

# Synthesis and characterization of new precursors to nearly stoichiometric SiC ceramics

## Part I *The copolymer route*

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Organosilicon polymers with a (C/Si (atomic ratio) < 1.28) exhibiting Si–Si and Si–CH<sub>2</sub>–Si linkages in their backbone have been prepared and characterized by multinuclear magnetic resonance and infrared spectroscopies, size exclusion chromatography and thermogravimetric analysis. These precursors give SiC ceramics with a C/Si (atomic ratio)  $\approx$  1.14 and a relatively low oxygen content (between 1.5–3 at %).

### 1. Introduction

Over the past twenty years, a considerable research effort has been devoted to ceramic-ceramic composite materials (e.g., SiC/SiC) obtained from the pyrolysis of organometallic precursors. This approach presents several advantages compared to the conventional powder sintering methods: (i) the formation of objects into complex shapes, (ii) access to matrices and continuous fibres with a small diameter, and (iii) an improved control over the elemental composition of the ceramics.

The presently available SiC(O) commercial fibres [1] have high free-carbon and oxygen contents. Oxygen is responsible for the degradation of the fibre when it is heated beyond 1100 °C, with silicon and carbon monoxides being evolved [2–8]. Curing the monofilaments via electron beam irradiation (E.B.) [9–11] allows the oxygen content to be reduced or even eliminated in the final ceramic, yielding a SiC(O) material which is stable at higher temperature. The fibre obtained, e.g., Hi-Nicalon [12], however still exhibits a substantial free-carbon content (20.5 at %). This might alter some properties, especially the creep resistance and the stability to oxidation.

During the course of the present research, the preparation of several experimental, quasi stoichiometric SiC fibres almost free of oxygen has been independently reported. However, none of them is presently commercially available. The Hi-Nicalon S fibre seems to have been prepared from a Yajima-type polycarbosilane (PCS) precursor according to a modified (but unspecified) procedure [13]. Sacks *et al.* [14] have also recently reported the preparation of a similar fibre via dry-spinning of a high molecular weight PCS, without disclosing the details of the processing. Lipowitz *et al.* [15], have shown that the introduction

of a small amount of boron into a PCS fibre could yield, after pyrolysis at high temperature (e.g., 1600 °C), a quasi stoichiometric, dense SiC fibre. Free carbon and oxygen are eliminated as CO by a carbothermic reduction, and boron acts as a sintering aid. Finally, Zhang *et al.* [16] have reported the preparation of a pure silicon carbide fibre from a polymethylsilane. This fibre displays a high Young's modulus (typically  $\approx$  400 GPa) with respect to the SiC(O) one (Nicalon standard grade), since all the low modulus secondary phases (i.e., free carbon and silicon oxycarbide) have been eliminated.

To obtain a nearly stoichiometric SiC fibre with a low oxygen content, our work has been focused on: (i) the synthesis of an original polymeric precursor which exhibits an atomic C/Si ratio  $\sim$  1.3, a moderate softening temperature (< 200 °C), and gives a high ceramic yield upon pyrolysis; (ii) the melt-spinning of this precursor in a dry glove-box, under an inert atmosphere; (iii) the curing of the green fibres via electron beam irradiation; and (iv) the physico-chemical and mechanical characterization of the ceramic monofilaments.

In this paper the synthesis and the characterization of the polymer and the intermediates are reported. In addition, some properties of the ceramic are described. The preparation and the mechanical characterization of the ceramic fibre will be detailed in the following paper [17].

### 2. Experimental procedure

#### 2.1. Characterization

##### 2.1.1. Infrared spectroscopy (IR)

The IR spectra were recorded between 4000–600 cm<sup>-1</sup> with a Perkin-Elmer 1420 spectrometer, or between

4000–400  $\text{cm}^{-1}$  with a Fourier transform Nicolet FT 20 SXC spectrometer. Low viscosity samples were placed between KBr plates, while solid samples were analysed as KBr pellets.

### 2.1.2. Nuclear magnetic resonance spectroscopy (NMR)

$^1\text{H}$  NMR spectra were recorded with a Hitachi Perkin-Elmer R24B (60 MHz) spectrometer in  $\text{CCl}_4$  or with a Bruker AC 250 (250 MHz) in  $\text{C}_6\text{D}_6$ .  $^{29}\text{Si}$  NMR spectra were obtained from a Bruker AC 200 at 39.73 MHz using the INEPT pulse sequence. Chemical shifts were calculated from tetramethylsilane (TMS) ( $\delta = 0$  ppm).

### 2.1.3. Size exclusion chromatography (SEC)

SEC profiles were obtained with four TSK-GEL H-type columns (from TOSO-Haas, USA) (porosity range: 4.0– $10^6$  nm), calibrated with narrow polystyrene standards and using ultra violet (UV) or refractometer detectors. Tetrahydrofuran (THF) was used as the eluent at a flow rate of  $1 \text{ ml min}^{-1}$ .

### 2.1.4. Thermogravimetric analysis (TGA)

TGA curves from 40–950 °C were recorded with a Perkin-Elmer model TGS2 thermobalance, then processed with a model 3600 data station (conditions: argon grade N56, flow rate:  $40 \text{ ml min}^{-1}$ ; heating rate:  $5^\circ\text{C min}^{-1}$ ; sample mass: 10–20 mg).

### 2.1.5. Pyrolysis

The pyrolyses of the precursors were carried out in a tubular furnace under an argon (N56) flow. The samples were put in an alumina boat. The heating rate was  $1^\circ\text{C min}^{-1}$  with a final plateau of 1 h.

