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Conversion process of chlorine containing polysilanes into silicon carbide

Part I *Synthesis and crosslinking of poly(chloromethyl)silanes–carbosilanes and their transformation into inorganic amorphous silicon carbide*

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Synthesis of chlorine containing polysilanes by catalytic redistribution is described and the obtained polymers are characterized by infrared (IR)-, magic angle spinning nuclear magnetic resonance (MAS-NMR)-spectroscopy and elemental analysis. The pyrolysis of such polysilanes was investigated by thermoanalysis, IR-, MAS NMR- and electron spin resonance (ESR)-spectroscopy. The conversion process from polysilane into polycarbosilane is described in terms of the results of the performed investigations and a model of the process is developed. Differences between this conversion process and those for chlorine free polysilanes or polycarbosilanes previously described by other authors are discussed.

1. Introduction

The conversion of organosilicon compounds into ceramic materials is a promising field of ceramic research. The application of such compounds as a precursor material for silicon carbide fibres which are used for manufacturing NICALON or TYRANNO fibres [1–4] is well investigated. However, chlorine containing polysilanes (PS) and polycarbosilanes (PCS) have been less studied.

With the exception of the publications of Baney *et al.* [5], Trandel and Urry [6], Calas *et al.* [7] and Gilbert and Cooper [8] chlorine containing PS/PCS were not the subject of investigations. Nevertheless, these polymers offer some advantages for application as ceramic precursors. These advantages result from the high reactivity of the Si–Cl bonds present in those polymers.

The synthesis of such chlorine containing polymers is economical in comparison with the synthesis described in references [1, 9, 10] and is similar to the synthesis which is described in reference [11]. A detailed description of our synthesis is given in reference [12, 13].

This paper will describe the processes involved in the conversion of the polymers and will specifically address the conversion from polysilanes into polycarbosilanes, the crosslinking process and the conversion of organosilicon compounds into an amorphous silicon carbide network. We exclude the crystallization process of silicon carbide at high temperatures e.g., more than 1200 °C, which will be reported in a future publication. IR-, NMR-, ESR-spectroscopy and thermoanalytical methods were used in the investigations.

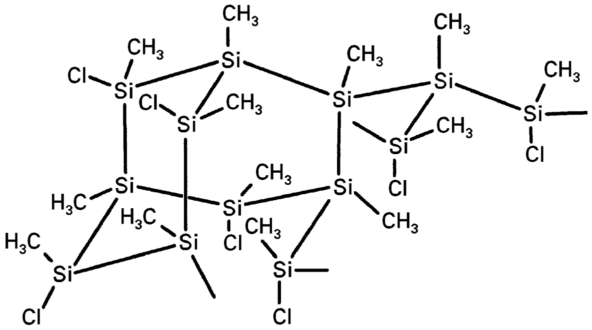


Figure 1 Part of the structure of polysilane as synthesized

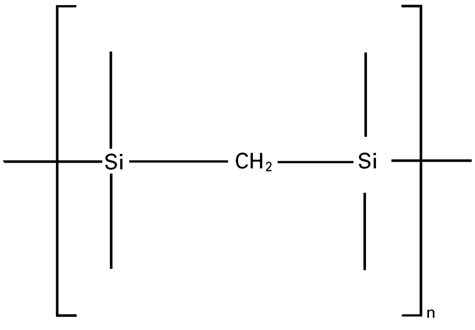


Figure 2 The principle structure of polycarbosilane

2. Experimental procedure

2.1. Synthesis of chlorine containing polysilanes/polycarbosilanes

The poly(chloromethylsilanes) were synthesized via a catalytic redistribution reaction of a mixture of chloromethyldisilanes that are by-products (DSF) of the direct synthesis of chloromethylsilanes and had the following average composition after careful distillation at 150–156 °C:

1.2 dichlorotetramethyldisilane	5.3 mol %
1.1.2 trichlorotrimethyldisilane	20.2 mol %
1.1.2.2 tetrachlorodimethyldisilane	74.5 mol %

2.1.1. Homogeneous catalytic redistribution reaction

2.5 g (0.5%) of the catalyst (imidazole) was added to 500 g of DSF. The mixture was heated up to 300 °C in a three-necked flask under an argon atmosphere. The methylchlorosilanes produced were continuously removed from the pot residue by distillation. Within 1 h the reaction was complete giving a powder-like polysilane/polycarbosilane. The PS/PCS yield was 20% with respect to the DSF.

