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One-Step Route to Silicon Carbide Precursors by a Tunable Catalytic Polycondensation

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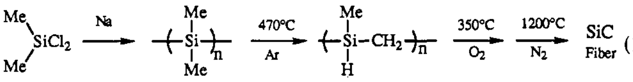
Polysilane polymers $(SiRR')_n$ have attracted a great deal of attention for various applications.[1] They were shown for the first time by Yajima et al.[2] to allow the preparation of ceramic material by a set of chemical transformations starting from organosilicon monomers (eq 1). This process allows the fabrication of a commercially available SiC-fiber.



$$Me_2SiCl_2 \xrightarrow{Na} -\!\!(\underset{Me}{\overset{Me}{Si}})_n\!\!- \xrightarrow[Ar]{470°C} -\!\!(\underset{H}{\overset{Me}{Si}}-CH_2)_n\!\!- \xrightarrow[O_2]{350°C} \xrightarrow[N_2]{1200°C} \underset{Fiber}{SiC} \quad (1)$$

Since then, preceramic polymers with various elemental compositions have been studied.[3,4] Ceramic precursors need appropriate rheological properties to fabricate them into useful forms: complex shapes, fibers, coatings, thin films, binder, or matrix matrials. The required properties are usually obtained by adjusting the degree of cross-linking of the preceramic polymer.[5]

It is clear that the chemical reactivity of preceramic polymers is of importance. Functional chain units will lead to early cross-linking (limiting volatile formation) and rearrangement reactions (facilitating the organization of a three-dimensional network), during the thermolysis. Polymers with Si-H functionalities are of particular interest, since they are stable and since they are easily obtained by using the transition-metal-catalyzed dehydrogenative coupling of trihydrogenosilanes.[6–10]

We wish to report here that 1,4-disilapentane (**1**, $H_3SiCH_2CH_2SiH_2Me$), a highly functionalized carbosilane monomer,[11] can directly serve as a ceramic precursor. The titanium-catalyzed dehydropolymerization gives rise to preceramic oligomers and polymers with a tunable degree of condensation. Whatever the molecular weight of the ceramic precursor, pyrolysis in the presence of titanium catalsyt gives high yields of silicon carbide residue.[12]

The reaction of **1**, at 20 °C, in the presence of 0.5 mol % of $(\eta\text{-}C_5H_5)_2TiMe_2$[6] or $(\eta^5\text{-}C_5H_5)_2TiCl_2/2n\text{-}BuLi$,[8] led to the formation of poly[(3-silabutyl)silane] (**2**) as a viscous liquid (Scheme 1). The dehydrocondensation reaction was monitored by measuring the volume of the hydrogen evolution. By gel permeation chromatography, an average degree of polymerization of 6.5 was determined. The formation of a linear polysilane **2** with dangling silabutyl functional groups was established by mean ^1H, ^{13}C, and ^{29}Si NMR analysis.[13]

At room temperature, only the SiH_3 functional group in **1** reacted. When the monomer was used up, the hydrogen evolution became slower and the $SiMeH_2$ began to condense. Thereupon the oligomers **2** cross-linked to give the high molecular weight polymer **3**. After 5 days of reaction in the presence of the catalyst, a highly viscous liquid was obtained with an average molecular weight M_w 20 000–35 000 and a polydispersity of 10–12. At 50 °C, crosslinking occurred very rapidly to give an insoluble solid within 30 min. IR and NMR spectroscopy distinguishes the linear oligomer **2** from the cross-linked polymer **3**. The ^1H NMR spectrum of **2** showed a triplet for the $Si(CH_3)H_2$ group. In the ^{13}C NMR spectrum, a single resonance was observed for this methyl group, whereas in **3** there is a second line slightly downfield. The relative intensities of the two $Si^{13}CH_3$ resonances in the spectrum of **3** can give an estimate of the degree of cross-linking in **3**. A value of 25% was estimated from the ^{13}C NMR spectrum of **3** ($M_n = 3260$, $M_w = 32\,900$).

Interestingly, it appears that the degrees of polycondensation and cross-linking can be adjusted by selecting the appropriate reaction time and temperature. The titanium-catalyzed dehdyrogenative polymerization of **3** produced a wide range of polymeric carbosilanes, from liquid, low oligomers, to viscous, soluble cross-linked polysilanes and up to a insoluble, nonmelting, highly cross-linked, polymeric material. Whereas the polycondensation

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(11) Schmidbaur, H.; Dörzbach, C. *Z. Naturforsch.* **1987**, *42b*, 1088. Compound **1** was obtained in two steps in a 85% overall yield from commercially available $(CH_2{=}CH)SiCl_3$ and $MeHSiCl_2$.

(12) A patent application covering the technology described herein has been filled by the authors of this communication.

