Silicon oxycarbide glasses derived from polymeric networks with different molecular architecture prepared by hydrosilylation reaction

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Abstract We have prepared two polysiloxane networks with different molecular structures and similar compositions as suitable precursors of silicon oxycarbide glasses (SiOC), in order to understand the influence of the molecular architecture of the polymeric networks on the structure of these glasses. The structural evolution from the polymeric precursor to glasses was followed by solid-state ^{29}Si magic angle spinning nuclear magnetic resonance (^{29}Si MAS NMR) and FTIR spectroscopies, X-ray diffraction, thermogravimetric analysis, and density measurements up to 1000 °C. The high-temperature behavior of SiOC glasses, up to 1600 °C, was studied by X-ray diffraction, and ^{29}Si MAS NMR spectroscopy. The formation of carbosilane bridges in the polymeric networks during the hydrosilylation reaction contributed to the generation of a larger amount of carbidic sites in the final products. An increase in the pyrolysis temperature led to a distribution of silicon sites and crystallization profiles that depended on the molecular architecture of the polymeric precursors.

Introduction

An impressive amount of research effort has been directed toward the synthesis of covalent ceramics from the pyrolysis of polymeric precursors [1–4]. This type of ceramics offers advantages such as applicability of polymer-processing techniques, homogeneity of precursors at the molecular level, lower processing temperatures as compared with conventional powder sintering methods, and possible synthesis of new compounds [5–7]. However, the main advantage of this approach is the possibility of building up polymers from molecular units and tailoring the molecular structure, so that the nano- and/or microstructure as well as the desired phases in the final glass or ceramic product can be dictated. Although the composition and the molecular structure of the polymeric network, the curing process, the pyrolysis cycle, and the atmosphere have been pointed out as variables that determine the properties of the product, and consequently their applications, it is still rather difficult to predict the appropriate polymeric architecture for the target glass or ceramic products under specific pyrolysis condition. The first paper dealing with a systematic structural characterization of silicon oxycarbide glasses (SiOC) regarding the above parameters was published by Babonneau et al. [8].
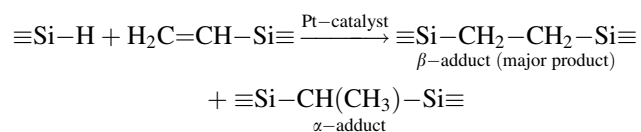
Control of the molecular architecture and knowledge about the structural evolution, through which the cross-linking and the polymer-to-ceramic transformation processes occur, are important parameters to consider if the performance of the material is to be improved. These parameters are particularly relevant in relation to the range of polymer-to-ceramic transformation temperatures and composition of the ceramic product.

Among some well-established methods for the processing of polymeric precursors is the hydrosilylation reaction, one of the most often employed routes in this area [9–13]. This reaction corresponds to the addition of a Si–H group to unsaturated moieties, usually in the presence of a catalyst [2, 10, 14, 15] or in a thermally-induced process [9, 16, 17]. Each reactive Si group gives rise to a Si–C$_x$–Si

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site, where $x = 1$ or 2, with high selectivity toward the ethylene bridges, as represented below:

$$\equiv Si-H + H_2C=CH-Si\equiv \xrightarrow{Pt-catalyst} \underset{\beta-adduct\ (major\ product)}{\equiv Si-CH_2-CH_2-Si\equiv}$$

$$+ \underset{\alpha-adduct}{\equiv Si-CH(CH_3)-Si\equiv}$$

Due to the large number of different commercially available building blocks, including monomers, oligomers, and polymers, a wide variety of precursors can be employed in this strategy [12, 14]. Hydrosilylation is a versatile reaction that provides many benefits in relation to other crosslinking mechanisms: It can occur at room temperature in the presence of a catalyst, but it can also be accelerated by heat. As a result, the time spent on preparation is reduced, and no byproducts are formed. Furthermore, the shrinkage in the "green body", the undesired feature usually observed in the sol–gel process, is minimized. However, the most important feature of the hydrosilylation reaction is the incorporation of carbosilane bridges ($Si-C_x-Si$) in the polymeric network. The preparation of silicon oxycarbide with an O/Si ratio equal to 1 ratio is not straightforward, although this ratio can be found in a linear polydiorganosiloxane, such as poly(dimethylsiloxane) (PDMS), in which pyrolysis leads to 0 % residue [15, 18]. Carbosilane bridges allow for better control of the carbon content without decreasing the crosslinking density of the polysiloxane networks, thereby culminating in materials with controlled O/Si ratios. The presence of these bridges has also been pointed out as being responsible for the better incorporation of carbon in the oxycarbide glasses, as compared with those derived from alkoxysilanes containing Si–H and/or Si–CH$_3$ groups by the sol–gel process [19–23]. In contrast to the hydrolysis-condensation reactions of alkoxysilanes commonly utilized during the sol–gel process, hydrosilylation reactions enables the formation of Si–C–C–Si or Si–C–Si bridges in the polymeric network, which contribute to the generation of a greater amount of SiC$_4$ molecular sites in the final product.