### 2.1.6. Chemical analysis

The elemental analyses of the ceramics were obtained by using an electron probe microanalyser (EPMA) Camebax Micro from Cameca. A pentaerythritol crystal (PET) crystal was used for silicon ( $\text{SiK}_\alpha$ ) and a multilayered pseudo crystal (PCI) for carbon and oxygen ( $\text{CK}_\alpha$  and  $\text{OK}_\alpha$ ).

### 2.1.7. Mass spectrometry

Mass spectra were recorded with a VG Micromass 16 F spectrometer (70 eV) equipped with a Data System 2040 data station.

### 2.1.8. X-ray diffraction (XRD)

XRD patterns of finely powdered samples were recorded with a Siemens D 5000 diffractometer. The average size of the crystallites,  $L_{111}$  was calculated from the Scherrer formula. [ $L_{111} = K\lambda/D \cos \theta$  where  $K$  is a constant taken as 0.9,  $\lambda$  the  $\text{CuK}_\alpha$  wavelength ( $\lambda = 0.154 \text{ nm}$ ),  $\theta$  the Bragg angle ( $\theta = 17.8^\circ$ ) and  $D$  the width at midheight in radius of the  $\beta\text{-SiC}$  (111)].

## 2.2. Solvents and reagents

Solvents were purchased from the “Solvants, Documentation, Synthèses” Company (SDS). Toluene was distilled over sodium and, then, over  $\text{LiAlH}_4$ . Diethyl ether was dried on  $\text{CaCl}_2$ , then distilled over sodium. Pentane and THF were distilled over Na/benzophenone. Dichloromethane was dried over alumina. Methylphenyldichlorosilane, a generous gift from Rhône-Poulenc, was distilled under vacuum ( $b_{40\text{Pa}}$ :  $65^\circ\text{C}$ ).  $\text{AlCl}_3$  (Aldrich),  $\text{LiAlH}_4$  (Aldrich), and  $\text{MeSiHCl}_2$  (Hüls) were used as received. Sodium (Pro-labo) was stored as lumps in paraffin oil. All solvents were kept on molecular sieves (0.4 nm) and stored in the dark under an inert atmosphere.

## 2.3. Apparatus

All filtrations and manipulations were carried out in a dry glove-box under a nitrogen atmosphere or with an argon line to avoid contamination by oxygen or moisture. Glassware was carefully dried and purged with argon before use. Gases were dried through potassium hydroxide columns.

## 2.4. Preparation of 2,4-Dichloro-2,4-disilapentane [18]

Magnesium turnings (49 g, 2 mols), zinc powder (20 g, 0.3 mol),  $\text{CH}_2\text{Cl}_2$  (85 g, 1 mol), and  $\text{MeSiHCl}_2$  (575 g, 5 mols) were introduced in a 2 l Sovirel reactor previously purged with argon. The reactor was equipped with a mechanical stirrer, a thermometric well, a pressure-equalizing funnel, and a reflux condenser at  $-20^\circ\text{C}$ , connected to a drying column. THF (750 ml) was added dropwise for 18 h, during which the temperature was maintained between 20–30 °C. The reaction mixture rapidly turned grey, as  $\text{MgCl}_2$  precipitated. Once the addition was completed, the mixture was stirred for 48 h. The excess  $\text{MeSiHCl}_2$  and THF were distilled off under vacuum. Dry pentane (1 l) was added to the grey solid residue, then the solution was filtered off under argon and the solid washed with pentane ( $3 \times 150 \text{ ml}$ ). The liquid fractions were evaporated, yielding 2,4-dichloro-2,4-disilapentane (60.5 g, yield 35%,  $b.p_{800\text{Pa}} = 42^\circ\text{C}$ ).

## 2.5. Synthesis of copolymer 1

Toluene (400 ml) and sodium chips (25.3 g, 1.1 mols) were introduced in a 1 l, three-necked round-bottomed flask equipped with an argon inlet, two pressure-equalizing funnels, a reflux condenser at  $-2^\circ\text{C}$ , and a drying column. Two funnels were used to avoid the formation of six-membered cyclosilane rings that could arise from the presence of an excess of  $\text{PhMeSiCl}_2$ . A mixture of 2,4-dichloro-2,4-disilapentane (35 g, 0.2 mol) and  $\text{PhMeSiCl}_2$  (15.3 g, 0.08 mol) were put in the first funnel, while the remaining  $\text{PhMeSiCl}_2$  (42 g, 0.22 mol) was introduced into the second funnel. After the vessel had been carefully purged with argon, the mixture was heated to reflux under magnetic stirring. The chlorosilanes were slowly added dropwise for 7–8 h. The reaction mixture

rapidly turned dark blue. After the addition was completed, the mixture was refluxed for 48 h, then allowed to cool under argon. Usually, two phases were observed: a liquid and a black precipitate. The solution was filtered off in a dry glove-box and the solid was washed with toluene (1 l). The solvent was partly evaporated under vacuum, and the concentrated solution of copolymer **1** was directly converted into copolymer **2**.

A second run gave similar results (SEC results: average molecular weight  $\bar{M}_n = 1280$ , polydispersity  $I_p = 3.9$ , TGA residue = 7 %).

## 2.6. Synthesis of copolymer 2

The toluene solution of copolymer **1** and a catalytic amount of  $\text{AlCl}_3$  (5 wt %) were introduced into a 500 ml, three-necked round-bottomed flask equipped with a magnetic stirrer, a gas inlet, and a reflux condenser. The vessel was first purged with argon, then the reaction mixture was heated at 70 °C. Gaseous HCl, dried through sulphuric acid, was bubbled for 15 h. The reaction was monitored by the disappearance of aromatic protons in the  $^1\text{H}$  NMR spectrum. After cooling, the solution was filtered off, then concentrated under vacuum. The concentrated solution of the chlorinated polymer **2** was immediately reduced into copolymer **3** to avoid hydrolysis or oxidation reactions.

