are very close to those reported by Lipowitz and Turner for $\underline{Si}O_xC_{4-x}$ sites in Nicalon silicon oxycarbide fibres pyrolysed at 1200 °C [16]. The percentage of each $\underline{Si}O_xC_{4-x}$ site, derived from the NMR spectra using integration and deconvolution, is reported in Table III. The good agreement between the O/Si ratio in the glasses derived from these data and the ratios obtained by elemental analysis confirms that the NMR spectra are reasonably quantitative. Actually, the only difficulty in the deconvolution of the spectra is the estimation of the amount of $\underline{Si}C_4$ sites, the concentration of which is very low, even in COVS glass.

The simplest structural model for silicon oxycarbide species would be a random distribution of Si–O and Si–C bonds. In such a model, the probability of finding a site $\underline{Si}O_xC_{4-x}$, $P(SiO_xC_{4-x})$, depends only on the probabilities of finding Si–O and Si–C bonds in the oxycarbide phase

$$P(SiO_xC_{4-x}) \quad = \quad \frac{4!}{x!(4-x)!}(p_{Si-O})^x(p_{Si-C})^{4-x} \quad (3)$$

Considering that practically all the oxygen atoms in the oxycarbide glasses are bonded to silicon atoms in Si–O–Si bridges and that silicon atoms are bonded to oxygen and carbon atoms only, p_{Si-O} and p_{Si-C} depend on the O/Si ratio of the glass

$$p_{Si-O} = (O/Si)/2$$

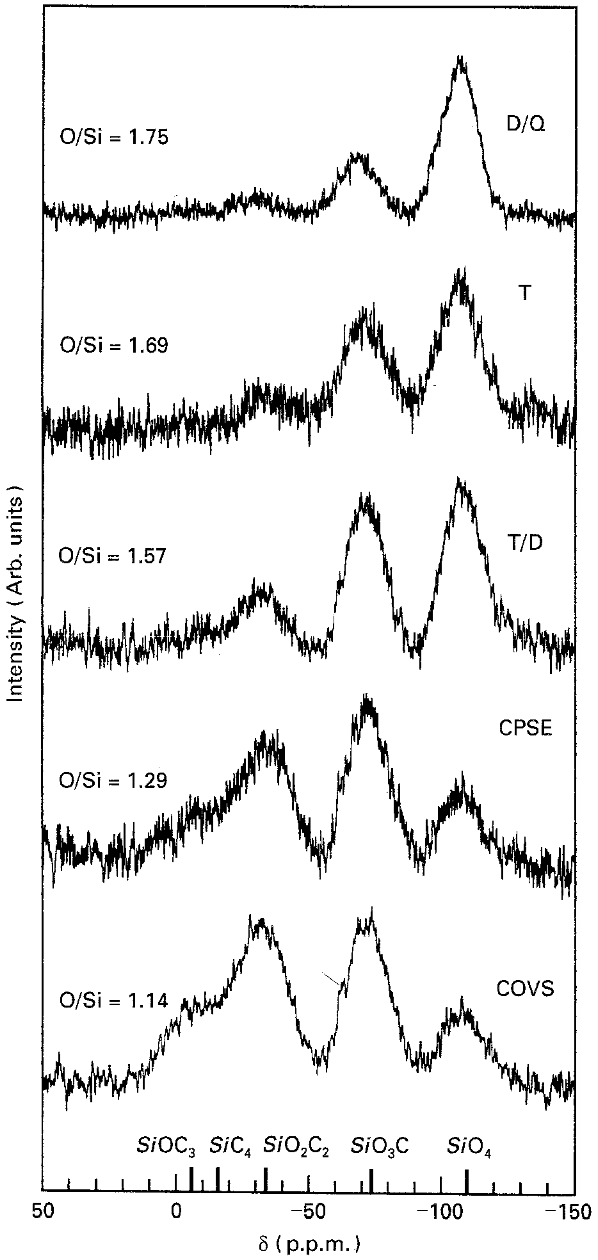


Figure 1 Experimental ^{29}Si MAS NMR spectra of the glasses. The name of the precursor is reported on the right of each spectrum, while the O/Si ratio (determined by elemental analysis) is shown on the left.