The current study focuses on a comparative study of the structural evolution from two different polymeric networks based on polysiloxane structures prepared by hydrosilylation reaction; i.e., polymers bearing Si–CH$_2$–CH$_2$–Si bridges as cross-linked units. We obtained the polymeric networks CP1 and CP2 via a Pt-catalyzed hydrosilylation reaction between 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D$_4$Vi) and poly(hydromethylsiloxane) (PMHS) or 1,3,5,7-tetramethylcyclotetrasiloxane (D$_4$H), respectively. We aimed to understand the influence of the molecular architecture on the structure of the final SiOC glasses. According to the previously published data [2, 9, 15, 18, 24–26], such kind of network is a promising ceramic precursor of SiOC glasses. We monitored the pyrolysis up to 1000 °C by thermal and spectroscopic techniques such as thermogravimetric analysis (TGA); Fourier transform infrared (FTIR) and ^{29}Si and ^{13}C magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopies; X-ray diffraction (XRD); and density measurements. We subjected the resulting silicon SiOC glasses to further pyrolysis at selected temperatures, up to 1600 °C, and evaluated their high temperature crystallization behavior by X-ray diffraction, and also by ^{29}Si MAS NMR for the CP2-derived samples. We compared the results with respect to the different molecular architectures of the precursors and the final products.

Experimental procedure

Preparation of the samples

Polysiloxane networks were obtained from homogeneous mixtures of PMHS ($\overline{M_n}$ = 2300 g/mol) (Dow Corning, Midland, WI, USA) and 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D$_4$Vi) (Dow Corning, Midland, WI, USA), coded CP1, and from 1,3,5,7-tetramethylcyclotetrasiloxane (D$_4$H) (Dow Corning, Midland, WI, USA) and