2.1.2. Heterogeneous catalytic redistribution reaction

The redistribution reactions of DSF were carried out in all glass apparatus with the strict exclusion of air and moisture. The apparatus consists of a three necked flask with a thermometer, magnetic stirrer and a column containing 15 g of the catalyst (phosphorylgroups fixed onto the surface of a silicate carrier [12]) and a distillation bridge.

2.2. Pyrolysis

Pyrolysis was performed with ground solid PS/PCS (derived from homogeneous catalytical redistribution) of about 2–5 g in weight under inert gas (argon). The sample was filled in an alumina crucible and placed into an alumina tube furnace (Severn Furnace Ltd., UK) over which argon flowed.

The samples were heated up at a rate of (10 K min^{-1}) to different pyrolysis temperatures. The dwell time was 1 h (except for investigations concerning the dwell time). The obtained pyrolysed samples (brownish or blackish powders) were used in the following investigations.

2.3. Spectroscopy and thermoanalysis

Thermoanalysis was performed on a polysilane sample placed into the analysis crucible which was contained in an inert atmosphere box. The sample was immediately placed into the analyser and a nitrogen flow was established. The heating rate of the thermoanalyser (MOM/Budapest) was 5 K min^{-1} and the maximum temperature was 1000 °C.

Fine grained samples were used for the IR-spectroscopy (FT-IR-spectrometer A 510, Nicolet). These samples were mixed with KBr and pressed into disks which were used for measurements in the range 4000–400 cm^{-1}.

For the NMR measurements fine grained samples were filled in zirconia rotors. ^{29}Si and ^{13}C solid state MAS-NMR was performed. The samples obtained from pyrolysis of less than 900 °C were measured by the cross-polarisation method (CP). The NMR-spectrometer used was a Bruker MSL 300 model.

The ESR experiments were carried out with fine grained samples. The ESR spectrometer used was an ESR 200 model (ZWG Berlin). Ruby and ultramarine were used as standards in the quantitative measurements.

3. Results and discussion

3.1. The synthesis of poly(chloromethylsilanes) (PCMS)

The PCMS is obtained by a catalytic redistribution reaction of both Si–Si– and Si–Cl– bonds of chloromethyldisilanes. In comparison with dehalocoupling reactions of alkyl- or aryldichlorosilanes forming polysilanes and -carbosilanes the absence of expensive metals and the avoidance of costly reduction steps with alkali or earth-alkali metals is obviously an advantage of this type of reaction. The redistribution of tetrachlorodimethyldisilane (I) to trichlorosilane (II) and oligo(chloromethylsilane) (III) is depicted as an example of a number of reactions in Fig. 3.

This reaction of chloromethyldisilanes can be carried out under different regimes: creating either a homogeneous or a heterogeneous catalytic conversion. In both cases basic and nucleophilic compounds were applied to act as a catalyst. In previous work some catalytic systems have been reported in particular hexamethyl-phosphoric triamide and quaternary phosphonium and ammonium salts [6–8]. In the case of the homogeneous redistribution reaction we have used heterocyclic compounds like imidazole or pyrazole as effective cracking catalysts for chloromethyldisilanes. The obtained poly(chloromethylsilane)s are highly branched and crosslinked and give ceramic yields of up to 70 wt%. The drawback of this reaction is that it is difficult to control the resulting polymer properties, however, it is easy to perform and gives products which are well suited for conversion into ceramic powders.

Furthermore we developed a heterogeneous catalysis for phase separation between the catalyst and the parent chloromethyldisilanes as well as the reaction products. This method allows the preparation of poly(chloromethylsilanes) free of the catalyst and gave PS with definite melting intervals strongly determined by the chosen reaction temperature [12–16].

Fig. 4 shows a ^{29}Si-NMR-spectrum of a poly(chloromethylsilane) after a reaction temperature of 220 °C. A considerable part of the silicon atoms form tertiary silicon structure units as indicated by the large

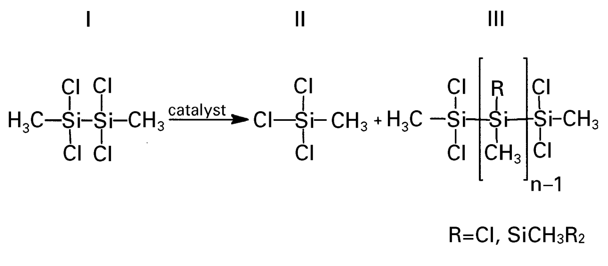


Figure 3 The redistribution of tetrachlorodimethylsilane (I) to trichloromethylsilane (II) and oligo(chloromethylsilane)s (III)