(13) A typical experiment, preparation of **2**: To a stirred mixed of 1.4-disilapentane (10.4 g, 100 mmol) and $(\eta^5\text{-}C_5H_5)_2TiCl_2$ (1.25×10^{-3} g, 0.5 mmol) were added 0.63 mL of a solution of *n*-BuLi in hexane (1.6 mol L^{-1}). The color changed to intense blue and hydrogen evolution was observed. After 48 h the reaction was stopped by bubbling air through the liquid until the intense color disappeared. GPC (detector: refractive index)[14] $M_w = 1041$, $M_n/M_w = 1.16$. ^1H NMR (80 MHz, δ, $CDCl_3$) 0.0 (t, $^3J(H,H) = 3.5$ Hz, 3H); 0.9 (m, 4H), 3.8 (m, 3H). ^{13}C NMR (62.9 MHz, δ, $CDCl_3$) 8.3 (CH_3), 1.4–5.5 (CH_2); 8.1–9.9 (CH_2). ^{29}Si NMR (49.7 MHz, δ, $CDCl_3$) –65 to –49 (SiH, SiH_2); –30.2 (t, $^2J(Si–H) = 189$ Hz). IR (hexane) $\nu = 2134\ cm^{-1}$ (SiH).

(14) Molecular weights are relative to polystyrene standards.

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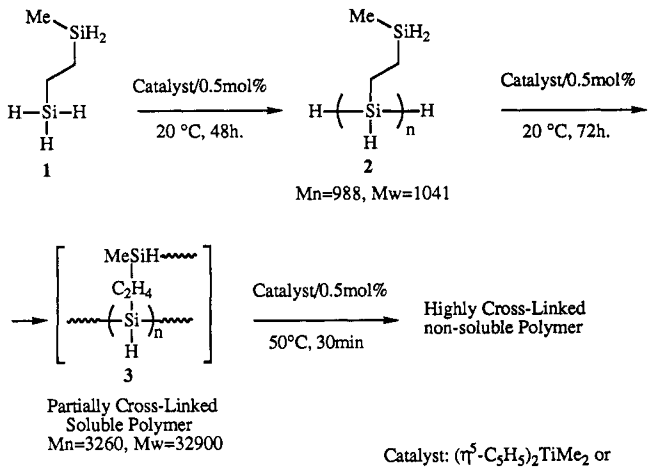
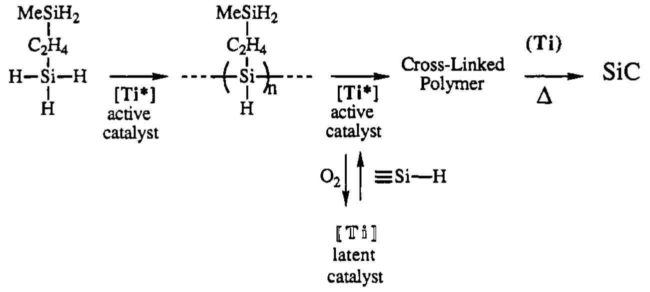
Scheme 1. Catalytic Dehydrogenative Polycondensation of 1



Scheme 2. Titanium-Catalyzed Route to Silicon Carbide from Monomer 1



of bis(trihydrogenosilyl) compounds, with two SiH_3 polymerizable groups, readily gives insoluble nonmelting materials,[15] a tunable polymerization reaction was observed from monomer 1 having a SiH_2 and a SiH_3 functional groups with different reactivities.

Moreover an additional possibility of controlling the polymerization reaction was found after a reversible deactivation by oxidation of the titanium catalyst (cf. Scheme 2). The catalytic polymerization or cross-linking reaction was stopped by oxidizing the active catalyst with O_2 or air. This is accompanied by the disappearance of the intense blue color of the reaction mixture containing the active catalytic species. Although the nature of the latter is not known, it might be indicative of the presence of Ti(III) complexes. Harrod et al. attributed the observed EPR resonances in the catalytic mixture, among others species, to a bimetallic mixed-valence species $(\eta^5\text{-}C_5H_5)_4Ti_2H_3$.[6] We did observe similar signals from the polymerization mixtures using both the $(\eta^5\text{-}C_5H_5)_2TiMe_2$[6] and $(\eta^5\text{-}C_5H_5)_2TiCl_2/2BuLi$[8] catalyst precursors.[16] Upon oxidation the resulting pale yellow reaction mixture was EPR silent. However, this oxidation was found to be reversible to some extent. In the presence of Si–H functional groups, the oxidized titanium compounds were reduced upon gentle heating or more slowly at room temperature. This reduction was observed by the appearance of an intense greenish color and new strong signals in the EPR spectrum.[17] The reduced catalyst was active for cross-linking the polymers, but at a rate slower than the initial one.

Thus, it appears that the initial dehydrogenative catalyst can be oxidized to a latent inactive, probably Ti(IV) species. From the latter, an active dehydrogenation catalyst can be regenerated; the reduction of the latent catalyst is presumably achieved by the residual Si–H functional groups in the oligomer **2** or polymer **3** (Scheme 2). The observed behavior seems consistant with a Ti(III) nature of active catalyst which would be reversibly oxidized to an inactive Ti(IV) species; however, no proof exists that the active catalyst is such a Ti(III) species, despite the observation of EPR signals. The regeneration of an active catalyst must be accompanied by some oxidation of the polymeric material. The oxidation of the catalyst is kinetically favored, whereas the oxidized polysilane is the thermodynamic product. This seems of particular interest from a practical view-point. Such a reversible deactivation of the polymerization and cross-linking catalyst opens interesting possibilities for processing the polymeric material.