## 2.7. Preparation of copolymer 3

$\text{LiAlH}_4$  (12 g, 0.3 mol) and dry diethyl ether (500 ml) were introduced in a 1 l, three-necked flask equipped with a magnetic stirrer, an argon inlet, a pressure-equalizing funnel, a reflux condenser at  $-5^\circ\text{C}$ , and a drying column. The suspension was vigorously stir-

red, and the solution of polymer **2** was slowly added, while the reaction temperature was maintained at 0 °C. At the end of the addition, the mixture was refluxed for 48 h, cooled, and finally filtered off in a dry glove-box. The filtrate was hydrolysed with aqueous HCl, separated from the water then dried over  $\text{MgSO}_4$ . After evaporation of the solvent, the crude copolymer was obtained (27 g). This polymer was devolatilized for 2 h at 180 °C under a pressure of 13 Pa to eliminate volatile oligomers, yielding copolymer **3** (24.3 g, 36 % yield).

## 2.8. Thermolysis of copolymer 3

Silica glassware was used to perform the thermolysis reaction.

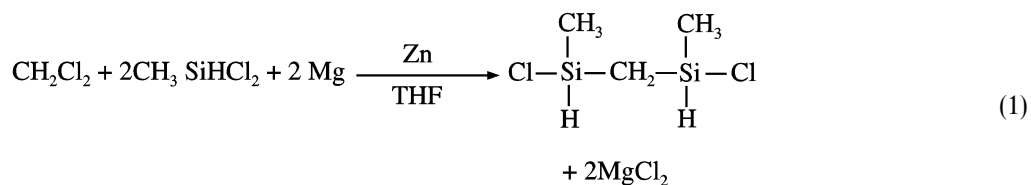
The copolymer **3** was introduced in a 250 ml, three-necked round-bottomed flask inside a dry glove-box. Then the flask was fitted to an argon inlet, a thermometric well, and a reflux condenser connected to a gas-meter. The vessel was carefully purged with argon, then heated with a fluidized sandbath at 400 °C. During the thermolysis, the internal temperature and the gas evolution were noted every 10–15 min. At 200–250 °C, white smoke, considerable vapour condensation, and gas evolution were observed. After 3 h, the internal temperature reached 300–350 °C, and the mixture was allowed to cool under an argon flow. The solid material was dissolved in pentane, then filtered off in a dry glove-box. After distillation of the solvent, the polymer was devolatilized for 2 h at 140 °C under a pressure of 13 Pa to eliminate volatile oligomers, yielding precursor **P I** with a 60 % yield. SEC results:  $\bar{M}_n = 1660$ , polydispersity index  $I_p = 2.3$ .

A second experiment was performed using apparatus modified to improve its air-tightness. The three-necked flask, the thermometric well, the argon inlet, and the condenser were equipped with silica-metal connections and copper seals. Moreover, argon N56 grade was used as the purge gas. Under these conditions, crude precursor **P II** was obtained also at a 60 % yield,  $\bar{M}_n = 1160$ , and  $I_p = 2.2$ . After devolatilisation under vacuum,  $\bar{M}_n = 1400$  and  $I_p = 1.8$ .

## 3. Results and discussion

### 3.1. Synthesis of 2,4-dichloro-2,4-disilapentane

This compound was synthesized according to a method developed in our laboratory [18] which consists of a direct silylation of methylene chloride using magnesium metal and zinc in THF:



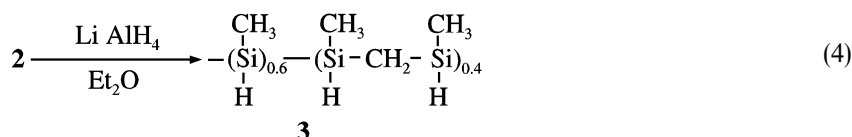
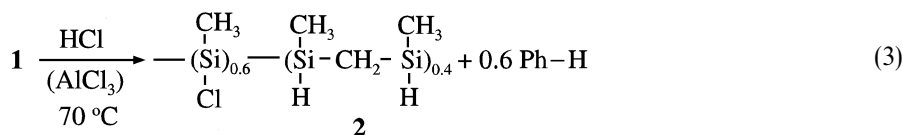
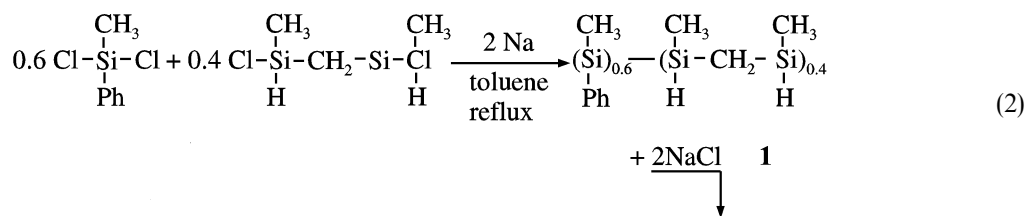
### 3.2. Synthesis of polysilacarbosilane

An earlier work performed in our laboratory had previously shown that the sodium co-condensation of methylchlorosilane and 2,4-dichloro-2,4-disilapentane in a 4:1 molar proportion gave a copolymer which rapidly oxidized in the presence of traces of oxygen. This oxidation led to an insoluble, infusible material. For this reason, methylphenyldichlorosilane has been used as a comonomer in the place of methylchlorosilane in this work. The polymers were prepared according to the route shown as Equations 2–5.