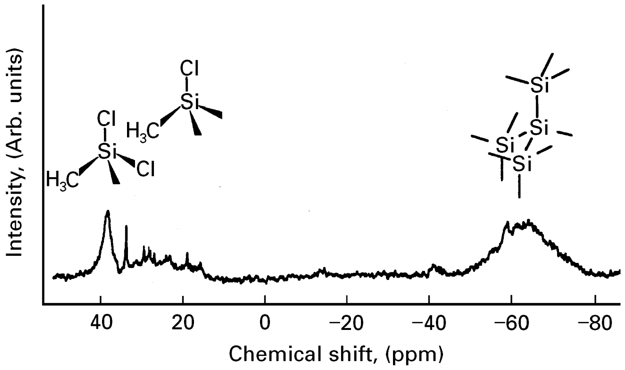


Figure 4 The ^{29}Si MAS-NMR-spectra of poly(chloromethylsilane)

broad resonance at -65 ppm. The comparatively narrow signal at 37 ppm is caused by $-SiCl_2CH_3$ groups bonded to branched Si units. A more detailed description of such polymers is already reported in [14].

3.2. Mass loss and gas evaluation during the pyrolysis process

The following results concern the polysilanes from the homogeneous reaction. The mass loss occurring during pyrolysis is caused by vaporization of oligosilanes and chlorosilanes, evolution of HCl and the formation of hydrogen and methane (detected by gas chromatography). Fig. 5 shows the mass loss curve for a thermogravimetric analysis of a poly(chloromethylsilane). A drastic mass loss is observed between 300–500 °C. Methyl insertion reactions (Kumada rearrangement) forming Si–H– bonds and methylene units are promoted with increasing temperature. This is shown in Fig. 6. These Si–H– bonds are consumed immediately by HCl formation or methane formation which lead to carbosilane structures and cross linking by Si-Si or Si-C bonding as shown in Fig. 7.

Furthermore it was noted that no other significant mass loss occurs at temperatures between 800–1000 °C. The mass loss must therefore be related to the progress of the crosslinking process which is completed at about 800 °C.

The mass loss including the loss caused by chlorine content is less than 30% which is small compared with the mass losses for chlorine free polymers reported by other authors [2, 3, 6]. This is caused by the rapid formation of highly crosslinked poly(silane/carbosilane) structures resulting from the HCl-formation reaction which enables an early crosslinking that retards the evaporation of low molecular weight polysilanes.

3.3. Structure change during pyrolysis process

The structure of pyrolysed PS/PCS was investigated by IR-, NMR- and ESR-spectroscopy. The measured IR-spectra are shown in Fig. 8. The bands at 3400 cm^{-1} and 1600 cm^{-1} are caused by OH vibrations that were derived from the KBr pressing technology. The absorption bands at around 2900 cm^{-1} characterize C–H vibrations of $-CH_3$ and $-CH_2$ groups. The methyl groups (CH_3) are characterized by absorption bands at 1410 cm^{-1} and 1270 cm^{-1}. Typical polycarbosilane absorption bands are found at 1000–1100 cm^{-1} (Si–CH_2–Si), 1350 cm^{-1} (Si–CH_2–Si). Si–Cl stretching vibrations are found between 600–470 cm^{-1} but they were observed to be significant only in as synthesized samples. Similar bands were found by Hasegawa and Okamura [1, 2], Bouillon *et al.* [18] and Babonneau *et al.* [19]. The vibration band at 2100 cm^{-1} (Si–H) which is commonly observed in chlorine free polycarbosilanes [1–3, 17, 18] was found only as a very weak band for the described polymers and pyrolysis products. The reason for this effect, as has already been explained, is the dehydrochloration process. The band intensity of polycarbosilane increases up to 500 °C at which point the original polysilanes are transformed into polycarbosilanes [1] whereas the IR-peaks of CH_3 groups

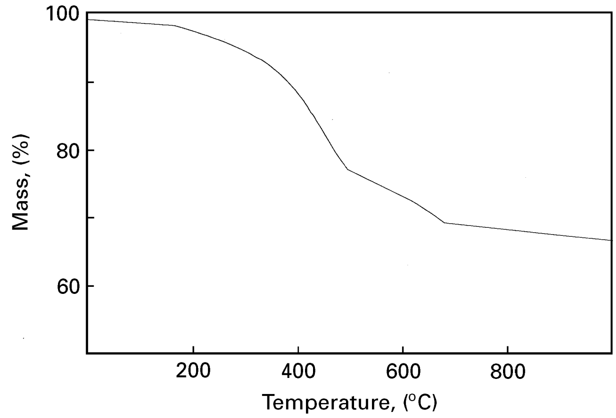


Figure 5 The TG-curve of a chlorine containing polysilane derived from a homogeneous catalytic redistribution heated in nitrogen (5 K min^{-1})

