Monatshefte für Chemie 125, 895–900 (1994)

Monatshefte für Chemie
Chemical Monthly

Short Communication

Preparation of a Cross-Linked Polycarbosilane and its Conversion to Silicon Carbide Ceramics**

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Summary. Cross-linked polycarbosilanes are obtained from the reaction of $Cl_2MeSiCHCl_2$ and Mg in tetrahydrofuran, followed by reduction with $LiAlH_4$. Analysis by NMR spectroscopy shows that most polycarbosilane is of the formula $[MeSiCH]_n$.

Keywords. Pre-ceramic polymer; Cross-linked; Polycarbosilane; Silicon carbide.

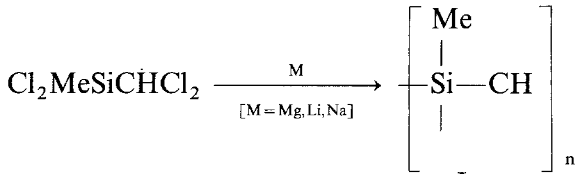
Herstellung eines vernetzten Polycarbosilans und seine Umwandlung zu Silikoncarbid-Keramik

Zusammenfassung. Durch Reaktion von $Cl_2MeSiCHCl_2$ mit Mg in Tetrahydrofuran und anschließende Reduktion mit $LiAlH_4$ erhält man vernetzte Polycarbosilane. NMR-spektroskopische Untersuchungen zeigen, daß das Polycarbosilan überwiegend als $[MeSiCH]_n$ vorliegt.

Polymer precursors to ceramic materials have been sought after in the hope they might allow some control over the processing and final shape of a ceramic green body [1]. These pre-ceramic polymers can be used as binders for SiC powders, can be pulled or spun into fibers, and can be infiltrated into shaped composites. Polycarbosilanes are pre-ceramic polymers which typically yield silicon carbide (SiC) upon firing; this area has been reviewed recently [1a]. The most widely used SiC pre-ceramic is the Nicalon polycarbosilane developed by *Yajima* in 1976 from thermal isomerization of poly(dimethyl)silane [2]. Polycarbosilanes can also be obtained by reductive coupling of $ClRR'SiCH_2Cl$ ($R,R' =$ Me, Me [3]; Me, Cl [4]; Cl, Cl [5]) using magnesium. In the case of $Cl_2MeSiCH_2Cl$ and Cl_3SiCH_2Cl, branched polymers and not cross-linked polymers are observed. We were interested in synthesizing cross-linked polycarbosilanes in the hope of obtaining a high char (ceramic) yield of SiC upon firing [6]. To investigate this possibility, we looked at the reductive coupling of $Cl_2MeSiCHCl_2$, a chlorosilane containing two potential reactive sites on both silicon and carbon which could lead to cross-linked systems.

** Contribution no. 6627

The polycarbosilane, **I**, was synthesized by the reaction of $Cl_2MeSiCHCl_2$ with magnesium in tetrahydrofuran (*THF*) [7, 8]. Little coupling takes place in refluxing diethyl ether. After cooling, the unreacted Si–Cl functionalities are reduced by $LiAlH_4$ prior to aqueous workup. In this manner yellow glassy solids are obtained in 50–99% yield which are soluble in common solvents such as hexane, *THF*, and toluene

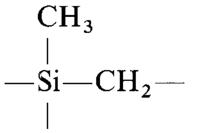


$$Cl_2MeSiCHCl_2 \xrightarrow[\text{[M = Mg, Li, Na]}]{M} \left[\begin{array}{c} Me \\ | \\ -Si-CH \\ | \end{array} \right]_n$$

I

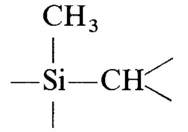
The 300 MHz proton NMR spectrum of **I** reveals broad resonances from −0.2 to 0.6 ppm (Si–CH) and from 3.5 to 4.8 ppm (Si–H) consistent with the formula of the polymer as mostly $[Me(H)_xSiCH]_n$. Other broad resonances between 1–2 ppm are also observed and are consistent with products resulting from some cleavage of the *THF* solvent; this incorporates at most 2% oxygen in the polycarbosilane [9]. No $SiCHCl_2$ is observed in the spectrum, however, resonances due to residual $SiCH_2Cl$ can be seen around 2.9 ppm [10]. The 75 MHz ^{13}C NMR spectrum of **I** shows a large broad Si–CH resonances from −10 to +10 ppm and peaks at 23, 30 and 32 ppm which can be assigned to $SiCH_2Cl$.