TABLE III Percentages of $\underline{Si}O_xC_{4-x}$ tetrahedral sites and O/Si ratio in the glasses derived from ^{29}Si MAS–NMR spectra

Precursor (O/Si) (elemental analysis)	%$\underline{Si}O_4$ – 108 p.p.m.	%$\underline{Si}O_3C$ – 72 p.p.m.	%$\underline{Si}O_2C_2$ – 32 p.p.m.	%$\underline{Si}OC_3$ – 5 p.p.m.	%$\underline{Si}C_4$ – 15 p.p.m.	O/Si (NMR)
COVS[a] (1.14)	15	33	35	15	3	1.22
CPSE[a] (1.29)	18	38	32	10	2	1.30
T/D[b] (1.57)	42	39	16	3	–	1.60
T[a] (1.69)	49	38	13	–	–	1.69
D/Q[b] (1.75)	65	27	8	–	–	1.79

Pyrolysed for 30 min under argon at [a] 900 °C, [b] 970 °C.

TABLE IV Percentages of $\underline{Si}O_xC_{4-x}$ tetrahedral sites calculated for various O/Si ratios assuming a random distribution of Si–O and Si–C bonds

O/Si	$\%\underline{Si}O_4$	$\%\underline{Si}O_3C$	$\%\underline{Si}O_2C_2$	$\%\underline{Si}OC_3$	$\%\underline{Si}C_4$
1.1	9.15	29.95	36.75	20.05	4.10
1.2	12.96	34.56	34.56	15.36	2.56
1.3	17.85	38.45	31.05	11.15	1.50
1.4	24.01	41.16	26.46	7.56	0.81
1.5	31.64	42.19	21.09	4.69	0.39
1.6	40.96	40.96	15.36	2.56	0.16
1.7	52.20	36.85	9.75	1.15	0.05
1.8	65.61	29.16	4.86	0.36	0.01

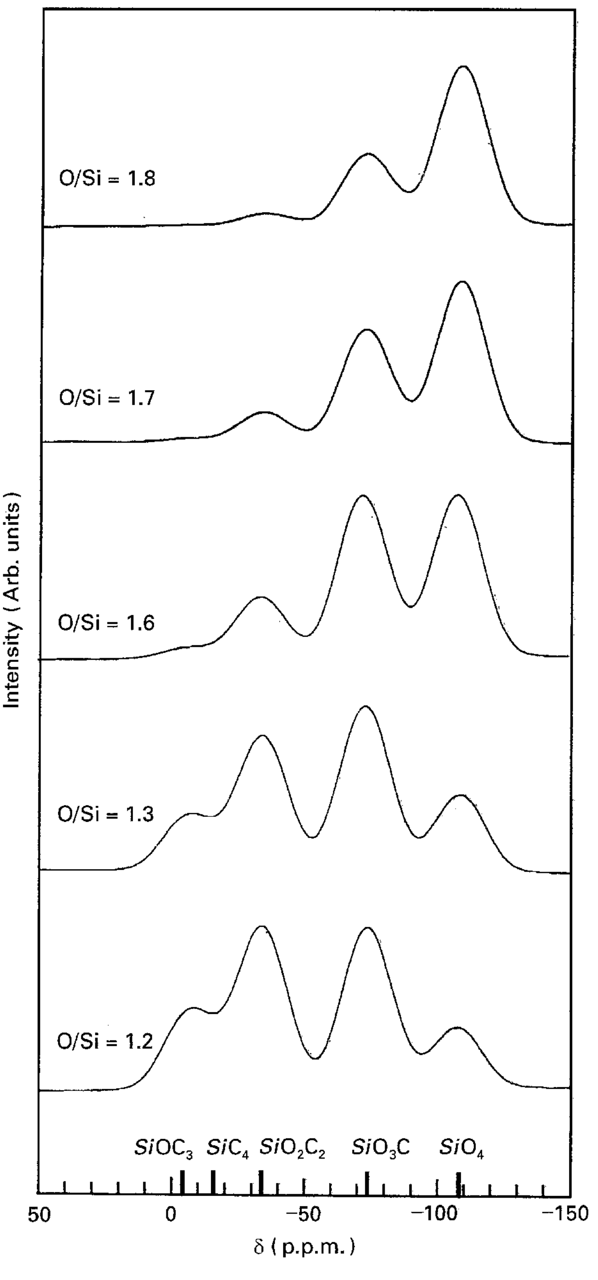


Figure 2 Theoretical ^{29}Si MAS NMR spectra of silicon oxycarbide glasses with different O/Si ratios, calculated assuming a purely random distribution of Si–O and Si–C bonds. The parameters used for the simulation are chemical shifts: $\underline{Si}O_4$, − 108 p.p.m., $\underline{Si}O_3C$, − 72 p.p.m., $\underline{Si}O_2C_2$, − 32 p.p.m., $\underline{Si}OC_3$, − 5 p.p.m., $\underline{Si}C_4$, − 15 p.p.m.; peak shape, gaussian; width at half-maximum, 22 p.p.m.