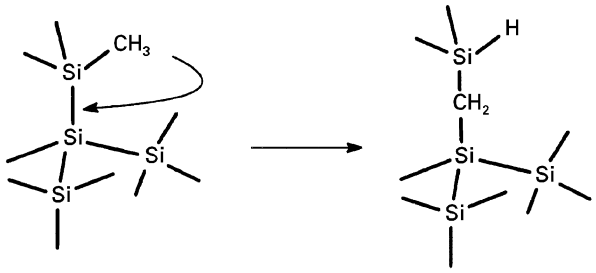
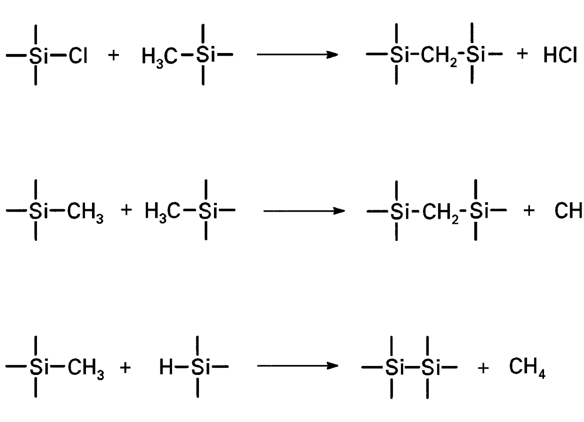


Figure 6 The methylene insertion (Kumada rearrangement) and formation of Si–H bonds during pyrolysis



$$-Si-Cl + H_3C-Si- \longrightarrow -Si-CH_2-Si- + HCl$$

$$-Si-CH_3 + H_3C-Si- \longrightarrow -Si-CH_2-Si- + CH_4$$

$$-Si-CH_3 + H-Si- \longrightarrow -Si-Si- + CH_4$$

Figure 7 HCl formation, methane formation and dehydrocoupling leading to Si–Si and Si-C crosslinking during pyrolysis processes decrease. An illustration of the progress of this transformation is given by Fig. 9 where the ratio of the band at 1250 cm^{-1} (for Si–CH_3) and the band at 800 cm^{-1} (for Si–C) is plotted as a function of the temperature.

The bands of the organic groups disappear with increasing temperature. There is no absorption peak except for that of Si–C in SiC at about 800 cm^{-1} at temperatures of more than 900 °C as is shown in Fig. 8.

A peak deconvolution procedure was performed on the IR-region between 1000–1100 cm^{-1}. It was assumed that a more crosslinked and larger structure (owing to the increase of the reduced mass) should shift the wavenumber of a certain vibration to a lower value, according to the simple model of vibrators

$$\tilde{\nu} \sim \left(\frac{k}{m_{\text{red}}}\right)^{1/2} \qquad (1)$$

where $\tilde{\nu}$ is the wavenumber, k is the force constant, and m_{red} is the reduced mass.
The following assumptions were made:

(1) the subband between 1090–1120 cm^{-1} is related to slightly crosslinked PCS
(2) the subband between 1050–1080 cm^{-1} is related to medium crosslinked PCS
(3) the subband between 1000–1030 cm^{-1} is related to well crosslinked PCS

This definition is useful to describe the crosslinking process. Nevertheless it is only a simplified model for a real description of the PCS-crosslinked structure. It should be emphasized once again that the described IR-band (1100–1000 cm^{-1}) disappears at temperatures of more than 700 °C giving a hint that no significant Si–O–Si vibrations (around 1080 cm^{-1}) influence this band as described by Hasegawa [3].