More detailed information on the structure of polycarbosilane can be obtained from its ^{29}Si NMR spectrum. Figure 1 shows the spectrum of **I** which reveals that 81% of the polycarbosilanes Si atoms are cross-linked as shown by the broad peak centered about 2 ppm [11]. Both cross-linked units shown below



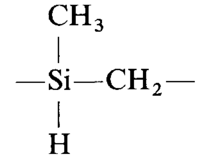
$$\begin{array}{c} CH_3 \\ | \\ -Si-CH_2- \\ | \end{array}$$

partially cross-linked unit



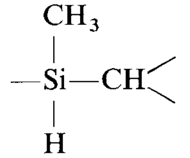
fully cross-linked unit

are presumably involved in the network structure of **I**. Using the DEPT pulse sequence [12], with a 45° *theta* pulse and assuming a Si–H coupling of 204 Hz, the protonated silicon portion of the spectrum can be isolated as shown in Fig. 2. Two regions are observed for the Si–H silicons, −15.1 to −18.1 and 2.0 to −8.2 ppm. The ^{29}Si resonances between −15.1 to −18.1 ppm are most likely due to the "SiH linear unit" shown below [13]. The broader peak between 2.0 and −8.2 ppm can be attributed to

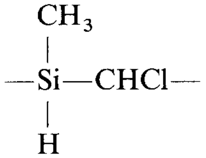


$$\begin{array}{c} CH_3 \\ | \\ -Si-CH_2- \\ | \\ H \end{array}$$

SiH linear unit



SiH cross-linked unit



$$\begin{array}{c} CH_3 \\ | \\ -Si-CHCl- \\ | \\ H \end{array}$$

chloromethyl linear unit

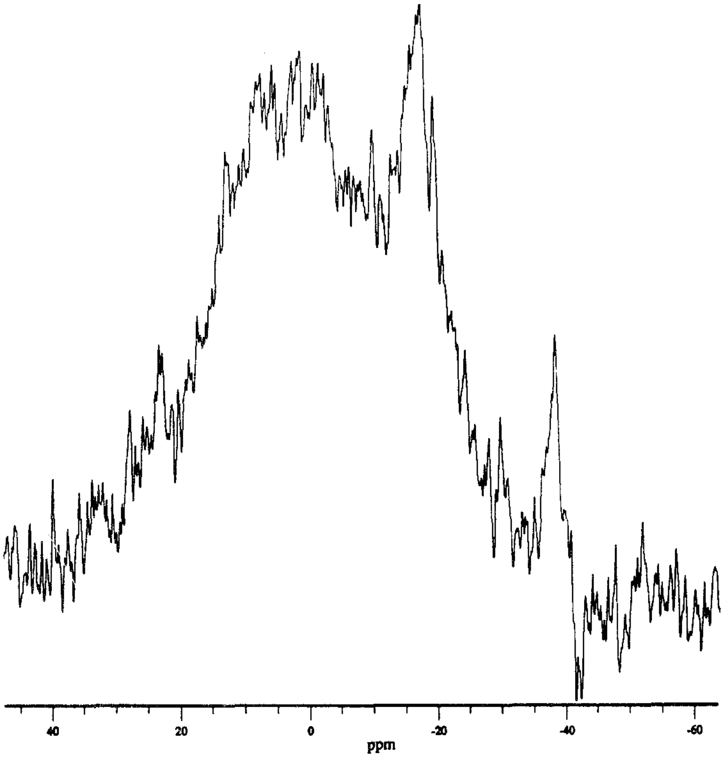


Fig. 1. ^{29}Si NMR spectrum (60 MHz) of polycarbosilane **I** in $CDCl_3$

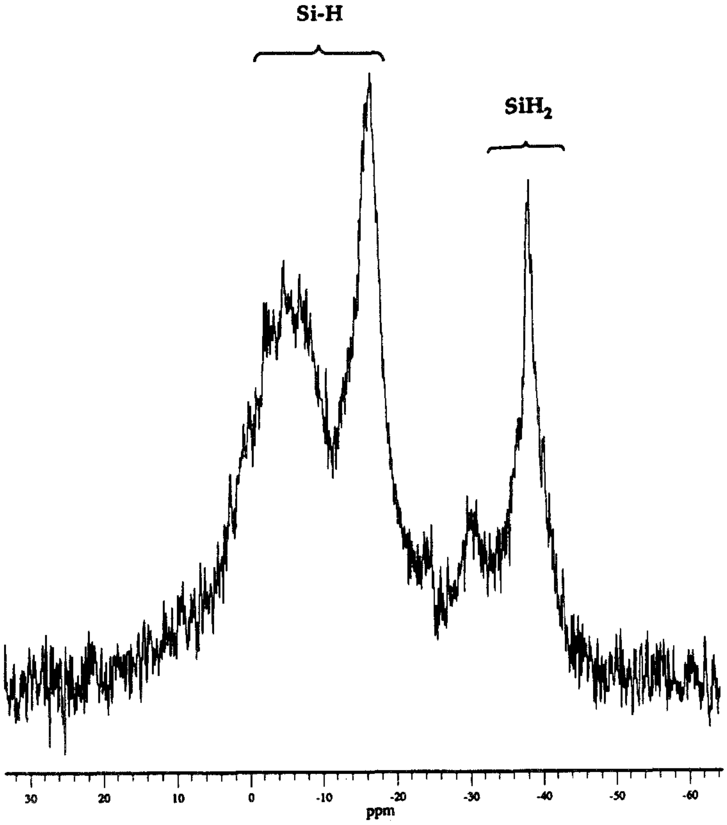
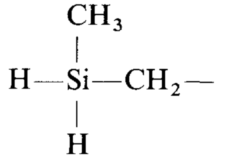
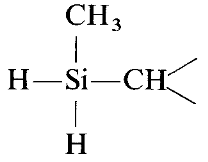


Fig. 2. ^{29}Si NMR spectrum of polycarbosilane **I** showing the SiH and SiH_2 regions



$$H{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{Si}}{-}CH_2{-}$$

SiH_2 end unit



$$H{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{Si}}{-}CH\langle$$

SiH_2 linear unit

