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Organosilicon Polymers: Pyrolysis Chemistry of Poly[(dimethylsilylene)diacetylene]

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The pyrolysis of $[-Si(CH_3)_2C\equiv CC\equiv C-]_n$ under a stream of argon to 1400 °C gives a β-SiC-containing ceramic in high yield (84%). The polymer-to-ceramic conversion chemistry was studied by means of thermal analysis, infrared spectroscopy, solid-state ^{13}C NMR spectroscopy, and X-ray powder diffraction. Gaseous products were analyzed by mass spectrometry. The polymer primarily undergoes low-temperature cross-linking through the diacetylene groups at about 200 °C, i.e., 300 °C below the mineralization stage. Decomposition reactions occur between 450 and 800 °C inside a highly cross-linked carbon network. The weight decrease arises only from loss of CH_4 and H_2. The total amount of silicon remains in the final residue. From a mechanistic point of view, $[-Si(CH_3)_2C\equiv CC\equiv C-]_n$ is of interest as a suitable model to explore the mechanism of the thermal conversion of silicon-containing polymers into silicon carbide. The formation of SiC takes place inside an amorphous carbon matrix and only involves silyl units that contain no Si–H or functional groups and that are separated from one another. Some implications are discussed. Pyrolysis under ammonia leads to Si_3N_4 with loss of carbon and evolution of HCN.

Introduction

As a part of our continuing studies of organosilicon (or -germanium) polymers containing a π-electron system in the polymer backbone,[1] we reported the synthesis of a new type of derivative,[2] 1, in which a regular alternating arrangement of a silylene (or germylene) unit and a diacetylene group is found.

$$[-(MR^1R^2)_mC\equiv CC\equiv C-]_n$$

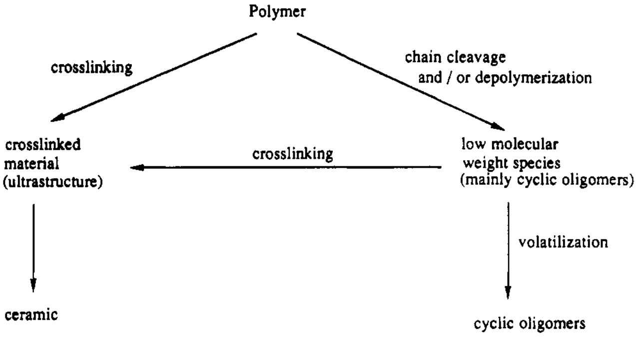
1

$$M = Si, Ge;\ R^1 = R^2 = \text{alkyl, aryl};\ m = 1, 2$$

Coupling reactions involving the use of the dilithiobutadiyne (or the corresponding di-Grignard reagent) and various dihalosilanes (or -germanes) afforded a general and selective route to a variety of the polymers 1. When they are doped with $FeCl_3$, these polymers exhibit conductivity values in the range 10^{-3}–10^{-5} S·cm^{-1}, characteristic of a conducting state.[2]

Besides their charge-transport properties consistent with a delocalization of the π-electron density along the main chain,[2] we were also interested in the thermal properties of compounds 1 and their evaluation as preceramic polymers.[3] As previously reported,[4,5] organometallic or inorganic polymers, even of high molecular weight, with a linear structure do not lead to high amounts of ceramic residue by pyrolysis. The polymeric chain is progressively broken into short fragments. In contrast, a polymer that undergoes cross-linking reactions in preference to skeletal cleavage will form a stabilized network system. On further pyrolysis, such a material will lead to a ceramic residue in good yield (Scheme I). Thus, the presence of appropriate reactive (or potentially reactive) functionalities whose reactivity will result in substantial cross-linking during the initial stages of the pyrolysis is one of the factors that determine the ceramic yields.[4,5] In this respect, the presence of the diacetylene units in the main chain of the polymer should be of interest. Polymers of the $[-XC\equiv CC\equiv C-]_n$ type, with X being either $(-CH_2)_n$ (n = 3, 5, 8)[6] or an aromatic group[7] have been reported to undergo thermally induced cross-polymerization reactions at relatively low temperature. A similar process would occur with poly[silylene (or germylene) diacetylenes] and could influence greatly their thermal behavior.