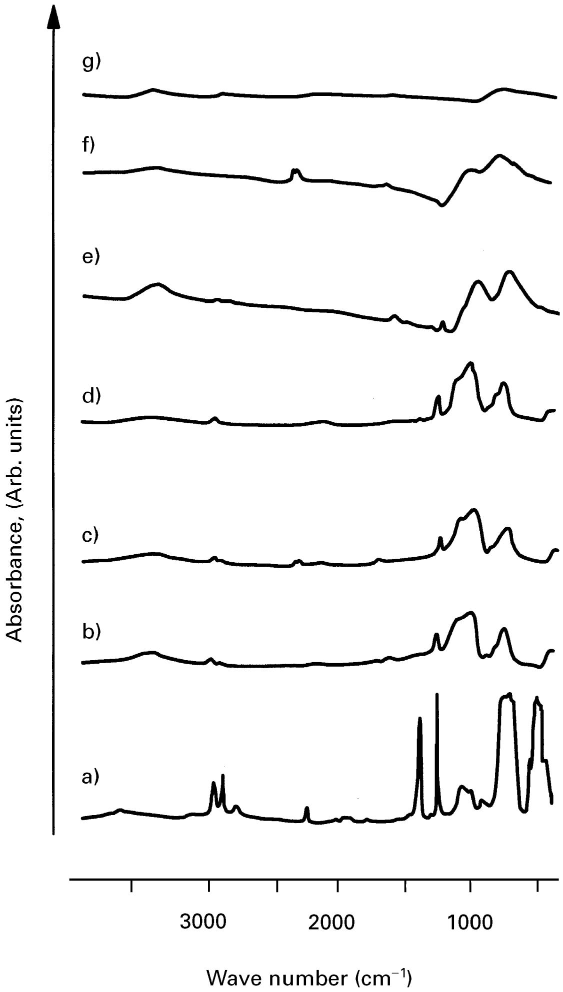


Figure 8 The IR spectra (absorption) of pyrolysed polysilane samples in dependence on the pyrolysis temperature (heating rate 10 K min^{-1}, dwell time 1 h), (a) as synthesized (b) 390 °C, (c) 450 °C, (d) 500 °C, (e) 600 °C, (f) 700 °C and (g) 900 °C

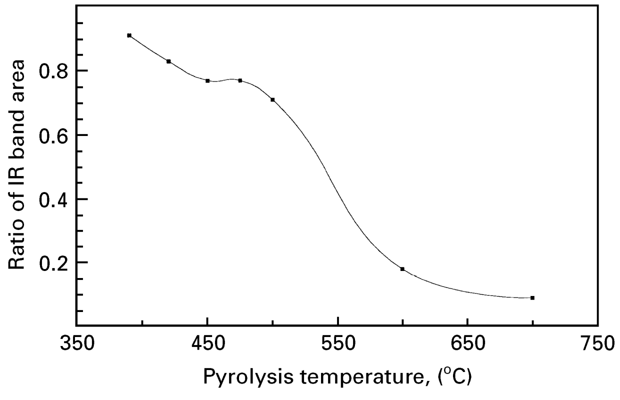


Figure 9 The ratio of the areas of the bands of Si–CH_3 (1250 cm^{-1}) and Si–C (780 cm^{-1}) in dependence on the pyrolysis temperature

Fig. 10 shows the relative amounts of the areas of the subbands which are related to the state of crosslinking of the polymer. At 390 °C there is a large amount of weakly cross-linked PCS but there is also a considerable amount of more crosslinked structures, which shows that the crosslinking process has already started. The amount of slightly cross-linked PCS is constant up to 450 °C although the amount of well crosslinked PCS increases. The reason for this is the continuous transformation of polysilane into polycarbosilane leading to the formation of new slightly crosslinked polycarbosilane structures.

This transformation is also also observed in the ^{29}Si-MAS NMR spectra (Fig. 11) where a signal around −50 ppm is found which is related to branched Si structures in polysilanes. At about 500 °C this signal disappears. This is obviously caused by transformation of the polysilane to polycarbosilane structures by Kumada rearrangement which is typical for that temperature.

TABLE I Typical IR-vibrations of polysilanes and polycarbosilanes

Wavenumber (cm^{-1})	Vibration
3000–2900	various C–H (stretching)
2100	Si–H (stretching)
1410	Si–CH_3 (def., antisym.)
1350	Si–CH_2–Si (def.)
1270	Si–CH_3 (def., sym.)
1100–1000	Si–CH_2–Si (wag.)
850–750	Si–C (stretching) Si–CH_3 (rocking)
550–470	Si–Cl (stretching)