the "SiH cross-linked unit" and not the "linear unit" due to the observed upfield chemical shift [14]; however, products due to Si–O incorporation can not be completely ruled out [15]. The resonances associated with SiH_2 groups are observed at -38.6 ppm and assigned to the "SiH_2 end unit" structure. The small hump centered at -30 ppm is tentatively assigned to the "SiH_2 linear unit". Using the NMR data, polycarbosilane **I** can be estimated to contain 14% SiH and 5% SiH_2 groups.

It appears that the reaction of $Cl_2MeSiCHCl_2$ with Mg metal forms a cross-linked soluble polycarbosilane. In a broad sense, the network structure of our polymer resembles the proposed structure for the Nicalon polycarbosilane [2].

GPC analysis of **I** revealed a broad bimodal distribution with $Mn = 1700$ and $Mw = 9500$ (polydispersity $= 5.5$). Elemental analyses of **I** showed about 5–8% residual chlorine, and were consistent with $[Me(H)_xSiCH]_n$ having the average formula $[MeSi(H)_{0.5}CHCl_{0.1}O_{0.1}]_n$. No melting of these polymers were observed up to 360°C. DSC analysis of **I** under N_2 gave two broad exothermic transitions: at 253°C and at 378°C. Pyrolysis of **I** at 1000°C under Ar produced black ceramics in 56–63% yields. TGA analysis of **I** gave similar ceramic yields with the major weight losses occurring in two steps (between 150–300°C and 400–550°C). Fibers of **I** could be pulled from hexane or toluene solution and retained shape when pyrolyzed at 1000°C under Ar. Analyses of the ceramics derived from **I** gave the ranges of $SiC + 0.44\text{–}0.50\ C + 0.21\text{–}0.26\ O$, roughly working out to an empirical formulation of $SiC_{1.5}O_{0.2}$.

When the reaction conditions were changed from Mg/*THF* to Na/toluene, insoluble powders were obtained. These polymers are probably cross-linked mixed polysilane/polycarbosilane systems. TGA yields of the isolated powders were 68–79%. Attempts at making these mixed systems soluble by thermal curing proved unsuccessful. If Li/*THF* is used, a yellow liquid is obtained in 88% yield which contains much residual CH_2Cl (NMR).