D$_4$Vi, labeled CP2. The preparation of these polysiloxane precursors involved a Pt-catalyzed hydrosilylation reaction having 2–3.5 % platinum divinyltetramethyldisiloxane in vinyl-terminated PDMS solution (ABCR GMBH Co., Kalsruhe, Germany) as catalyst, without the use of a solvent. The preparation is described in detail in refs. [2, 10, 26]. The PMHS/D$_4$Vi and D$_4$Vi/D$_4$H weight ratios employed during the synthesis of the polymeric networks CP1 and CP2 were 50:50 and 59:41, respectively, in order to obtain the same number of Si–H/Si–Vi groups. After the curing procedure, the polymeric networks were subjected to pyrolysis under Ar atmosphere. Bulk pyrolysis experiments of the polymeric networks were carried out in a tube furnace (EDGcon 5P, EDG, SP, Brazil) equipped with an internal alumina tube and a temperature controller, under atmosphere of flowing argon (100 mL/min), up to 1000 °C. A typical heating cycle involved heating of the sample to 200 °C, at 5 °C/min; maintenance of the sample at 200 °C for 60 min; further heating of the sample to 400 °C, at 5 °C/min; maintenance of the sample at this plateau for 90 min; additional heating of the sample to 1000 °C, at 2 °C/min, followed by maintenance of the sample at this temperature for 120 min. Finally, the samples were cooled down to room temperature at 2 °C/min. Samples were also submitted to pyrolysis at final temperatures ranging between 1200 and 1600 °C. Pyrolysis was carried out in a Thermolyne F59340-CM instrument, in the same conditions described above.
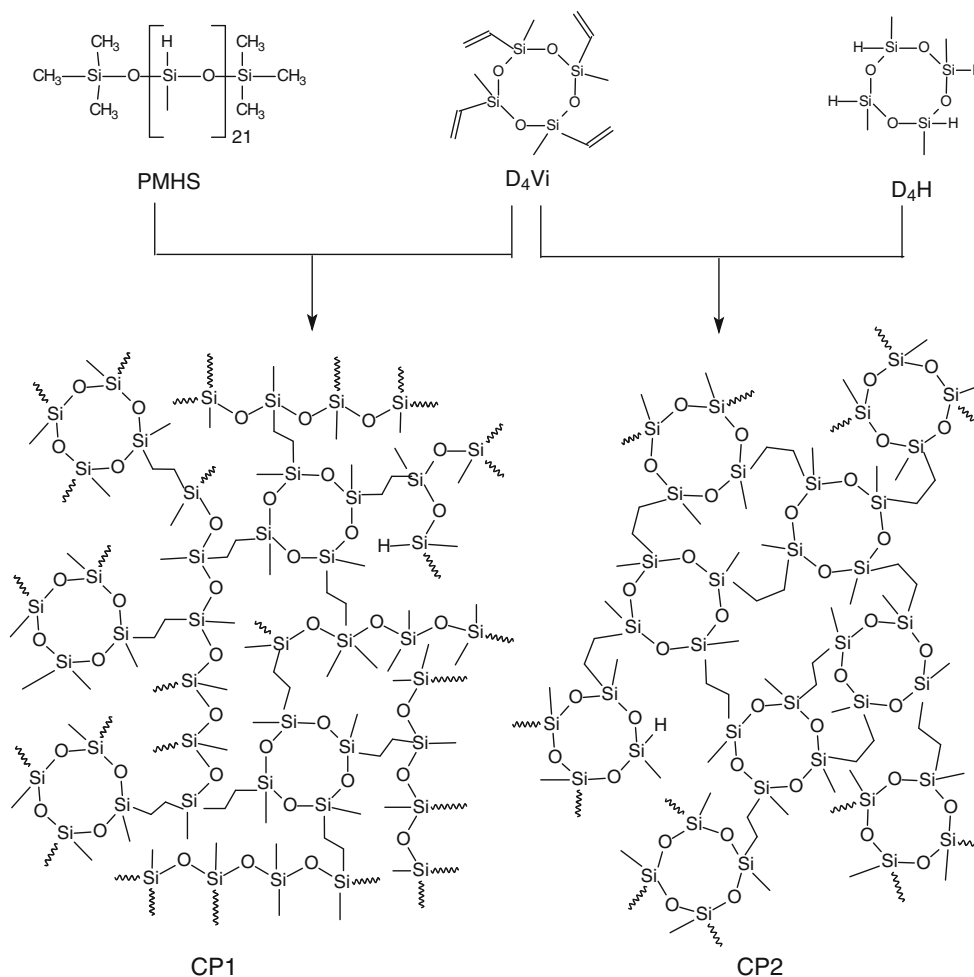
Fig. 1 Molecular structure of the siloxanes PMHS, D_4Vi, and D_4H and the corresponding idealized molecular structure of the polymeric networks CP1 and CP2 obtained by hydrosilylation reaction
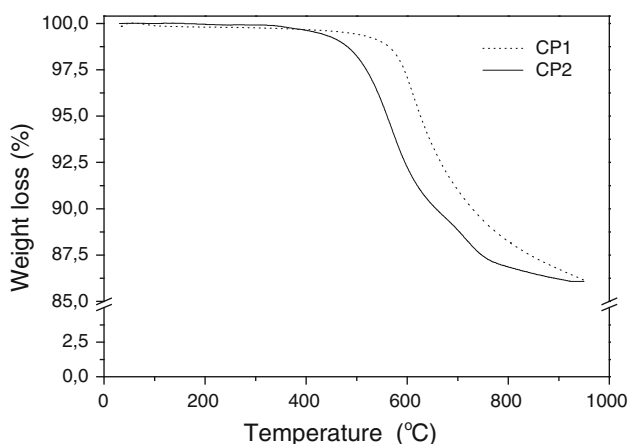