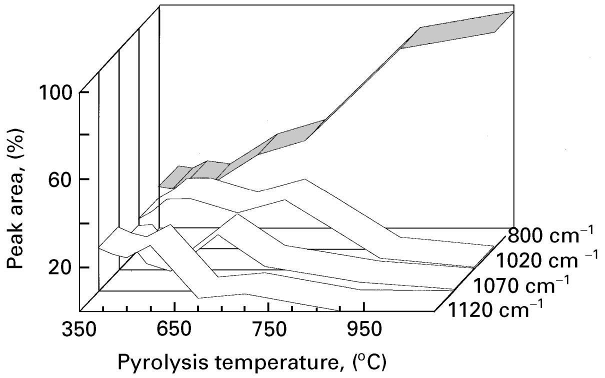


Figure 10 The IR subbands of the Si–CH_2–Si vibration band around 1040 cm^{-1} derived from deconvolution of this band and the Si–C band and its dependence on the pyrolysis temperature

The amount of well crosslinked polycarbosilane increases up to 500 °C. This effect results from crosslinking processes of medium and weakly crosslinked polycarbosilane structures. Although the mass loss achieved its maximum (which is related to the crosslinking) the crosslinking process seems to be retarded as shown by the IR-results which suggests a crosslinking at higher pyrolysis temperatures than could be expected by the mass loss.

A larger amount of weakly crosslinked polycarbosilane was observed at 500 °C subsequently followed by a drastic decrease of this subband at 600 °C. The transformation of polysilane into polycarbosilane reached its maximum and final interval which is in agreement with NMR-spectroscopy results.

The amount of well crosslinked polycarbosilane decreases slightly at 600 °C because of the beginning of the formation of an inorganic network consisting of silicon and carbon atoms that is indicated by the IR-band between 700–900 cm^{-1} which is related to Si–C vibrations. The relative area of this band increases slowly with heating of the samples from 500 to 700 °C and then increases very rapidly at temperatures of more than 700 °C (Figs. 9 and 10). This broad band includes the vibrations of the Si–C bonds of the Si–CH_3 and Si–CH_2 groups which cause this peak at lower temperatures in addition to those of Si–C bonds in silicon carbide which cause this band at temperatures of 600–700 °C. Nevertheless this process is characterized by the intensity ratio of the bands of Si–CH_3 vibrations (1250 cm^{-1}) and Si–C vibrations (780 cm^{-1}) which are shown in Fig. 9. The drastic decrease of the quotient at pyrolysis temperatures between 500–600 °C indicates a crosslinking process which additionally includes carbon atoms (as CSi_4 units).

In addition the NMR spectra of samples which were treated at these temperatures imply a change of structure. The ^{29}Si-signals characterize the entity of SiC_4 groups (Fig. 11). This signal at about 0 ppm is shifted to –15 ppm with increasing temperature. This shift is related to an inorganic SiC structure as described in