and

$$p_{\text{Si-C}} = 1 - p_{\text{Si-O}} \tag{4b}$$

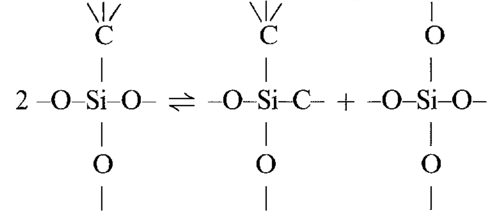
The percentages of $\underline{Si}O_xC_{4-x}$ sites thus calculated for an O/Si ratio between 1.1 and 1.8 are given in Table IV. These values have been used to simulate the ^{29}Si NMR spectra expected for oxycarbide glasses with a perfectly random environment of the silicon atoms. Thus, the spectra reported in Fig. 2 have been obtained assuming gaussian shapes and standard chemical shifts and widths for the five $\underline{Si}O_xC_{4-x}$ peaks. From these spectra it may be seen that even a slight modification of the O/Si ratio leads to a significant modification of the distribution of the peaks.

3. Discussion

The experimental and calculated values reported in Tables III and IV as well as the experimental and calculated spectra reported in Figs 1 and 2, agree quite well considering the experimental uncertainties. Thus, the silicon oxycarbide phase in our glasses may be described as a purely random distribution of Si–O and Si–C bonds, building an independent single phase whatever the composition. In all cases, the structure of the oxycarbide phase depends on the O/Si ratio of the glass only, and is not reminiscent of the non-random structure of the precursor. This indicates that the environment of silicon atoms has reached a metastable equilibrium state under our pyrolysis conditions.

If we assume that all the carbon atoms in the oxycarbide phase are bonded to silicon atoms only, as in silicon carbide [19], these oxycarbide phases may be seen as an assembling of $\underline{C}Si_4$ tetrahedra and Si–O–Si bridges as structural units. Schematic representations of such a structure in two dimensions are given in Fig. 3. However, the environment of carbon atoms is still open to question and the actual structure is probably more complicated, incorporating many defects such as residual C–H bonds, dangling bonds or even C–C bonds.

We have recently reported the occurrence of solid-state, reversible redistribution reactions involving the exchange of Si–O bonds with Si–C bonds during the pyrolysis of cross-linked methylpolysiloxanes [11]. These reactions leads to a modification of the environment of the silicon atoms as examplified in scheme I



$$2\ \begin{array}{c} \backslash|/ \\ \text{C} \\ | \\ -\text{O}-\text{Si}-\text{O}- \\ | \\ \text{O} \\ | \end{array} \rightleftharpoons \begin{array}{c} \backslash|/ \\ \text{C} \\ | \\ -\text{O}-\text{Si}-\text{C}- \\ | \\ \text{O} \\ | \end{array} + \begin{array}{c} | \\ \text{O} \\ | \\ -\text{O}-\text{Si}-\text{O}- \\ | \\ \text{O} \\ | \end{array}$$

Scheme I Schematic representation of the redistribution of Si–O and Si–C bonds between two $\underline{Si}O_3C$ units, leading to the formation of one $\underline{Si}O_2C_2$ and one $\underline{Si}O_4$ unit.

The exchange of Si–O and Si–C bonds starts at about 500–600 °C, before the degradation of the organic groups, and may lead to the formation of volatile silanes or siloxanes, which entails a decrease in the pyrolysis yield and an increase in the O/Si ratio of