Fig. 2 TGA curves recorded during pyrolysis of CP1 and CP2 under argon atmosphere

Characterization techniques

The structural evolution from the polymeric network precursors to ceramic materials was investigated by FTIR using a transmission Fourier transform spectrometer (Bomem Hartmann & Braun, MB series, Quebec, Canada) operating between 4000 and 400 cm^{-1}, at 4 cm^{-1} resolution, by means of the conventional KBr pellet method. ^{29}Si and ^{13}C solid-state nuclear magnetic resonance (NMR) experiments were carried out on a spectrometer (Bruker AC 300/P MHz, Karlsruhe, Germany) operating at 59.62 and 75.48 MHz, respectively. Spectra were recorded by applying magic angle spinning (MAS), with a 30° pulse of 7 μs and 60-s delay between pulses. On average, 1200 scans were necessary for a good signal-to-noise ratio to be achieved. ^{29}Si MAS NMR spectra were adjusted using Gaussian fit multi-peaks available

Fig. 3 FTIR spectra of CP1 and CP2 obtained at room temperature and after pyrolysis at 1000 °C
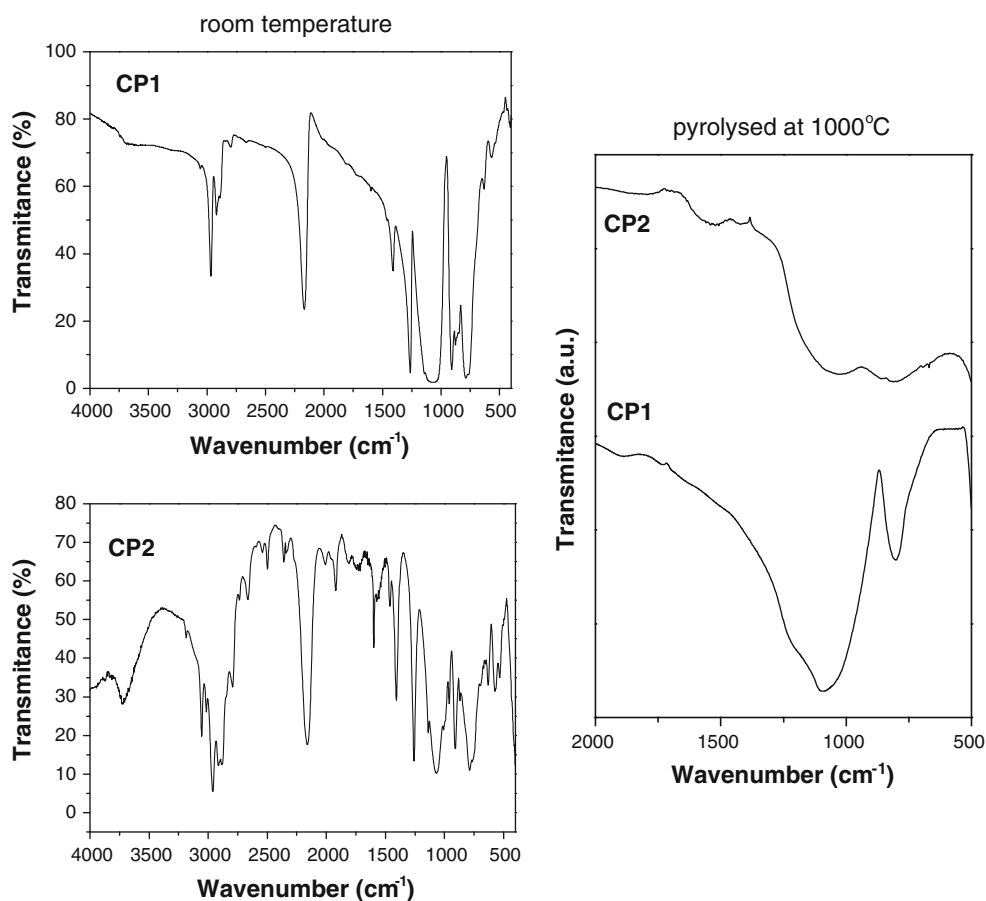
in Microcal Origin^{TM} 7.0 software. Thermogravimetric analyses (TGA) were performed in a thermobalance (2950 Thermal Analysis Instrument, TA Instrument, New Castle, DE, USA). Analyses were conducted using ∼10 mg of the polymer samples, in flowing nitrogen (100 mL/min), at a heating rate of 10 °C/min, up to 1000 °C. Density measurements were accomplished on a picnometer (Micromeritics 1305, Norcross, GA, USA). Samples were exhaustively purged with He before measurements. X-ray diffraction patterns (DRX) were recorded on a diffractometer (Shimadzu, model XRD-6000, Kyoto, Japan), using Cu Kα radiation. Carbon and hydrogen elemental analyses were carried out in an elemental analyzer (Perkin Elmer, model 2400) employing the procedure suggested in [27]. The accuracy was checked with reference samples, and the deviation was estimated to be around 5 %. The Si content in the ceramic products was evaluated by X-ray fluorescence in an X-ray equipment (Spectrace 5000, Tracor), using a cellulose filter. The oxygen content was estimated by difference.

Results and discussion

We prepared the polymeric networks CP1 and CP2 at room temperature via a Pt-catalyzed hydrosilylation reaction

between D$_4$Vi and PMHS or D$_4$H, respectively. Figure 1 displays an idealized molecular structure for the precursors as well as for the networks CP1 and CP2. Both polymeric networks consist of shaped transparent rubbery samples. CP1 and CP2 have the same O/Si = 1 molar ratio, a C/Si molar ratio of ≈1.5, but distinct molecular architecture. CP1 is a traditional silicon network based on a linear polymeric chain cross-linked by D$_4$Vi oligomers, whereas CP2 is a polycyclic silicon network similar to a "molecular sponge." Indeed, small angle X-ray scaterring (SAXS) measurements of this network revealed a low fractal dimension value (D parameter from the power-law region), which implies an open structure that probably results from the great steric hindrance experienced by the precursors during formation of the the network as well as the free volume of the cycles [10].

The polymeric networks CP1 and CP2 exhibit similar thermogravimetric behavior (Fig. 2). Although the network of CP1 is slightly more stable than that of CP2, the maximum degradation temperature obtained for CP1 is 10 °C (from DTG curves not shown) higher than the one observed for CP2. However, both samples furnish the same ceramic yield at 1000 °C (86 wt %), which is a direct consequence of the crosslinking density in the preceramic precursors [15].