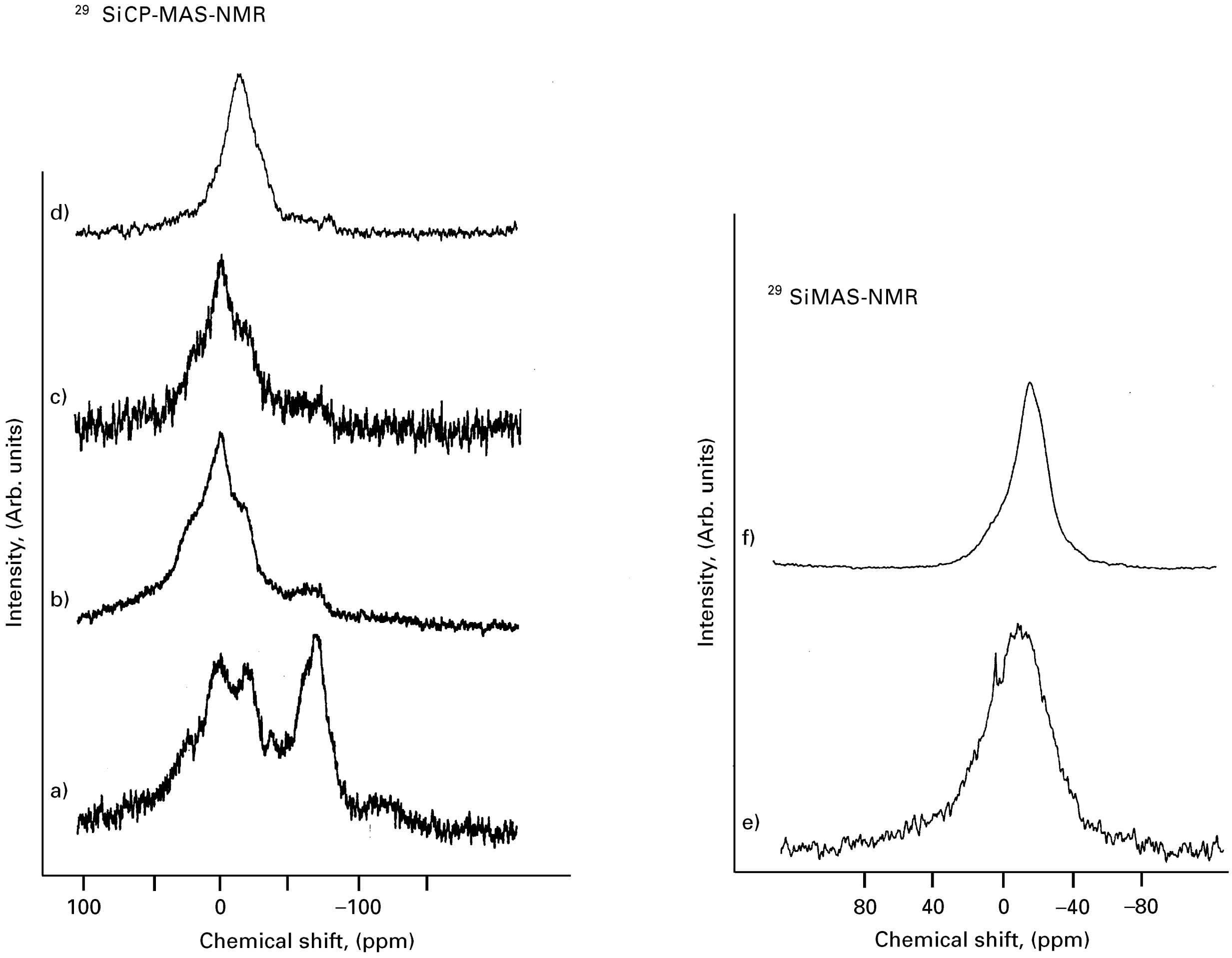


Figure 11 The ^{29}Si-MAS-NMR spectra of pyrolysed polysilane samples as a function of the pyrolysis temperature; (a) 390 °C, (b) 450 °C, (c) 500 °C, (d) 600 °C, (e) 900 °C and (f) 1100 °C

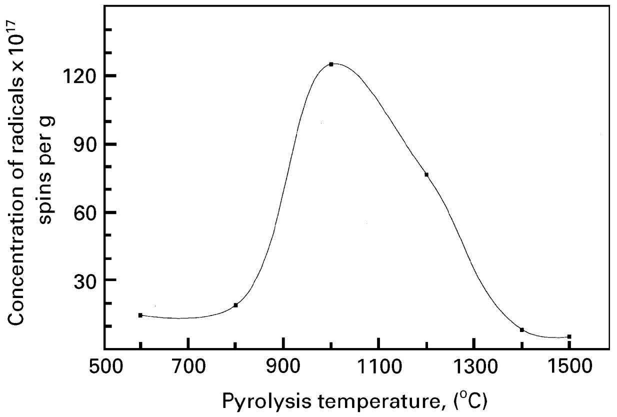


Figure 13 The concentration of radicals measured by ESR experiments of pyrolysed polysilane samples as a function of the pyrolysis temperature

reference [12]. The original signals at about 35 and 50 ppm are assumed to be related to chlorine containing groups. The disappearance of these NMR signals at pyrolysis temperatures below 500 °C prove that the Si–Cl bonds play an active part in the crosslinking process.

Nevertheless the ^{13}C-spectra (Fig. 12) show that the environment of the carbon atoms changes giving CSi_4 groups between 600–900 °C. This implies once again that the progress of crosslinking and the structure alters between the organosilicon state and the inorganic state. The observed increase in Si–C-band intensity in the IR spectra is in agreement with the observations of the NMR spectroscopy.

The data of the ESR-spectroscopy experiments show that new structural defects are created during the conversion process (Fig. 13). Probably the conversion of the crosslinked polycarbosilanes into inorganic amorphous silicon carbide is connected with the formation of carbon radicals or the so called "dangling bonds" [18]. The concentration of these radicals is shown in Fig. 13. The radical concentration reaches a maximum at the pyrolysis temperature of about 1000 °C. The number of radicals decreases at higher temperatures which is probably due to the crystallization of silicon carbide.

4. Conclusions

The investigated chlorine containing polysilanes show a more effective crosslinking process during the pyrolysis than that described for organosilicon polymers.