The first step consists of the sodium co-condensation of methylphenyldichlorosilane and 2,4-dichloro-2,4-disilapentane to give the copolymer **1**. Substitution of phenyl groups by hydrogen atoms is performed in two steps: (i) substitution of the phenyl groups by chlorine atoms with  $\text{HCl}/\text{AlCl}_3$  at 70 °C [19],

affording copolymer **2**, then (ii) reduction of Si–Cl bonds with LiAlH<sub>4</sub>, yielding copolymer **3**. The volatile fraction of copolymer **3** is eliminated under vacuum.

The *r* ratio can be written as:  $r = 5 - 5x/5x + 3 = 0.64$ , from which the value of *x* is 0.38 (*x* calculated = 0.4, regarding the proportions of the monomers).



### 3.3. Characterization of copolymers 1, 2, and 3

#### 3.3.1 Copolymer 1

3.3.1.1. <sup>1</sup>H NMR. The 250 MHz <sup>1</sup>H NMR spectrum of copolymer **1** exhibits three broad signals (Fig. 1): between –0.6–0.8 ppm (Si–CH<sub>3</sub> and Si–CH<sub>2</sub> protons); between 3.2–4.6 ppm (Si–H protons); and between 6.6–7.6 ppm (aromatic protons); a weak signal at 5 ppm which is assigned to chlorinated end-groups –SiMeHCl. The Si–C<sub>6</sub>H<sub>5</sub>/Si–(CH<sub>3</sub> + CH<sub>2</sub>) integration ratio *r* is close to the theoretical value: assuming the following composition for the copolymer **1**:

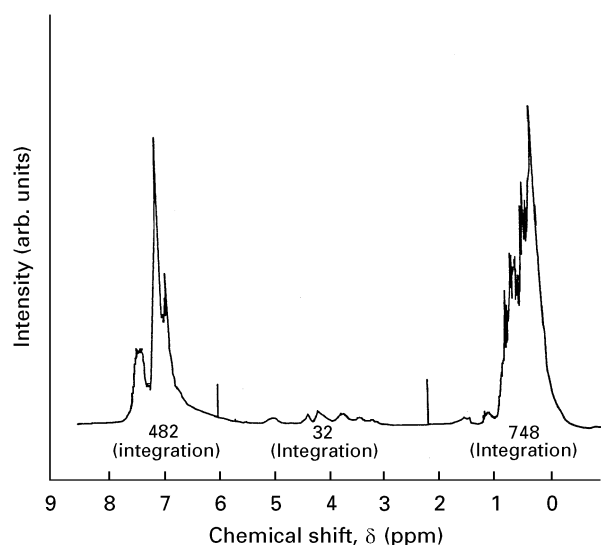
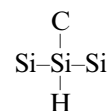


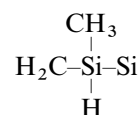
Figure 1 The <sup>1</sup>H NMR spectrum of copolymer 1.

On the other hand, the comparison of the experimental (23.3), and calculated (6.25), Si–CH/Si–H integration ratios indicates that the Si–H bonds partly react in our reaction conditions. Similar results have been reported by Schilling and Williams [20] and Seyferth *et al.* [21] who observe that 60–80% of Si–H bonds are consumed when MeHSiCl<sub>2</sub> is condensed, with or without another chlorosilane, in the presence of an alkali metal (sodium or potassium). However, no details are given concerning the structure of the products.

3.3.1.2. <sup>29</sup>Si NMR. <sup>29</sup>Si INEPT NMR data gives valuable information. Using polarization on Si–H protons, four signals centred at –70, –36, –16, and –6 ppm are observed (Fig. 2). The signal at –70 ppm, assigned to SiSi<sub>2</sub>CH sites, is characteristic of polysilane linkages [22]. Their presence could be explained by disproportionation reactions between phenyl groups and hydrogen



The signal at –36 ppm was assigned to SiSiC<sub>2</sub>H sites [23]:



The signals at –16 and –6 ppm could be assigned to SiC<sub>3</sub>H sites and SiMeHCl end-groups respectively.

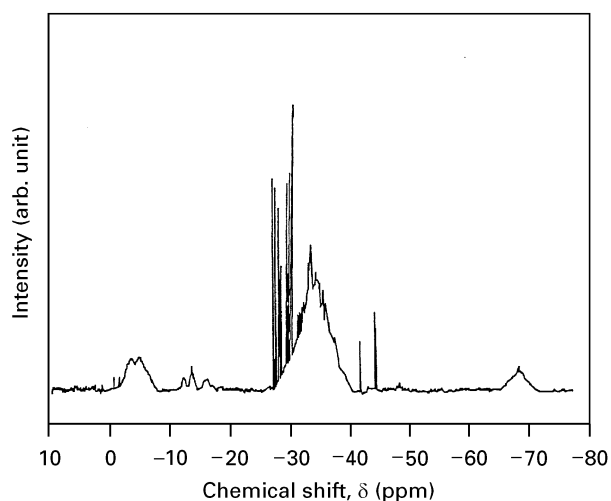


Figure 2 The  $^{29}\text{Si}$  spectrum of copolymer 1 (INEPT, Si-H polarization).