Fig. 4 ^{29}Si MAS NMR spectra of the polymeric networks CP1 and CP2 submitted to pyrolysis for 2 h at various temperatures between 200 and 1000 °C
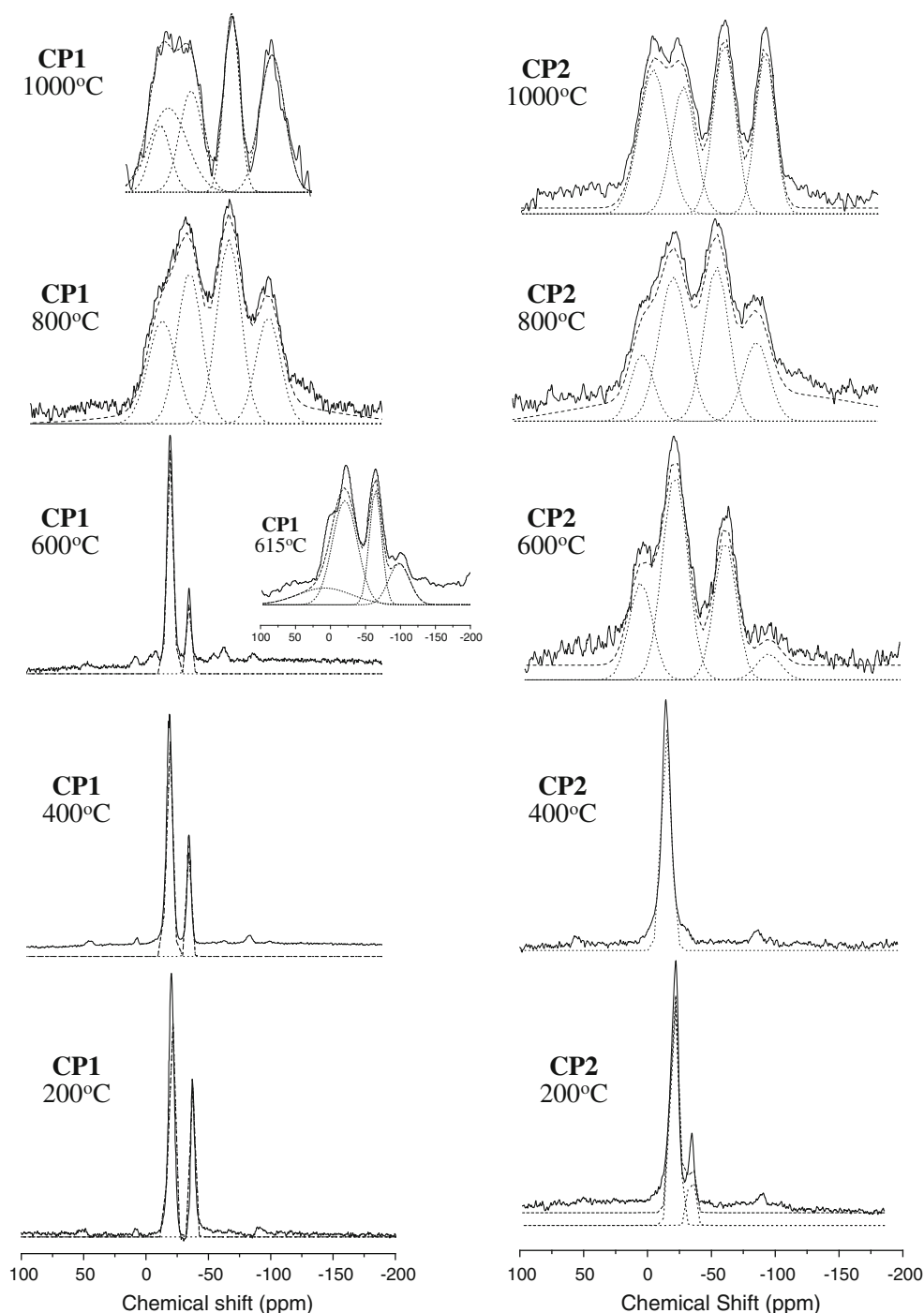
Figure 3 contains the FTIR spectra of CP1 and CP2 obtained at room temperature as well as the spectra of the resulting SiOC glasses obtained at 1000 °C. The spectra are similar and present the typical absorptions related to the C–H, Si–H, Si–O, C=C, and Si–CH$_3$ bonds of D$_4$Vi, PMHS, and D$_4$H [10, 15, 23]. The absorptions in the ranges 2960–2800 cm^{-1} and 1402–1261 cm^{-1} are related to aliphatic C–H (CH$_3$ and CH$_2$ groups). The band at 1080 cm^{-1} corresponds to v(Si–O–Si), and the one at 791 cm^{-1} can be

assigned to v(Si–C) and has contribution from Si–O–Si bonds. The most characteristic absorptions of the vinyl group in D$_4$Vi are v(C–H) and v(C=C) at 3061 and 1595 cm^{-1}, respectively. The strong band at 2160 cm^{-1} is typical of v(Si–H) absorption, suggesting that part of both groups still remain in the cured network, due to incomplete reaction. The spectra of samples CP1 and CP2 submitted to pyrolysis at 1000 °C display only two broad bands centred at 1030 and 800 cm^{-1}, which can be attributed to v(Si–O–Si)