In order to gain more information on the polymerization pathway, the reaction of $Me_3SiCHCl_2$ with Mg was investigated. We were also interested in observing *Grignard* reagents of the type $Me_3SiCHCl(MgCl)$ or $Me_3SiCH(MgCl)_2$ [16]. Reaction of $Me_3SiCHCl_2$ with an excess of Mg produced a brown solution with precipitated salts. Similar products were obtained whether this reaction was quenched by MeI or by protons during aqueous workup. The major products were found to be $Me_3SiCH(Cl)SiMe_3$ (16%) and $Me_3SiCH_2SiMe_3$ (8%) [17]. The *Wurtz*-coupled products, $Me_3SiCH(Cl)CH_2SiMe_3$ and $Me_3SiCH(Cl)CH(Cl)SiMe_3$, were found in low yield (<1%). No Me_3SiCH_2Cl was observed. The formation of $Me_3SiCH(Cl)SiMe_3$ and $Me_3SiCH_2SiMe_3$ can be understood as arising from attack of $Me_3SiCHCl(MgCl)$ at the silicon atom of unreacted starting material. We did not observe any products derived from the required leaving group $-CHCl_2$. We conclude that competitive chemistry similar this might be operating to some extent in the preparation of **I** leading to cleavage of some polymer Si–C bonds as well as formation of Si–C linkages by reductive coupling.

Acknowledgements

We would like to thank Dr. *R. Zubyk* for GC/MS analyses. The expert technical assistance of *C. Adams*, *L. Harrison*, and *J. Nguyen* is greatly appreciated.

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[6] Cross-linking of the pre-ceramic polymer is thought to be necessary to obtain high ceramic yields, see reference 1b.

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[8] A typical preparation of the polycarbosilane is as follows: To a stirred solution of 43.0 ml (0.307 mol) of $Cl_2MeSiCHCl_2$ in 400 ml *THF* was added 15.62 g (0.643 mol) of dried magnesium turnings over a 1 h period at 25°C. After the addition, the reaction mixture was refluxed for 2 h, and the resulting orange-brown mixture was cooled and stirred at room temperature for 16 h. After cooling to 0°C, 3.20 g of lithium aluminum hydride was added slowly to quench any residual Si–Cl. After stirring for 1 h, the slurry was slowly quenched with 10% aqueous hydrochloric acid solution until the evolution of gas ceased. The bulk of the solids were filtered and the filtrate was extracted with hexane and washed once with saturated ammomium chloride solution, then twice with distilled water and dried over magnesium sulfate. Removal of the volatiles *in vacuo* left 17.8 g (93% based on $(MeH_{0.5}SiCHCl_{0.11}O_{0.11})_n$) of a golden brown solid. The polymer is soluble in most common organic solvents. ^1H NMR ($CDCl_3$, ppm): -0.4–0.6 (br, MeSi, SiCH), 3.6–4.6 (br, SiH); ^{13}C NMR ($CDCl_3$, ppm): -10 to $+8$ (br, Si–CH), 14.3 (s), 22.9 (s), 29.9 (s), 31.8 (s); ^{29}Si NMR ($CDCl_3$, ppm) $+20$ to -20 (br, MeSiCH), $+1$ to -20 (br, $Me(H)SiCH_2$), -10 to -20 (br, Me(H)SiCH), -28 to -34 (br, $Me(H)_2SiCH_2$), -34 to -42 (br, $Me(H)_2SiCH$). Analysis: calcd. for $C_2H_{4.5}Cl_{0.11}SiO_{0.11}$: C, 38.56; H, 7.28; Cl, 6.26; found: C, 38.53; H, 7.24; Cl, 6.20.

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[10] In our hands the CH_2Cl resonance of Me_3SiCH_2Cl occurs at 2.74 ppm ($CDCl_3$) and 2.44 ppm (C_6D_6), and the $CHCl_2$ resonance of $Me_3SiCHCl_2$ occurs at 4.80 (C_6D_6).

[11] Cross-linking in this paper can also refer to cyclic structures within the polycarbosilane.

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[14] Related silicon-29 shifts (ppm) are: $(H_2PhSi)_2CH_2 = -33.48$; $(H_2PhSi)_3CH = -30.87$; $(H_3Si)_2CH_2 = -59.97$; $(H_3Si)_3CH = -53.30$; Hager R., Steigelmann O., Muller G., Schmidbaur H.

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[15] Note: $HMe_2SiOSiMe_2H$ has a ^{29}Si resonance at -4.42 ppm; Helmer B., West R. (1982) Organometallics **1**: 877

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[17] An internal hexadecane standard was used to determine the absolute yields

Received February 1, 1994. Accepted February 7, 1994