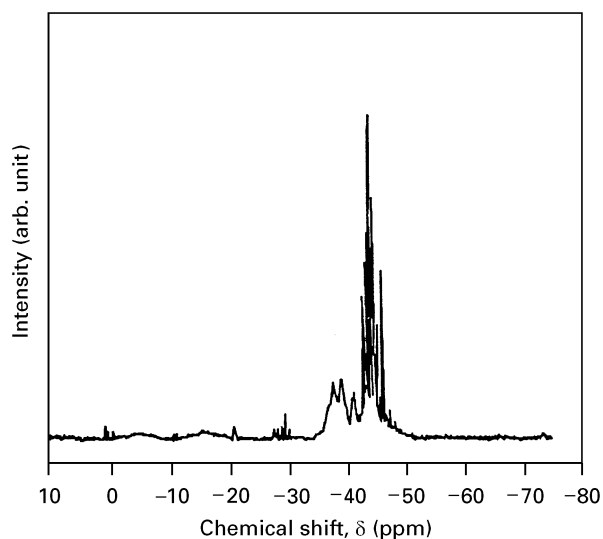
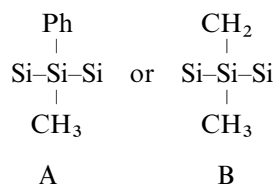


Figure 3 The  $^{29}\text{Si}$  spectrum of copolymer 1 (INEPT, Si- $\text{CH}_3$  polarization).

Using polarization on Si- $\text{CH}_3$  protons, apart from the signals at  $-36$ ,  $-16$ , and  $-6$  ppm, an additional signal centred at  $-44$  ppm was observed, which could be assigned to  $\text{SiSi}_2\text{C}_2$  units (Fig. 3):



The unit B could explain the consumption of Si-H bonds observed by proton NMR spectroscopy. A broad, weak signal at  $-80$  ppm, corresponding to polysilane linkage, can also be hardly detected. These results reveal that side reactions occurred and the structure of polymer 1 is more complex than expected.

**3.3.1.3. IR spectroscopy.** The IR spectra clearly show the presence of the expected bands (Fig. 4). The results are listed in Tables I and II, where the bands are assigned in accordance with published literature data

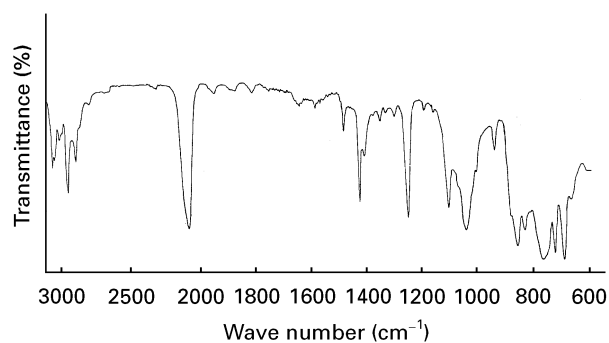


Figure 4 The IR spectrum of copolymer 1.

TABLE I Main absorption bands observed in the IR spectrum of the phenyl group

Wavenumber ( $\text{cm}^{-1}$ )	Intensity	Assignment
3000–3100	m	$\nu\text{C-H}$
1480	m	$\delta\text{C-H}$
1425	s	$\nu\text{C=C}$
1375	vw	
1330	w	$\delta\text{C-H}$
1295	w	$\nu\text{C=C}$
1190	w	$\delta\text{C-H}$
1155	w	$\delta\text{C-H}$
1100	s	$\delta\text{C-H}$
1000	vw	$\delta\text{CCC}$
830	w	$\gamma\text{C-H}$
725	s	$\gamma\text{C-H}$
665	w	$\gamma\text{C-H}$

s: strong; m: medium; w: weak; vw: very weak

TABLE II Main absorption bands observed in the IR spectrum of the  $-(\text{HMeSi-CH}_2-\text{SiMeH})-$  group

Wavenumber ( $\text{cm}^{-1}$ )	Intensity	Assignment
2980	w	$\nu\text{aCH}_3$
2940	s	$\nu\text{aCH}_2$
2880	m	$\nu\text{sCH}_3$
2850	w	$\nu\text{sCH}_2$
2120–2090	s	$\nu\text{Si-H}$
1410	m	$\delta\text{aCH}_3$
1350	m	$\delta\text{CH}_2(\text{Si-CH}_2-\text{Si})$
1250	s	$\delta\text{sCH}_3$
1035	s	$\text{WCH}_2(\text{Si-CH}_2-\text{Si})$
935	m	
855	m	$\delta\text{Si-H}$
770	m	$\text{rCH}_3$
675	m	$\nu\text{Si-CH}_3$

[24–29]. Moreover, this technique gives us information about the environment of the Si-H sites as noted in the work of Lucovsky [30]. Thus, from data obtained for silanes, we could establish three relationships of the type  $\nu = b_1 + b_2 \sum E_j$  (where  $b_1$  and  $b_2$  are constants and  $E_j$  is a measure of the electronegativity):

$$\nu(\text{Si-H}) = 1740 + 34.7 \sum_{j=1}^3 SR(R_j) \quad (6)$$

$$\nu(\text{SiH}_2) = 1953.3 + 25.4 \sum_{j=1}^2 SR(R_j) \quad (7)$$

$$\nu(\text{SiH}_3) = 2086.1 + 22.5 SR(R_j) \quad (8)$$

where  $SR(R_j)$  are the Sanderson electronegativities of the substituents, defined in the following equation [32]:

$$SR(R_j) = \left( \prod_j SR(A_j) \right)^{n^{-1}} \quad (9)$$

where  $SR(A_j)$  are the electronegativities of the group constituents and  $n$  is the number of atoms in the group. The two maxima for the Si–H stretching band could be rationalized as follows: (i) a Si–H vibrator is surrounded by Si, CH<sub>2</sub>, and CH<sub>3</sub> for which Equation 6 gives a wavenumber value of 2083 cm<sup>-1</sup> (experimental value: 2120 cm<sup>-1</sup>). (ii) A Si–H group is linked to 2 silicon atoms and 1 methyl group for which the calculated wavenumber from Equation 6 is 2047 cm<sup>-1</sup> whereas the experimental value is 2090 cm<sup>-1</sup>. It must be noted that the deviation between the experimental and calculated values is about 2%. One can conclude that the Lucovsky model satisfactorily represents the environment of every Si–H oscillator. These results are consistent with the <sup>29</sup>Si NMR data.