Table 1 ^{29}Si MAS NMR characterization of SiOC glasses submitted to pyrolysis in flowing Ar at different temperatures

| Temperature °C	Sample	SiO$_4$ (%) δ (ppm)	SiO$_3$C (%) δ (ppm)	SiO$_2$C$_2$ (%) δ (ppm)	SiC$_4$ (%) δ (ppm)	SiOC$_3$ (%) δ (ppm)
800	CP1	21	32	30	17	–
		(−104)	(−71)	(−37)	(−14)	–
	CP2	18	27	26	29	–
		(−101)	(−69)	(−33)	(−7)	–
1000	CP1	26	21	18	24	11
		(−109)	(−70)	(−32)	(−10)	(−3)
	CP2	22	27	21	30	–
		(−105)	(−71)	(−37)	(−11)	–

Fig. 5 XRD patterns of ceramic products generated by pyrolysis for 2 h at various temperatures between 1000 and 1600 °C (peak assigned with *filled inverted triangle* corresponds to quartz from the mortar used to crush the sample)
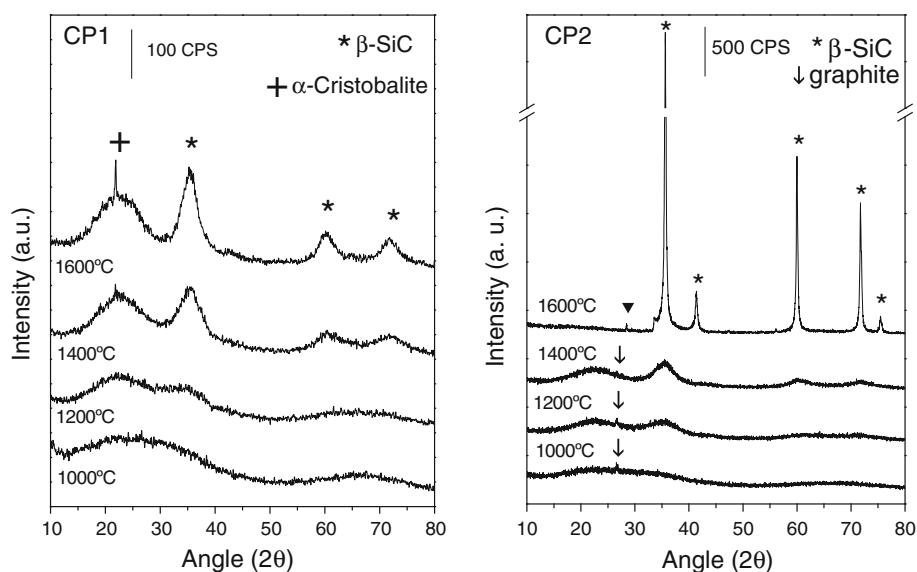
and ν(Si–C–Si), respectively [2, 15, 26, 28, 29]. The relative intensity of the band ascribed to Si–C bonds is higher for CP2 than CP1, indicating that the total amount of sites containing Si–C is larger in CP2.

The structural evolution of the polymeric networks CP1 and CP2 as monitored by ^{29}Si MAS NMR spectra can be found in Fig. 4. At 200 °C, the resonances at $\delta = -20$ and −37 ppm for CP1 and $\delta = -19$ and −33 ppm for CP2 can be assigned to D (C$_2$SiO$_2$) and D^H [C(H)SiO$_2$] or D^V [C(C=C)SiO$_2$] units, respectively [2, 9, 30–32]. At this temperature, 70 and 83 % of the functional groups of the precursor units are directly involved in the formation of the network (peaks at −20 and −19 ppm) in polymers CP1 and CP2, respectively. The remaining Si–H or Si–Vi groups (peaks at −37 and −33 ppm) were not able to participate in the hydrosilylation reaction. No residual Si–H or Si–C=C groups are detected for CP2 at 400 °C, whereas 20 and 12 % of these groups can be verified for CP1 at 400 and 600 °C, respectively. These results suggest that the organic-to-inorganic transformation is faster in CP2 compared with CP1. The more open structure of CP2 culminates