Scheme I



In this paper, we describe the thermal decomposition of poly[(dimethylsilylene)diacetylene] (2) under an inert or a reactive atmosphere and our attempts to understand the polymer-to-ceramic conversion.

$$[-Si(CH_3)_2C\equiv CC\equiv C-]_n$$

2

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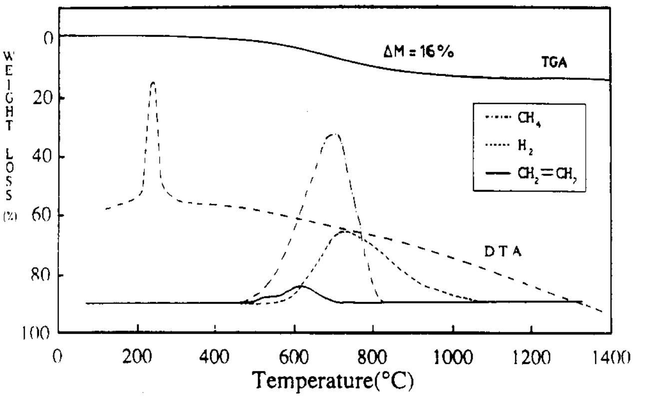

Figure 1. Pyrolysis of **2** under argon: TGA, DTA, and mass spectrum traces.

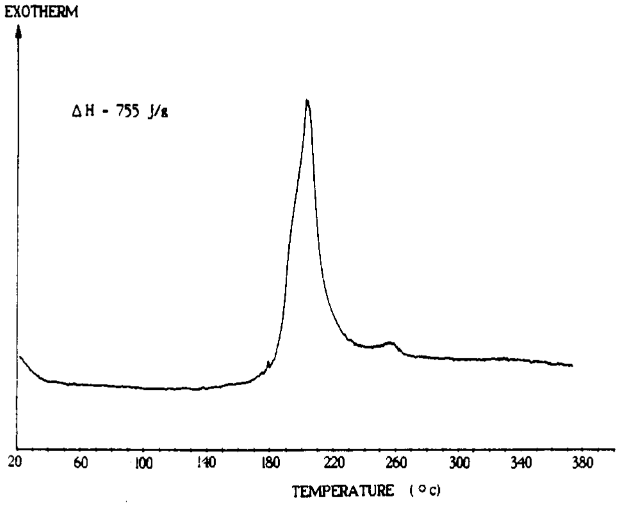

Figure 2. DSC curve for poly[(dimethylsilylene)diacetylene] (**2**) under argon (5 °C/min).

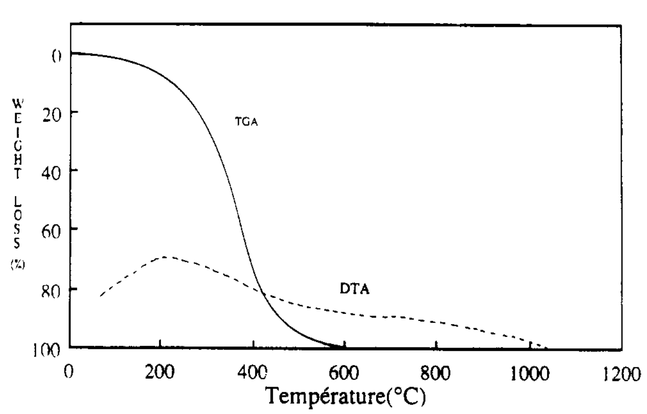

Figure 3. Pyrolysis of **3** under argon: TGA and DTA traces.

Results and Discussion

Thermal Analysis. Thermogravimetric analysis (TGA) and thermal differential analysis (TDA) measurements under argon were obtained by using a thermogravimetric analyzer (TGA/TDA) interfaced with a mass spectrometer (Figure 1).