**3.3.1.4. TGA.** TGA of a sample of copolymer **1** free from solvent gives only a 7% ceramic yield at 950 °C. This indicates that copolymer **1** is mainly made of volatile low-mass oligomers and is not significantly cross-linked.

### 3.3.2. Copolymer 2

The substitution by chlorine atoms of the phenyl groups in copolymer **1** was monitored by proton NMR spectroscopy. The reaction was achieved after bubbling gaseous HCl for 15 h. The progressive disappearance of aromatic protons around 7 ppm was observed. This intermediate copolymer **2** has not been further characterized to avoid any oxygen contamination from hydrolysis or oxidation reactions.

### 3.3.3. Copolymer 3

**3.3.3.1. IR spectroscopy.** The Si–H valence band is still double. In addition, no variations in the wavenumber values is observed. The characteristic vibrations of the carbosilane group, –(HMeSi–CH<sub>2</sub>–SiMeH)–, have been previously discussed. The sharp W<sub>CH<sub>2</sub></sub> band around 1040 cm<sup>-1</sup> exhibits no high-frequency shoulder (1060–1080 cm<sup>-1</sup>), characteristic of Si–O bonds. This suggests that the oxygen concentration is very low (Fig. 5). On the other hand, a new band is observed at 953 cm<sup>-1</sup>, which is assigned to the SiH<sub>2</sub> end-groups vibrating [26].

The chemical stability of this polymer has also been verified via IR spectroscopy. After keeping a sample of polymer **3** in air for 1 and 3 h, the absorption band at 1040 cm<sup>-1</sup> becomes broader with a maximum at 1077 cm<sup>-1</sup>, clearly indicating the presence of Si–O bonds. The sensitivity towards oxygen (or moisture) of this copolymer can be due to SiH–SiH sequences observed in the <sup>29</sup>Si NMR at –70 ppm.

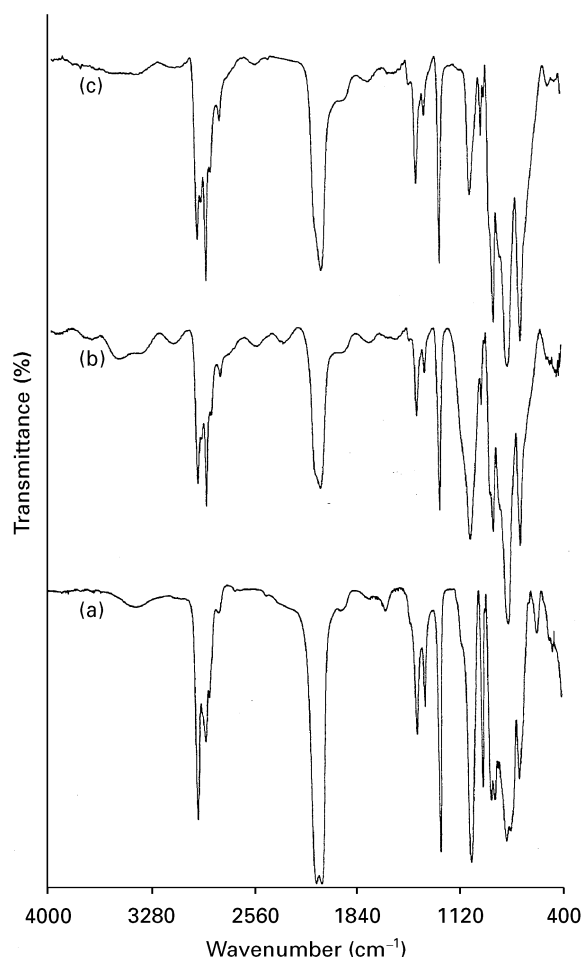


Figure 5 The IR spectra of (a) copolymer **3**; (b) precursor P I and (c) precursor P II.

**3.3.3.2. NMR spectroscopy.** In the proton NMR spectra (Fig. 6), the signal near 5 ppm, assigned to chlorinated end-groups, disappeared, showing that the reduction was quantitative. The experimental Si–CH/Si–H ratio is close to the expected value (observed: 4, calculated: 3.6). Regarding the experimental value for copolymer **1**, this result suggests that the cleavage of Si–Si bonds by LiAlH<sub>4</sub> occurred to some extent [31].

The <sup>29</sup>Si INEPT NMR spectrum, polarized on Si–H protons, exhibits 3 signals near –70, –33, and –13 ppm, assigned to SiSi<sub>2</sub>CH, SiSiC<sub>2</sub>H, and SiC<sub>3</sub>H environments respectively (Fig. 7). The broadening of the signal at –33 ppm was attributed to the SiSiMeH<sub>2</sub> end-groups [23].

**3.3.3.3. TGA.** The ceramic residue at 950 °C of the polymer was only 14.5%, so the poorly cross-linked copolymer **3** could not be considered as a precursor. Due to the presence of Si–H bonds, it was easily converted into a suitable precursor with a higher ceramic yield by a thermal treatment at atmospheric pressure.