The transformation of polysilane into polycarbosilane was observed in the temperature range from 200–500 °C. The crosslinking of polycarbosilane occurs in the temperature range from about 300–800 °C. That means that the crosslinking is partly performed in the same interval where the transformation of polysilane into polycarbosilane takes place. The crosslinking is realized by cleavage of hydrogen, chlorine and CH_3 groups which results in a pyrolysis gas consisting mainly of HCl, CH_4 and H_2. This pyrolysis behaviour enables new methods of manufacturing ceramic materials such as silicon carbide, silicon nitride and even mixed carbides of silicon compounds with other metallic carbides e.g. SiC/TiC or SiC/WC. In addition to

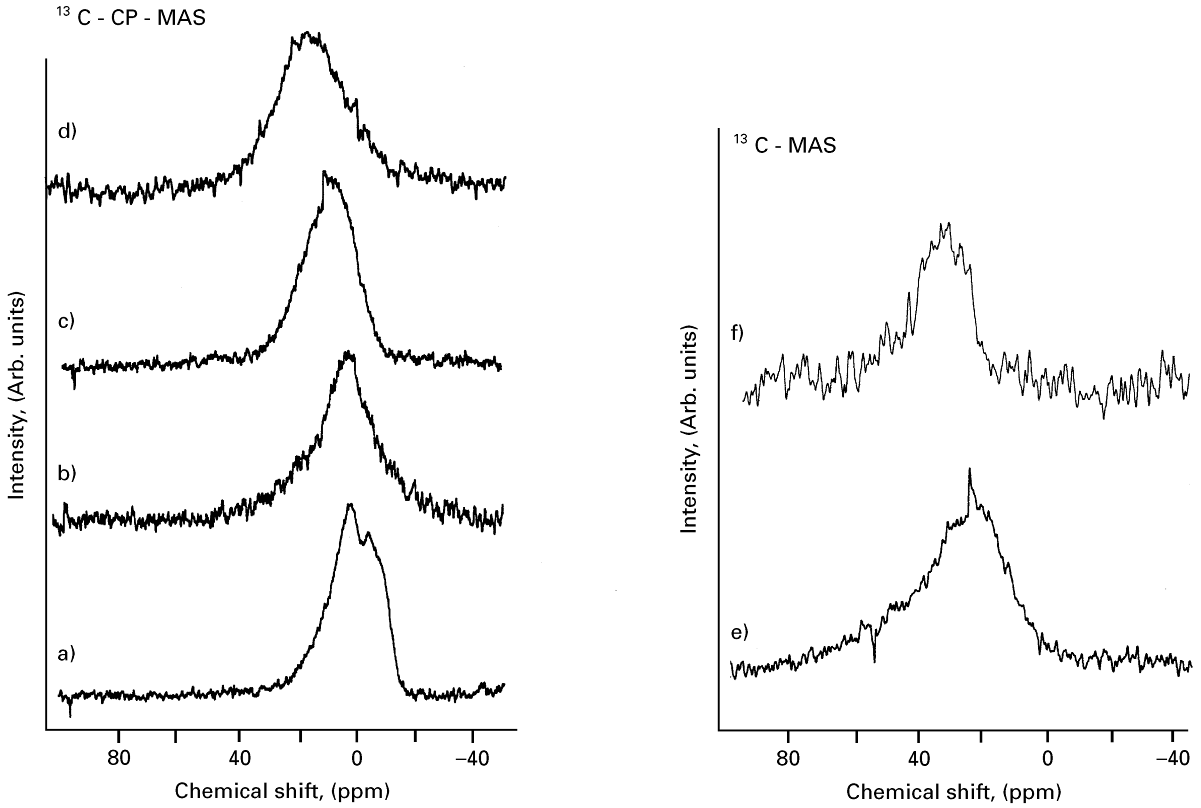


Figure 12 The ^{13}C MAS-NMR spectra of pyrolysed polysilane samples as a function of the pyrolysis temperature; (a) 390 °C, (b) 450 °C, (c) 500 °C, (d) 600 °C, (e) 900 °C and (f) 1100 °C

this there are some new opportunities for fibre manufacturing especially with regard to the curing process and the composition of the final fibres [22, 23]. All these advantages are a result of the highly reactive silicon–chlorine bond in the polymer.

The final step of the crosslinking process is the conversion of the well crosslinked polycarbosilane into an inorganic amorphous silicon carbide network which is connected with the creation of radicals especially carbon "dangling bonds".

During this later stage only a very small mass loss was found that results from the well crosslinked state of the polysilane/polycarbosilane.

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