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Preliminary communication

## Organosilicon polymers: pyrolysis of poly[(silanylene)diethynylene]s

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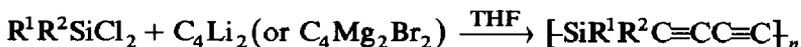
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### Abstract

The pyrolysis of  $\{Si(CH_3)_2C\equiv CC\equiv C\}_n$  in a stream of argon to 1400 °C gives a SiC-containing ceramic in high yield (85%). TGA, TGA-mass spectrometry and solid state <sup>13</sup>C NMR studies are reported, and show that: (1) a low-temperature cross-linking process involving the diacetylenic units occurs at about 300 °C below the mineralisation stage and (2) the weight decrease between 400 °C and 800 °C arises only from loss of H<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>. Pyrolysis under NH<sub>3</sub> leads to Si<sub>3</sub>N<sub>4</sub> with loss of the carbon.

In an earlier work [1], we reported the preparation of various poly[(silanylene)diethynylene]s by the reaction of the dilithium or di-Grignard reagent of the diacetylene with a dichlorosilane:



When doped with the Lewis acid FeCl<sub>3</sub>, the polymers had relatively high conductivities, reaching the range of 10<sup>-5</sup> to 10<sup>-3</sup> S cm<sup>-1</sup>, characteristic of a conducting state.

We were also interested in pyrolysis of the polymers as a possible route to ceramic materials [2]. The presence of appropriate functionalities (H or vinyl groups) on the main chain of the polymer is one of the factors that determine the ceramic yields [2,3]. They allow cross-linking, which inhibits depolymerisation. Our compounds bear no such reactive groups at silicon, but they contain diacetylenic units, which are known to induce crosslinking reactions in the case of diacetylenes or poly(aromatic diacetylene)s at relatively low temperatures [4,5]. Thus a similar process should occur with poly[(silanylene)diethynylene]s, and we decided to see whether the  $\{SiR^1R^2\}$  units would provide SiC under these conditions.

Heating of  $\{Si(CH_3)_2C\equiv CC\equiv C\}_n$  ( $M_w = 4063$  relative to polystyrene standards,  $M_w/M_n = 1.24$ ) in a stream of argon (50 ml/min) to 1400 °C at 10 °C/min, gave a