## 3.4. Thermolysis of copolymer 3 into precursor P I

The thermolysis of copolymer **3** was performed at atmospheric pressure without a catalyst, and it was

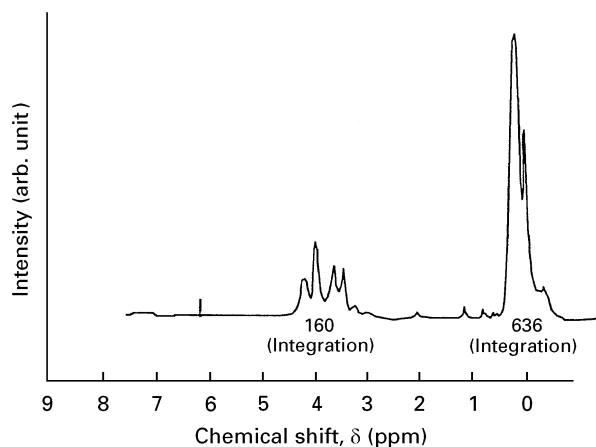


Figure 6 The  $^1\text{H}$  NMR spectrum of copolymer 3.

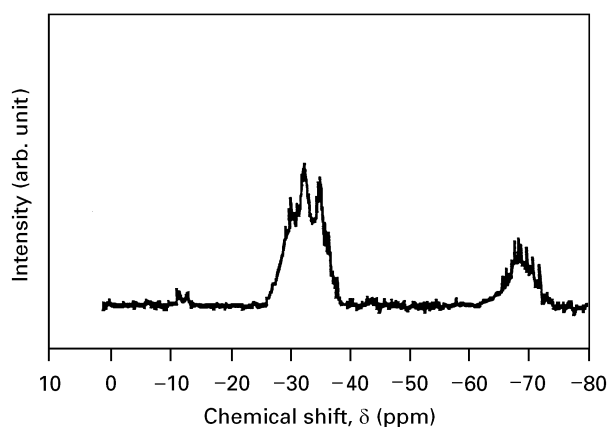


Figure 7 The  $^{29}\text{Si}$  spectrum of copolymer 3 (INEPT, Si-H polarization).

monitored by measuring the volume of the evolved gases (essentially hydrogen and methylsilanes). The SEC profile of **P I** exhibits a moderately narrow mass distribution, with  $\bar{M}_n = 1660$ , and  $I_p = 2.3$ . The ceramic yield of the precursor **P I** increased to 64 %, clearly showing that the precursor was branched. A softening temperature of 160 °C was measured by differential scanning calorimetry (DSC). The experimental Si-CH/Si-H integration ratio of **P I**, determined by proton NMR spectroscopy, increased to 6 (Fig. 8), which confirmed the partial consumption of the Si-H bonds during the thermal treatment, involving silicon atoms. In addition, modifications to the infrared spectra appeared in the low-frequency domain, (spectrum b on Fig. 5). The intensity of the band at 955  $\text{cm}^{-1}$ , assigned to SiH<sub>2</sub>, decreased. This result corroborated the proton NMR data.

From the  $^{29}\text{Si}$  NMR spectroscopy data two facts could be observed (Fig. 9): (i) the intensity of the polysilane signal near -70 ppm decreased, and (ii) the intensity of the peak at -14 ppm assigned to SiC<sub>3</sub>H sites increased confirming the conversion of the polysilane chain into polycarbosilane.

The elemental chemical analysis of the ceramic obtained from the precursor **P I** pyrolysed at 1000 °C is: Si = 45.5 at %; C<sub>total</sub> = 51.5 at %; O = 3 at %; free

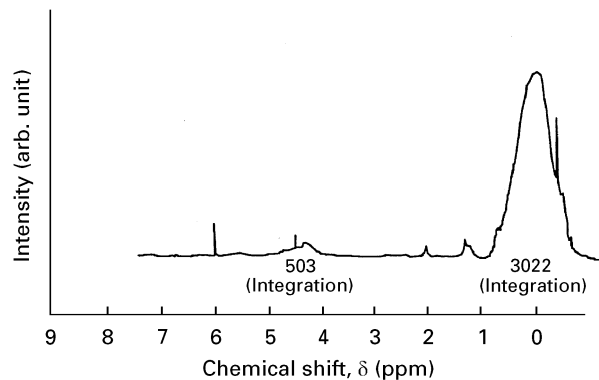


Figure 8 The  $^1\text{H}$  NMR spectrum of precursor P I.

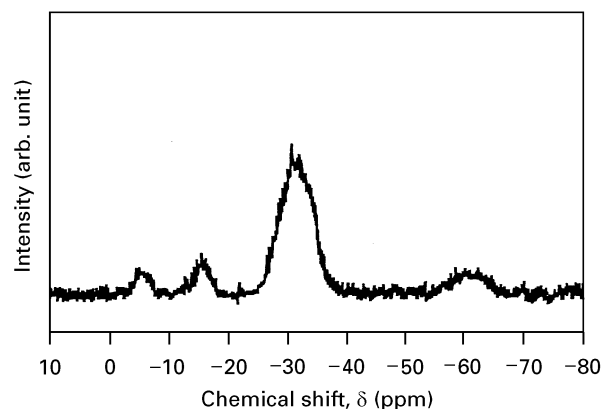


Figure 9 The  $^{29}\text{Si}$  spectrum of precursor P I (INEPT, Si-H polarization).

carbon = 7.5 at % (assuming oxygen is combined as SiO<sub>2</sub> and the SiC is stoichiometric C/Si = 1.13).