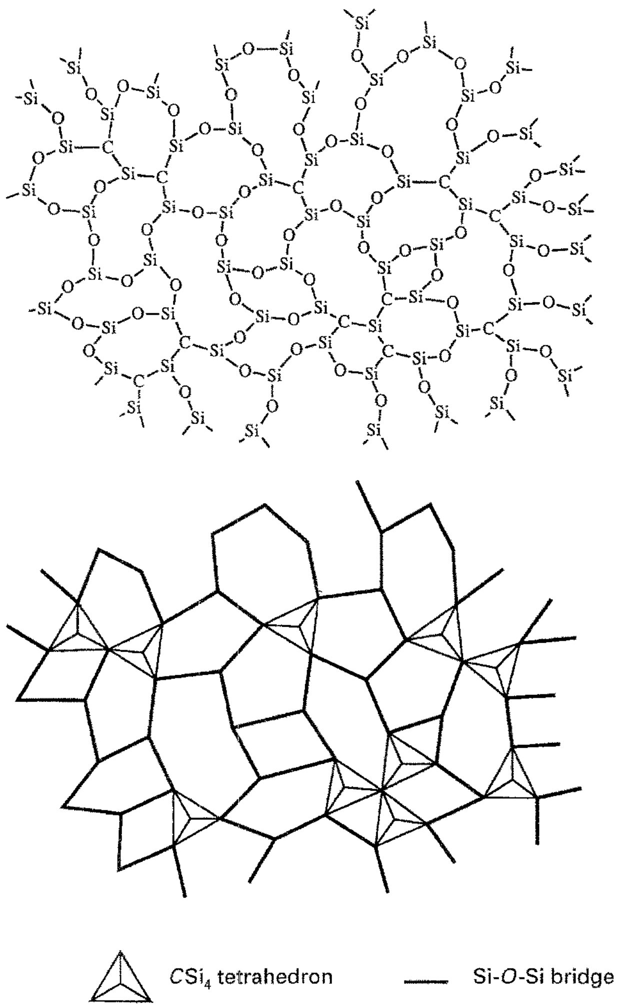


Figure 3 Schematic two-dimensional representation of a random silicon oxycarbide network (fourth bond to silicon and carbon omitted).

the glass [13, 14]. These reactions go on at higher temperature, during and after the degradation of organic groups, leading to a continuous modification of the environment of the silicon atoms in the solid residue [6, 7, 15].

The occurrence of these redistribution reactions during the pyrolysis treatment provides an explanation for the formation of the random environment of silicon atoms in oxycarbide glasses. This may be illustrated by the example of the glasses derived from the D/Q and the T precursors. The environments of the silicon atoms in these precursors are completely different: the D/Q precursor contains $\underline{Si}O_2C_2$ and $\underline{Si}O_4$ sites and the T precursor contains $\underline{Si}O_3C$ sites only. On the other hand, the environments of the silicon atoms in the glasses are similar due to the very close O/Si ratio in these glasses. This situation may readily be accounted for by the exchange of Si–O and Si–C bonds; in the case of the T precursor, $\underline{Si}O_4$ and $\underline{Si}O_2C_2$ units may be formed from $\underline{Si}O_3C$ units according to [6, 13, 14]

$$2\underline{Si}O_3C \rightarrow \underline{Si}O_2C_2 + \underline{Si}O_4 \qquad (5)$$

In the case of the D/Q precursor, the formation of the $\underline{Si}O_3C$ units may simply arise from the reverse reaction [5, 13, 14]

$$\underline{Si}O_2C_2 + \underline{Si}O_4 \rightarrow 2\underline{Si}O_3C \qquad (6)$$

The continuation of the redistributions should lead to the formation of $\underline{Si}OC_3$ or $\underline{Si}C_4$ sites, as for instance

$$\underline{Si}O_2C_2 + \underline{Si}O_3C \rightarrow \underline{Si}OC_3 + \underline{Si}O_4 \qquad (7)$$

$$SiOC_3 + SiO_3C \rightarrow SiC_4 + SiO_4, \text{ etc.} \qquad (8)$$

The fact that no $\underline{Si}OC_3$ or $\underline{Si}C_4$ peaks are detected in the ^{29}Si MAS NMR spectra of the glasses may simply be ascribed to the high O/Si ratio in these glasses (about 1.7–1.8), leading to very low concentrations of these sites, lower than 2% (see Table IV). Actually, the spectrum of the glass obtained from the CPSE precursor (O/Si $\cong$ 1.3) shows the formation of such sites from the starting $\underline{Si}O_2C_2$ sites [15]. Thus, all the following redistribution equilibria must be involved in the pyrolysis of polysiloxane precursors

$$\underline{Si}O_xC_{4-x} + \underline{Si}O_yC_{4-y} \rightleftharpoons \underline{Si}O_{x-1}C_{5-x} + \underline{Si}O_{y+1}C_{3-y} \qquad (9)$$

where $0 < x \leq 4$ and $0 \leq y < 4$.

The redistribution equilibria of organometallic compounds in the liquid or the gaseous state have been extensively studied for synthetic purposes and thermochemistry studies [20–22]. It was shown that the enthalpy change, (ΔH), due to the redistribution is usually small. Actually, as there is no generation nor loss of any bonds due to the substituent exchanges, ΔH is equal to zero if the bond energies are additive. In that case (ideal random case), the yields of the redistribution products *at the equilibrium* are given by the law of random statistics (if the reaction is performed under homogeneous conditions). Conversely, deviations from the random distribution provide a measurement of the ΔH values, i.e. of the non-additivity of bond energies. If the reaction is performed under heterogeneous conditions, for instance if one of the reaction products is distilled or precipitates, the equilibria are displaced towards the quantitative formation of this product, according to the Le Chatelier's principle.