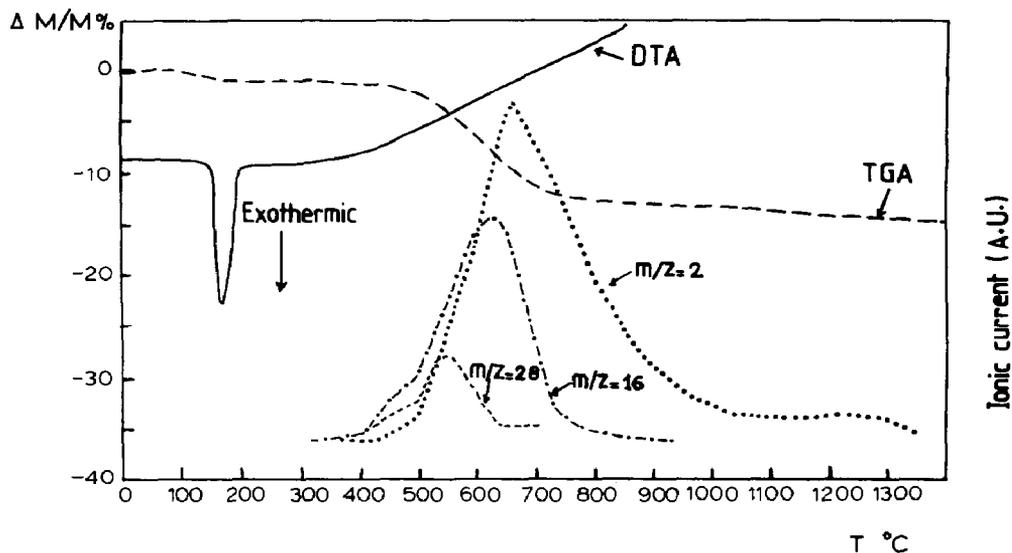


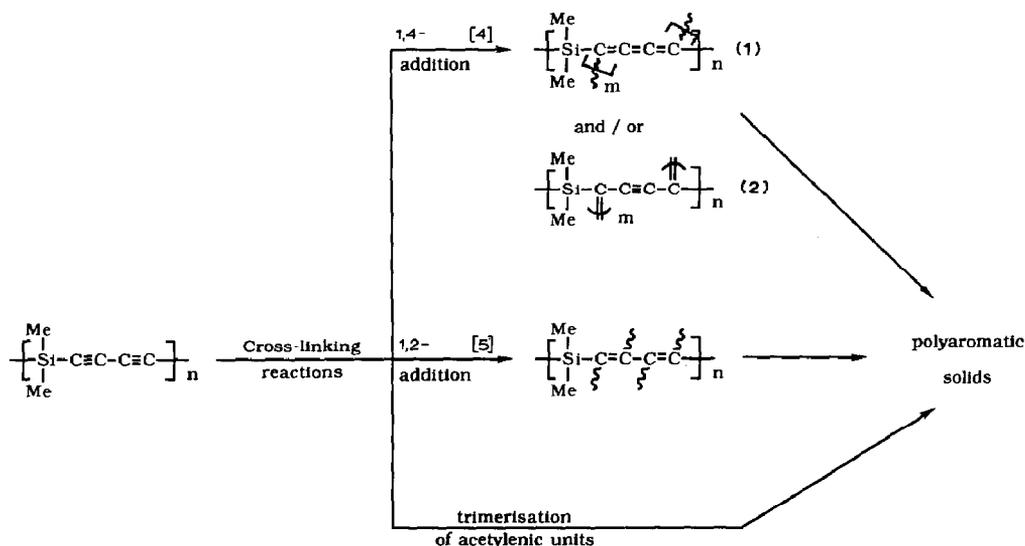
Fig. 1. Pyrolysis of  $\{\text{Si}(\text{Me})_2\text{C}\equiv\text{CC}\}_n$ : DTA and TGA/MS analysis. For DTA and TGA/MS analysis see ref. 9.  $m/z = 2, 16$  and  $28$  are attributed to  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{CH}_2=\text{CH}_2$ , respectively. Calibration of the mass spectrometer was done using standard compounds such as  $\text{H}_2$ , Ar,  $\text{N}_2$  and  $(\text{C}_2\text{H}_5)_2\text{O}$ .

black powder as a ceramic residue in 85% yield [6\*]. Elemental analysis of the pyrolysis product gave 33.1% Si, 65.9% C, and 1.3% O, and the ceramic blend may be represented as  $(\text{SiC})_1(\text{C})_4$  on a molar basis. The material contains a large excess of free carbon (compare SiC: calc. 70% Si, 30% C), as observed previously for polyacetylenes  $\{\text{SiR}^1\text{R}^2-\text{C}\equiv\text{C}\}_n$  [7]. Examination of this material by X-ray powder diffraction showed the presence of crystalline  $\alpha$ -SiC.

The results of TDA and TGA studies under argon are shown in Fig. 1. Exothermic transformation (800–1000 cal/g determined by differential scattering calorimetry, DSC [8\*]) was observed at about 200°C without weight loss, suggesting a cross-linking process involving the diacetylenic units. Decomposition of the sample occurred between 450°C and 800°C with loss of  $\text{H}_2$ ,  $\text{CH}_4$  and a small quantity of ethylene, as indicated by mass spectrometric analysis [9\*] of the gases evolved during the pyrolysis (Fig. 1).

Solid-state  $^{13}\text{C}$  NMR spectroscopy suggests that the initial stages of the cross-linking process involve conversion of the  $sp$  carbons into  $sp^2$  centers [10]. The resonances at 82.3 and 89.3 ppm, assigned to the diacetylenic carbons of the starting material [1], are replaced by a broad envelope of signals in the 130–160 ppm region. In addition, when a sample is heated above 200°C, the infrared spectra show two new absorptions at 2114 and 1872  $\text{cm}^{-1}$ , attributed respectively to enyne and triene structures such as **1** and **2** (Scheme 1) along with a broad absorption at 1529  $\text{cm}^{-1}$  in a frequency range characteristic of aromatic groups. When the sample is heated to 400°C, the gradual disappearance of the two former absorptions is observed while the latter increases. Thus the data are consistent with cross-linking reactions

\* Reference number with asterisk indicates a note in the list of references.



Scheme 1. Cross-linking of poly[(silanylene)diethynylene].

via either 1,2- or 1,4-addition of acetylenic groups, leading [4,5] ultimately to the amorphous  $sp^2$  carbon matrix (Scheme 1). However, we cannot exclude the possibility that aromatic species may be formed directly by trimerisation of the acetylenic units.

The pyrolysis of  $\{\text{Si}(\text{CH}_3)_2\text{C}\equiv\text{CC}\equiv\text{C}\}_n$  in a stream of  $\text{NH}_3$  (50 ml/min) to  $1400^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$  was found to occur with weight loss above  $450^\circ\text{C}$ . We obtained a white powder as residue in 38% yield. X-ray diffraction showed the presence of  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$ .

We conclude that the data described demonstrate the feasibility of using poly[(silanylene)diethynylene]s to produce SiC-containing materials. The following features should be pointed out:

(i) The cross-linking reactions occur at about three hundred degrees Celsius below the mineralisation stage. Thus the formation of SiC occurs inside the amorphous carbon matrix.

(ii) All the silicon contained in the dimethylsilyl groups of the starting polymer was quantitatively present in the ceramic as SiC. The weight decrease arises only from loss of  $\text{H}_2$ ,  $\text{CH}_4$  and a small amount of  $\text{C}_2\text{H}_4$ . SiC is formed from silicon units that contain no Si-H bonds and which are separated from one another inside a carbon matrix present in the final material. This is illustrative of a ceramic formation process which must be different from the usual one, such as occurs for instance in the case of polycarbosilanes [3,11]. The latter contain reactive Si-H groups which are known to determine the reticulation of the polymer and the subsequent mineralisation stage.

(iii) Pyrolysis under  $\text{NH}_3$  leads to  $\text{Si}_3\text{N}_4$  with loss of the carbon.

Studies now under progress are directed towards gaining a better understanding of this solid-state cross-linking process and its influence on the structure of the final ceramic material.

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