### 3.5. Thermolysis of copolymer 3 into precursor P II. The preparation of a ceramic with low free-carbon and oxygen contents

The IR spectra of copolymer 3 and precursor **P I** (spectra a and b on Fig. 5 respectively) clearly showed that contamination by oxygen occurred during the thermal treatment (the formation of a shoulder near 1080  $\text{cm}^{-1}$  is characteristic of Si-O bonds). Therefore as previously discussed the air tightness of the thermolysis device was improved and a second precursor **P II** was prepared. As a result of these modifications, the atomic oxygen content in the ceramic was decreased from 3 at % to 1.5 at %.

#### 3.5.1. Characterization of the precursor P II

In the IR spectroscopy data, the carbosilane group Si-CH<sub>2</sub>-Si was characterized by two absorption bands at 1350  $\text{cm}^{-1}$  ( $\delta_{\text{CH}_2}$ ) and 1040  $\text{cm}^{-1}$  ( $\text{W}_{\text{CH}_2}$ ). The latter band was sharp, indicating that contamination by oxygen did not significantly occur under our reaction conditions (spectrum c on Fig. 5).

### 3.5.2. Gas analysis

The pyrolysis was carried out under argon at temperatures up to 1000 °C and the gases produced were analysed by mass spectrometry. The major components were hydrogen and methane. Methane was released between 350–830 °C (Fig. 10). This could be explained by the condensation of two Si–CH<sub>3</sub> groups leading to the formation of the carbosilane backbone, Si–CH<sub>2</sub>–Si, and the elimination of methane. The hydrogen evolution started at 350 °C and ended around 1000 °C, two maxima being observed near 510 and 865 °C (Fig. 11). The first evolution of hydrogen between 350–780 °C could be due to the reaction of the Si–H bonds with Si–CH<sub>3</sub> groups, to form Si–CH<sub>2</sub>–Si motifs. The second evolution, between 780–990 °C, could be explained by the transformation of  $\overline{\text{C}}\text{Si}_2\text{H}_2$  and  $\overline{\text{C}}\text{Si}_3\text{H}$  groups into  $\overline{\text{C}}\text{Si}_4$ .

### 3.5.3. Ceramic study

The precursor **P II** was pyrolysed under an argon flow at 1000 °C. The elemental analysis of the ceramic obtained is: Si = 46 at %; C = 52.5 at %; O = 1.5 at %; C/Si = 1.14. The calculated, atomic free-carbon content, assuming oxygen is combined as SiO<sub>2</sub>, is equal to 7.25%. At 1000 °C, the peaks assigned to β-SiC (111), (220), and (311) were observed in the XRD patterns.

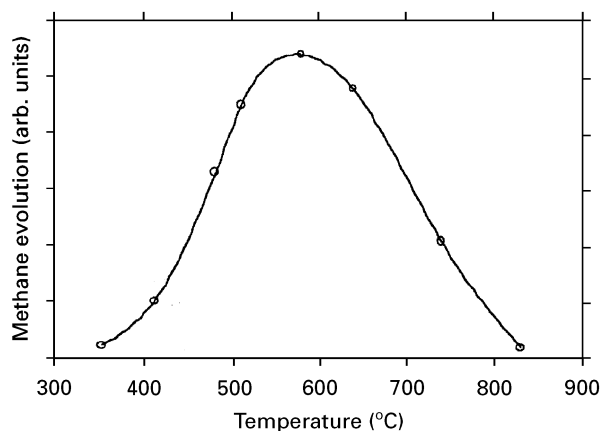


Figure 10 The methane evolution during the pyrolysis of precursor P II.

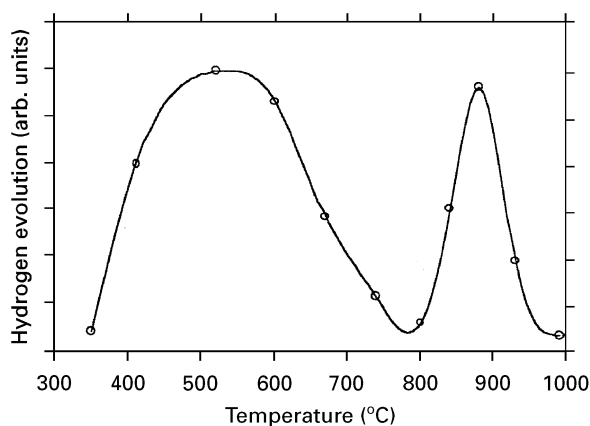


Figure 11 The hydrogen evolution during the pyrolysis of precursor P II.

The calculated average size of the crystallites was about 3 nm.

## 4. Conclusions

An original route for the synthesis of organosilicon copolymers having a reduced carbon content, compared to the commercial PCS, has been proposed. The copolymers can be easily thermally branched, at atmospheric pressure and without the use of a catalyst, due to the presence of Si–H bonds. They give soluble, fusible precursors in good yields, which can be spun and converted into ceramic residues with high yields. The pyrolysis of these precursors leads to nearly stoichiometric SiC ceramics. In addition, the use of proper synthesis conditions allowed us to reduce the atomic oxygen content to a level as low as 1.5 at %.

During the heat treatment of the polymers, the formation of carbosilane sequences Si–CH<sub>2</sub>–Si, accompanied with the evolution of hydrogen and methane takes place from 350 °C rather than 500 °C in the case of the commercial polycarbosilane. This result suggests that the transformation of the precursor still goes on in the first stage of the pyrolysis.

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