This reasoning may be applied to the redistributions of Si–O and Si–C bonds involved in our case. The fact that a random distribution of $\underline{Si}O_xC_{4-x}$ sites is observed whatever the starting distribution in the precursors suggests that a metastable equilibrium state is reached in our glasses. It also shows that the redistributions are *entropically controlled*, i.e. the ΔH of these reactions are negligible. Thus, for moderate pyrolysis temperatures (< 1000 °C), the only driving force for the formation of the environment of silicon atoms in the glasses is the increase of the entropy. Actually, this random environment may be formed only because the phase separation to the stable SiO_2 and SiC phases requires extensive diffusion, and is only possible at higher temperature.

Indeed, for high pyrolysis temperatures the environment of silicon atoms is no more random: the NMR spectra of the glasses obtained at 1200 °C show a significant increase in the relative amount of $\underline{Si}O_4$ and $\underline{Si}C_4$ sites, and the silicon oxycarbide phase in glasses obtained at 1400 °C may rather be described as a mixture of amorphous silica and silicon carbide crystallites [6, 15, 17, 23]. The conversion of a random mixture of Si–O and Si–C bonds to a mixture of SiC and SiO_2 implies a decrease of the configurational entropy, and the driving force for this process is provided by the exothermic crystallization of silicon carbide.

The phase separation to SiC and SiO_2 may be viewed as a continuation of the redistribution reactions, involving the same equilibria. However, the exchange of Si–O and Si–C bonds between a $\underline{Si}O_xC_{4-x}$ site and a $\underline{Si}C_4$ site incorporated in a SiC crystal would be an endothermic reaction, and therefore the redistribution would be no longer random. In other words, the redistributions take place under heterogeneous conditions, and the growth of SiC crystals is equivalent to a consumption of the $\underline{Si}C_4$ sites, which displaces the equilibria towards the formation of a mixture of $\underline{Si}C_4$ and $\underline{Si}O_4$ sites.

The composition of the oxycarbide phase should also play an important role in the crystallization of SiC, and thus on the possibility of obtaining random glasses. However, we observe a random structure for all our glasses whatever their composition. It must be noted that, even for the lowest O/Si ratio investigated here (O/Si = 1.2), the percentage of $\underline{Si}C_4$ tetrahedra in the random glass is very low, less than 3%. Consequently, the probability of finding several adjacent $\underline{Si}C_4$ units and thus of reaching a critical size allowing the growth of SiC crystals is low. In addition, defects in the environment of the carbon atoms (dangling bonds, residual C–H bonds), as well as the presence of excess carbon, might also hinder the crystallization of SiC.

We have no proof concerning the mechanism of the redistribution reactions involved in the formation of the environment of silicon atoms in oxycarbide glasses. Concerted mechanisms involving four-centre intermediates are commonly accepted for redistribution reactions performed at moderate temperature [1, 2]. In our case, such a mechanism might be operative in the temperature range 500–700 °C, before the complete degradation of the organic groups. On the other hand, at higher temperature (800–900 °C), extensive cleavage of Si–C and Si–O bonds take place, and a free-radical mechanism (not necessarily concerted), involving the formation and the combination of the free-radicals Si·, Si–O·, C·, and Si–C· appears more probable.

5. Conclusions

The environment of silicon atoms in metastable oxycarbide glasses obtained by pyrolysis at moderate temperatures (< 1000 °C) of polysiloxane precursors may be described as a purely random distribution of Si–O and Si–C bonds. This result shows that, although the nature of the precursor governs the composition of the glass (O/Si ratio and excess carbon content) the environment of silicon atoms in these glasses depends on the O/Si ratio of the glass only and is not related to the structure of the precursor.

The formation of the environment of silicon atoms in the glasses may be accounted for by the occurrence of reversible, entropically controlled redistributions of Si–O and Si–C bonds, which start at ~ 500 °C and reach a metastable equilibrium state at about 900 °C. The random distribution of Si–O and Si–C bonds observed shows that, in the absence of crystallization, the bond energies may be considered as additive. At higher temperature, the increased diffusion of the atoms allows for the energetically favoured crystallization of silicon carbide, which leads to a consumption of the Si–C bonds and to the phase separation to SiC and SiO_2.

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