Finally, we examined the thermal behavior of both linear and cross-linked polysilanes **2** and **3**. The thermogravimetric analysis of carefully purified (titanium-free) samples, as well as that of titanium catalyst containing samples were performed from 20 to 1200 °C under argon. Samples of **2** and **3**, containing 0.5 mol % of the initial titanium catalyst, either as its active (blue) form or as its latent oxidized form, exhibited a similar first weight loss at ca. 160 °C, ranging from 6 to 10%. The GC–mass analysis of the volatile products evolved at this temperature only showed hydrogen and the monomer **1**. At temperatures higher than 350 °C, a second weight loss ranging from 19 to 24% was observed. The final yield of ceramic residue, ca. 73% is close to the theoretical value of 78% for the conversion of a ceramic precursor with a $(Si_2C_3H_{10})_n$ stoichiometry to SiC. The analysis of the residue[18] revealed an elemental composition close to silicon carbide (Si/C = 1.01/1) indicating that more than 90% of the silicon was retained in the final ceramic. At 1400 °C crystalline β-SiC was formed.[18] It is interesting to note that the pyrolysis of **2** or **3** (regardless of the degree of cross-linking) in the presence of the titanium polymerization catalyst gave a similar composition and ceramic yield.[19] The separation of the titanium species from the oligomer **2** was achieved by filtration through a silica gel column.[20] Titanium-free samples of **2** were stable up to 200 °C. The TGA analysis then revealed an abrupt weight loss to give a ca. 30% final ceramic yield. The highly functionalized oligomer **2** thus gave a quite high yield of residue with respect to its molecular weight. However, in the presence of catalyst, a much higher yield was observed. The TGA curves for linear oligomers **2** both with and without catalyst are shown in Figure 1. The titanium catalyst plays an important role in the thermolysis. Changes in ceramic yield and

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(16) During the polymerization, the EPR spectrum changed, but there was always a multiplet consisting of six lines at $g = 1.99$, which was assigned to $(\eta^5\text{-}C_5H_5)_4Ti_2H_3$[6] and at the end of the polymerization only the latter was observed.

(17) The EPR spectrum of the reactivated catalyst consisted of several lines in the range 1.95–2.00, probably not corresponding to a single titanium species.

(18) After pyrolysis at 1200 °C: Found: C, 29.0; Si 68.3. Calculated for SiC: C, 29.95; Si, 70.05. Crystallization of the sample started at 1100 °C and after heating at 1400 °C, the sample exhibited the diffraction lines characteristic of β-SiC (2θ = 35.64°, 59.97°, 72.32°).

(19) The catalyst present can be in its active form or its oxidized form, since upon heating under argon, it is always reactivated by reaction with Si–H functional group.

(20) From cross-linked samples, the catalyst could not be removed completely by silica gel filtration.

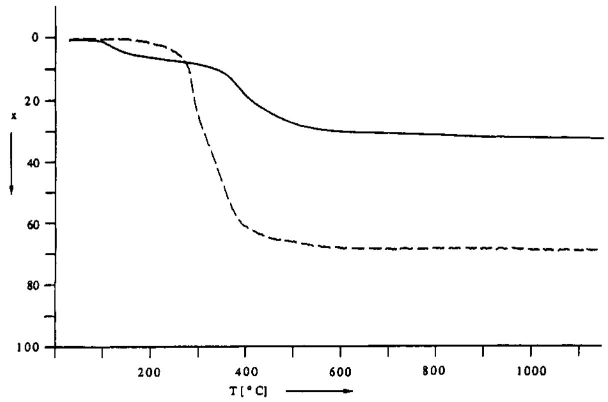

Figure 1. Thermogravimetric analysis of polymer **3** (— in the presence of titanium catalyst, - - - without titanium catalyst). *x* = weight percent.

composition were also previously observed upon using small amounts of transition metal complexes to process polymeric SiC precursors.[21] In the present work, extensive cross-linking with hydrogen evolution probably occurred at the early stage of the thermolysis. Some depolymerization also occurs at 160 °C as evidenced by the evolution of small amounts of monomer 1. However, this titanium-catalyzed fragmentation is probably associated with the formation of a reactive silyltitanium species.[7,22] Such species may lead to highly cross-linked or rearranged polymer to give a more thermally stable network which is responsible for the high ceramic yield.

In conclusion, as shown in Scheme 2, the use of the hydrogenosilane monomer 1 offers a straightforward route to silicon carbide ceramic. Linear or cross-linked polysilane readily resulted from the titanium-catalyzed dehydropolycondensation of 1. Polymeric material with various degrees of condensation or cross-linking and therefore presenting a variety of rheological properties can be obtained from a single monomeric precursor. An easy processing of such polymeric material should result by adjusting the reaction conditions as well as by reversible deactivation of the titanium catalyst. For example, we prepared silicon carbide films on carbon from these precursors. An interesting point is that whatever the molecular weight of the polymeric precursor, the pyrolysis in the presence of catalytic amounts of titanium gives a high silicon carbide ceramic yield.

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