in complete crosslinking at 400 °C, affording a structure with 100 % of SiC$_2$O$_2$ sites. Moreover, in the case of CP2, heating at 600 °C is enough to promote reorganization reactions of the siloxane sites, as demonstrated by two other additional broad resonances centered at δ 6 and −63 ppm, assigned to C$_3$SiO and CSiO$_3$ sites. In contrast, some functional groups can be inaccessible to the hydrosilylation reaction in CP1. In this polymeric network, the organic-to-inorganic conversion starts only at 615 °C. Following the structural evolution promoted by pyrolysis, the redistribution of the Si sites is similar for both CP1 and CP2 up to 800 °C, with increase in the relative intensity of the resonances at δ −10 and −106 ppm, attributed to SiC$_4$ and SiO$_4$, respectively [2, 9, 26, 31, 32]. At 1000 °C, the products display the characteristic silicon oxycarbide glass spectrum with random distribution of the SiO$_4$, SiO$_3$C, SiC$_2$O$_2$, and SiC$_4$ sites for CP1 and CP2 [33]. The composition of each site is described in Table 1 for the samples obtained at 800 and 1000 °C. For both CP1 and CP2, the abundance of SiC$_4$ sites is higher than those usually observed in glass products obtained from the pyrolysis of alkoxysilane gels, which
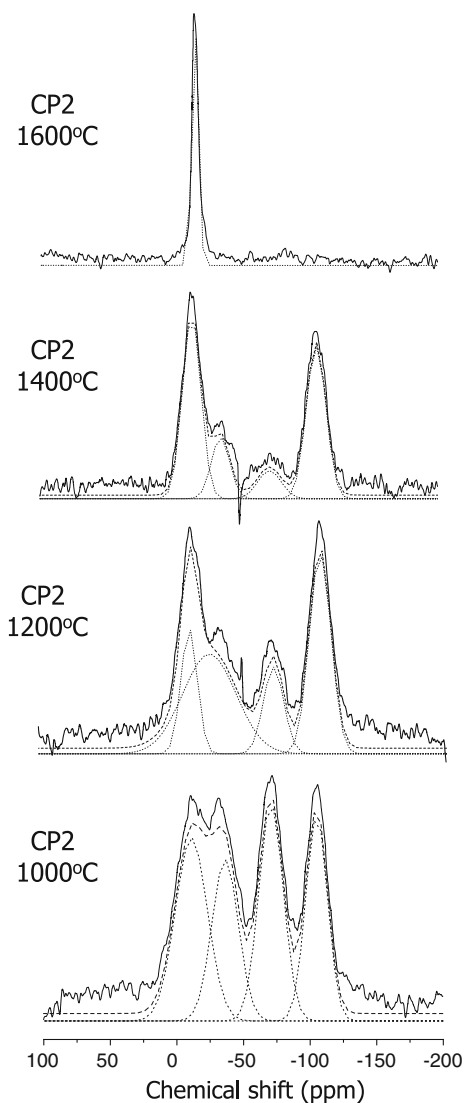
Fig. 6 ^{29}Si MAS NMR spectra of the CP2-derived sample submitted to pyrolysis for 2 h at various temperatures between 1000 and 1600 °C

consist primarily of SiO$_4$, SiO$_3$C, and SiC$_2$O$_2$ and contain a lower amount of or no SiC$_3$O and SiC$_4$ sites [21, 34]. In addition, the distribution of silicon sites in the CP1 and CP2-derived glasses is similar to the one observed in Blackglas^{TM} [35].

The densification processes up to 1000 °C undergone by CP1 and CP2 as a function of the temperature are similar. There is a higher increase in the density values from 600 to 800 °C, which is in agreement with the ^{29}Si MAS NMR data. The density values of CP1 and CP2 at 1000 °C are 2.1 ± 0.2 and 2.2 ± 0.2 g/cm^3, respectively. The XRD patterns of the CP1 and CP2 glass samples subjected to pyrolysis at 1000 °C are given in Fig. 5. The patterns are characteristic of amorphous materials, as expected for silicon oxycarbide glasses. At 1200 °C, the main diffractions

associated with β-SiC can be observed as very broad peaks with low intensity. This suggests the beginning of the crystallization process, as a consequence of the continuous reorganization of the silicon sites. These diffractions become more intense with rising pyrolysis temperatures, up to 1600 °C. At this final temperature, the CP2-derived product has pattern typical of pure β-SiC, with peaks at 35.6°, 41.3°, 60.0°, and 72.0° (2θ). It was observed before that for SiOC samples with an excess of "free" carbon phase in the glass network are better stabilized, at least until 1500 °C, toward the formation of β-SiC [36]. Such behavior is quite similar to the one observed for CP2. The CP1-derived product presents less intense and broad peaks relative to β-SiC, in addition to a broad halo centered at 21.9° (2θ), assigned to α-cristobalite, suggesting that the amorphous phase is a near-silica-structure for the silicon oxycarbide network [36]. The XRD pattern of CP2 obtained between 1000 and 1400 °C contains a very low intense peak centered at 26.5° (2θ), assigned to a lamellar structure, such as graphitic carbon [24]. The mean size of the β-SiC crystals as estimated by the Scherrer equation is 40 and 140 Å for CP1 and CP2, respectively.

