An Original Route to Precursors of Silicon Carbide-based Ceramics Possessing Low Free Carbon Content

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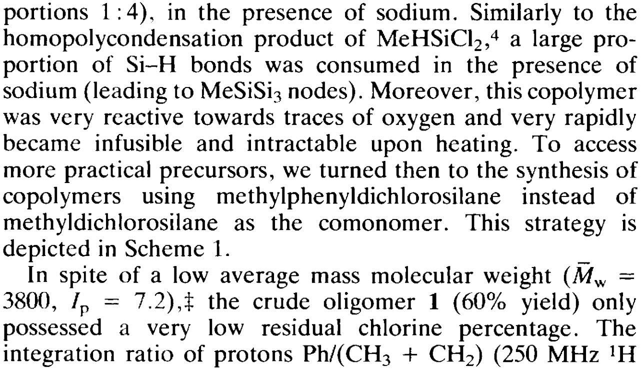
2,4-Dichloro-2,4-disilapentane is used as starting material in the synthesis of novel polycarbosilane precursors of silicon carbide-based ceramics containing low free carbon excess.

Since it has been recognised that an excess of free carbon is responsible for a decrease in the thermomechanical stability of ceramic fibres,[1–3] there is current interest in the preparation of stoichiometric silicon carbide from the pyrolysis of organosilicon polymers.[4,5] But there exists a paucity of precursors leading to SiC-based ceramics possessing an atomic ratio C : Si $\approx$ 1 : 1 and most of them exhibit drawbacks.[6] For example, the polycarbosilane derived from disilacyclobutane[7,8] requires an expensive multistep synthesis whilst the direct pyrolysis of poly(methylsilane)s leads to ceramics containing free silicon.[9,10] In addition, the preparation of fibres is tedious or not possible because of poor rheological properties of the corresponding preceramic polymers. In a recent approach in this field, Yajima's polycarbosilane[11] has been used for the preparation of nearly stoichiometric silicon carbide fibres, according to a modified 'Hi-NICALON' process, has been reported.[12] Very recently, the transition metal-catalysed dehydrocondensation has been applied to the synthesis of polycarbosilanes possessing Si–CH$_2$–CH$_2$–Si linkages, yielding nearly stoichiometric SiC upon pyrolysis.[13]

We had pointed out previously that chlorinated bis(silyl)methanes could be used for the preparation of silicon carbide precursors possessing Si–Si and Si–CH$_2$–Si linkages in their backbones.[14,15] In order to control the C : Si ratio, here we report an original molecular building-block approach to preceramic polymers consisting of the synthesis of poly[silylene-*co*-(2,4-disilapentane-2,4-diyl)]s using 2,4-dichloro-2,4-disilapentane as starting monomer (or comonomer).† Firstly, we carried out the copolycondensation of 2,4-dichloro-2,4-disilapentane and MeHSiCl$_2$ (respective molar proportions 1 : 4), in the presence of sodium. Similarly to the homopolycondensation product of MeHSiCl$_2$,[4] a large proportion of Si–H bonds was consumed in the presence of sodium (leading to MeSiSi$_3$ nodes). Moreover, this copolymer was very reactive towards traces of oxygen and very rapidly became infusible and intractable upon heating. To access more practical precursors, we turned then to the synthesis of copolymers using methylphenyldichlorosilane instead of methyldichlorosilane as the comonomer. This strategy is depicted in Scheme 1.

In spite of a low average mass molecular weight ($\bar{M}_w$ = 3800, I_p = 7.2),‡ the crude oligomer **1** (60% yield) only possessed a very low residual chlorine percentage. The integration ratio of protons Ph/(CH$_3$ + CH$_2$) (250 MHz ^{1}H NMR spectrum) was consistent with the starting value of x (0.38 *cf.* 0.4). But the integration ratio (CH$_3$ + CH$_2$)/SiH of 23.0 was higher than expected (6.45) showing that Si–H bonds of the bis(silyl)methane comonomer were consumed to a large extent.

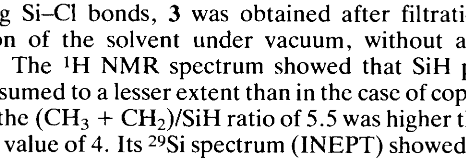


Scheme 1 *Reagents and conditions*: i, Na in refluxing toluene, 48 h (x = 0.4); ii, gaseous anhydrous HCl/AlCl$_3$ (5 mol%), toluene, 60 °C, 15 h; iii, LiAlH$_4$/ether, 48 h, reflux, filtration, then H$_2$O/H$_3$O$^+$ work-up, neutralisation and drying (MgSO$_4$)