For the CP2-derived sample, we also monitored the structural evolution promoted by the further rise in the firing temperature by ^{29}Si MAS NMR (Fig. 6). For the samples subjected to pyrolysis at 1200 and 1400 °C, there is an increase in the relative amounts of SiC$_4$ and SiO$_4$ sites. The redistribution reactions of silicon sites are essential steps for carbothermal reactions, as discussed by some authors [9, 28, 37, 38]. These reactions afford crystalline β-SiC, which is characterized by a narrow resonance peak at −16 ppm in the ^{29}Si MAS NMR spectrum. For CP2, density growth depends on the pyrolysis temperature. At 1600 °C the density value is 3.21 g/cm^3, which corresponds to pure SiC phase.

The ^{13}C MAS NMR spectra recorded for the polymeric networks CP1 and CP2 submitted to pyrolysis at 1000 °C are illustrated in Fig. 7. The spectra of both samples are similar, with a broad signal centered at 133 ppm. This signal is assigned to unsaturated and probably conjugated species, such as aromatic carbons and carbon structure units with double or triple bonds, which may not be directly attached to silicon sites [28, 29]. In addition, another peak centered at 32 ppm may be ascribed to structures like –Si–CH$_2$– units [28, 29]. The carbon phase is dispersed in the SiOC matrix, which is more significant in CP2. Consequently, at high temperatures, the carbothermal reduction of SiO$_2$ can take place, thereby consuming the carbon phase [26]:

$$SiO_{2(s)} + C_{(s)} \rightarrow SiO_{(g)} + CO_{(g)} \qquad (1)$$
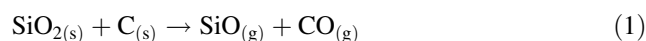
This reaction results in the evaporation of CO and SiO gaseous species. However, the above equation is only valid for low levels of free carbon in the material. In the presence
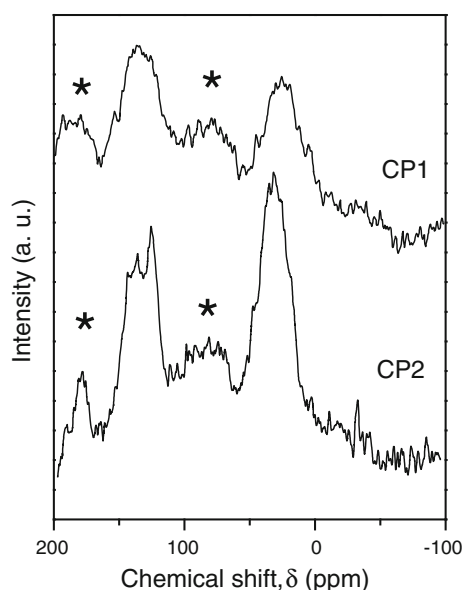
Fig. 7 ^{13}C MAS NMR spectra of the CP1- and CP2-derived sample submitted to pyrolysis for 2 h at 1000 °C (peak assigned with *asterisk* corresponds to spinning side bands)

Table 2 Composition of the silicon oxycarbide glass obtained at 1000 °C

Sample	Elemental composition[a]
CP1	$SiO_{1.01}C_{1.59}H_{0.37}$
CP2	$SiO_{1.02}C_{2.38}H_{0.49}$

[a] O was not analyzed

of high carbon contents, $SiC_{(s)}$ and $CO_{(g)}$ are the major decomposition products, according to:

$$SiO_{(g)} + 2C_{(s)} \rightarrow SiC_{(s)} + CO_{(g)} \tag{2}$$
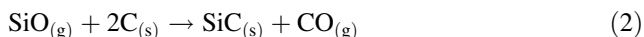
The above equations show that the SiO species plays an important role as intermediate species in the reduction of silica. For samples with high C amounts, the carbothermal reduction of SiO_2 will preferentially produce SiC, as observed for CP2. The larger amount of total carbon in the CP2-derived glass is also supported by the chemical composition of the derived-glasses obtained at 1000 °C (Table 2) as well as by the more intense absorption band at $\sim 800 \text{ cm}^{-1}$ in the FTIR spectrum of CP1 (Fig. 3). Similar results have been observed before for samples derived from phenylsilsesquioxanes, which showed higher amount of total carbon, when compared to vinylsilsesquioxane [39].

Conclusions

We obtained polysiloxane networks with distinct molecular architectures and similar compositions by hydrosilylation

reaction. These networks are suitable precursors of SiOC glasses. At 1000 °C, these polymers give rise to silicon oxycarbide glasses with higher amounts of SiC_4 sites than similar ceramics usually prepared by hydrolysis-condensation reaction of alkoxysilanes. Our results indicated that the polysiloxane network prepared from polycyclic oligomers (CP2) has faster organic-to-inorganic transformation compared with the linear precursor (CP1). The higher amount of total carbon in the CP2-derived glass compared with the CP1-derived glass might be related to the molecular architectures of CP1 and CP2, which are strictly related to the crosslinking density observed during pyrolysis. The amount of free carbon is able to drive the synthesis toward a ceramic phase constituted exclusively by β-SiC, in good ceramic yield, as observed for CP2.

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