As expected, the ^{29}Si NMR spectrum (INEPT) of **1** showed two main broad signals (δ ppm) centred at δ −36 [–CH$_2$–*Si*(Me)H–Si] and δ −42 [Si–*Si*(Me)Ph–Si]. However, overlapping sharp peaks in the region δ −28 to −30 (SiC$_2$H$_2$) and additional signals at δ −6 (weak), (SiC$_3$H) and δ −70 (*Si*CSi$_3$) revealed that side reactions took place and that the structure of **1** was more complex than expected. In order to avoid any contamination by oxygen during the process, the chlorinated intermediate material resulting from the splitting of phenyl groups[16] was rapidly treated with an excess of lithium aluminium hydride in anhydrous diethyl ether as the solvent without further characterisation (overall yield of **2** was 45% based on the starting comonomers). SEC results: $\bar{M}_w$ = 1600, I_p = 2.6; char yield = 14.5%.§ From the ^{1}H NMR spectrum, no remaining aromatic proton signal was observed while the integration ratio (CH$_3$ + CH$_2$)/SiH of 3.9 was close to the expected value (3.6). To account for this observation, it might be inferred that not only Si–Ph bonds but also some of the Si–CH$_2$ bonds were cleaved during treatment with HCl–AlCl$_3$, leading to Si–Cl chain ends, which are reduced in the final step. This is in good agreement with the fact that the M_w value underwent a marked decrease. The ^{29}Si NMR spectrum of **2** showed two broad signals in the regions δ −30 to −40 (*Si*SiC$_2$H) and δ −65 to −70 (*Si*CSi$_2$H and *Si*CSi$_3$). It is of note that the product was not contaminated by oxygen during the overall process and more particularly in the final aqueous work-up. Thus, only a sharp FT-IR absorption band at 1040 cm^{-1} [ω(Si–CH$_2$–Si)] was observed with no shoulder in the region 1060–1100 cm^{-1} indicative of ν(Si–O).

Homopolycondensation of 2,4-dichloro-2,4-disilapentane yielded poly(2,4-disilapentane-2,4-diyl) **3**, *i.e.* oligomers formed of repetitive Si–CH$_2$–Si units (Scheme 2) (61% yield, $\bar{M}_w$ = 4300, I_p = 3.1, char yield = 14%).

After a final treatment with LiAlH$_4$ to remove any remaining Si–Cl bonds, **3** was obtained after filtration and distillation of the solvent under vacuum, without aqueous work-up. The ^{1}H NMR spectrum showed that SiH protons were consumed to a lesser extent than in the case of copolymer **1**. Thus, the (CH$_3$ + CH$_2$)/SiH ratio of 5.5 was higher than the expected value of 4. Its ^{29}Si spectrum (INEPT) showed signals at δ −36 (sharp peaks) [–CH$_2$–Si(Me)H–Si], and δ −40 (broad m) (*Si*Si$_2$C$_2$). In addition, a weak signal at δ −6 was assigned to *Si*C$_3$H nuclei. Thus, the structure of **3** is more complex than expected owing to the occurrence of side reactions. Owing to



Scheme 2 *Reagents and conditions*: i, Na in refluxing toluene, 48 h, then filtration and devolatilisation under high vacuum, 80 °C; ii, LiAlH$_4$/diethylether, reflux, 48 h, then filtration

Table 1 Ceramic yields and elemental composition (atom%) of ceramics obtained at 1000 °C

Polycarbosilane	Ceramic yield (%)	Analysis (%) C	Si	O	C/Si ratio
4	60	52.5	46	1.5	1.14
5	79	51.3	47.5	1.1	1.08

the thermal instability of Si–H and Si–Si bonds, oligomers **2** and **3** were readily converted into polycarbosilanes **4**[¶] and **5**[||] respectively. Thus, treatment at temperatures in the range 300–350 °C yielded solid materials that could be melted without decomposition. This transformation proceeded smoothly under atmospheric pressure, in the absence of catalysts. Controlling the mixture viscosity and the volume of gas (mainly hydrogen and methylsilanes) led to reproducible results. IR, ^{29}Si and ^{1}H NMR spectra showed that some of the Si–H bonds disappeared during this conversion, with concomitant insertion of methylene groups into Si–Si bonds.

SiC-based ceramics possessing a slight excess of free carbon and low oxygen content (Table 1) were prepared by placing the polycarbosilane **4** or **5** in a graphite crucible and heating under a high purity argon flow at a pressure of 100 kPa with a radiofrequency coil up to 1000 °C (heating rate: 5 °C min^{-1}).

Moreover, it was shown that these polycarbosilanes are well-suited for the melt-spinning process. Investigations concerning curing and pyrolysis of the resulting fibres, and study of their thermomechanical properties are in progress.

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Footnotes

[†] The synthesis of ClSiMeHCH$_2$SiMeHCl had previously been reported from dibromomethane.[17] We have prepared this compound according to an original and cheaper route using dichloromethane, in the presence of magnesium powder and zinc (30% mass) and a large excess of dichloromethylsilane. The solvent (anhydrous THF) was added dropwise over the mixture of the reactants at 25–30 °C. After the end of the addition, the mixture was kept at this temperature under stirring for 72 h, then an excess of chlorosilane and THF were trapped at −150 °C under vacuum. Finally, the crude bis(chlorosilyl)methane was trapped at low temperature under vacuum. The pure product was recovered in 35% yield upon distillation [66 °C (42 mm Hg)] and gave satisfactory microanalysis. Its ^{29}Si NMR spectrum showed that two diastereoisomers were present.

[‡] Size exclusion chromatography (eluent: THF, polystyrene standards).

[§] Char yields were measured from TGA analyses up to 950 °C (heating rate = 5 °C min^{-1}, argon flow rate = 50 ml min^{-1}).

[¶] Yield = 60%, $\bar{M}_w = 2550$, $I_p = 1.8$, softening range 160–170 °C.

[||] Yield = 58%, $\bar{M}_w = 7650$, $I_p = 3.0$, softening range 240–250 °C.

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