The thermograms clearly suggest that two different steps take place successively when the temperature of a sample (M_w = 4063 relative to polystyrene standards, M_w/M_n = 1.24) was progressively increased up to 1200 °C. The following comments can be made.

(1) The TDA curve exhibits a strong exothermic peak at about 200 °C without weight loss. This feature did not appear in the case of a sample of **2** previously heated at about 300 °C. The differential scanning calorimetry (DSC) analysis under argon also reveals a strong exotherm with an onset between 180 and 230 °C centered at 200 °C (Figure 2). This exothermic transformation is related to a chemical process, i.e., a thermally induced cross-polymerization through the diacetylene groups which will modify irreversibly the backbone of the starting material. The integral under the DSC curve yields the heat of reaction, which amounts to 755 $J{\cdot}g^{-1}$.

(2) The TGA trace shows that the weight loss was only 16% and occurred mainly between 450 and 750 °C. This second step is related to the extensive thermal degradation of the cross-linked material formed during the exothermic transformation of the diacetylene units. The off-gases from the pyrolysis were analyzed by mass spectroscopy, and the major compounds were identified as CH_4 and H_2 (Figure 1). A small amount of ethylene was observed. Although the yields of the individual volatiles are difficult to quantify, we never detected gaseous silicon species during the pyrolysis. The weight decrease arised mainly from loss of CH_4 and H_2.

The observed high char yield, i.e. 84%, is almost certainly due to the thermally induced cross-polymerization through the triple bonds. Chemical evidence of the influence of the cross-linking step on the ceramic yield was afforded by the study of the fully saturated polymer **3**. **3**

$$[\text{-Si(CH}_3)_2(\text{CH}_2)_4\text{-}]_n$$
3

was obtained by the hydrogenation of **2** on Pd/C. When heated to 1400 °C, **3** exhibits a progressive thermal decomposition that is almost complete by 500 °C (Figure 3). No solid residue was recovered at the end of the pyrolysis. Due to its purely linear structure and the lack of reactive centers, the polymeric chain fragments during the pyrolysis and forms very low molecular weight species.

Finally, the degree of polymerization seems to have a slight effect on the ceramic yield. Compared to **2** (M_w = 4063 relative to polystyrene standards, M_w/M_n = 1.24), silylene–diacetylene polymers of higher weight average molecular weights ($10^4 < M_w < 2 \times 10^4$) recently reported by Barton et al. led to quite similar ceramic yields.[8]

Cross-Polymerization of Poly[(dimethylsilylene)diacetylene] (2). Poly(diacetylenes) have been intensively studied.[9] These polymers have traditionally been prepared using a solid-state, free-radical polymerization initiated by heating or ultraviolet irradiation of the crystalline monomers. The reaction proceeds via 1,4-addition of the diacetylenes in the crystal lattice and leads to the two extreme backbone structures in the polymer, i.e., a mesomer ene–yne structure or a butatriene structure.[9,10]

The occurrence of such a process during the pyrolysis of **2** was studied by IR and ^{13}C NMR spectroscopy. Some X-ray powder diffraction experiments are also reported.

Evidence was at first obtained through a study of the thermolysis of the 1,4-bis(trimethylsilyl)-1,3-butadiyne[11]

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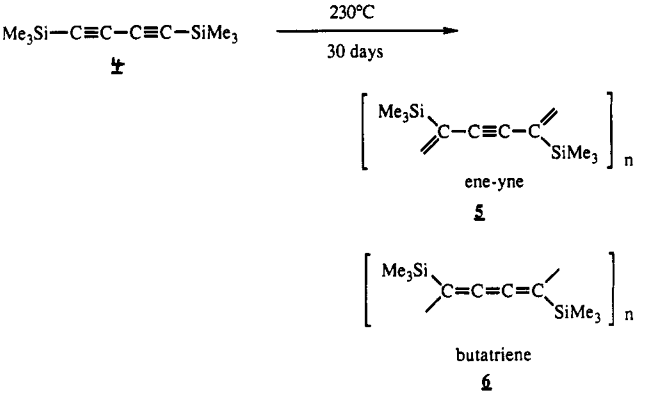
Scheme II



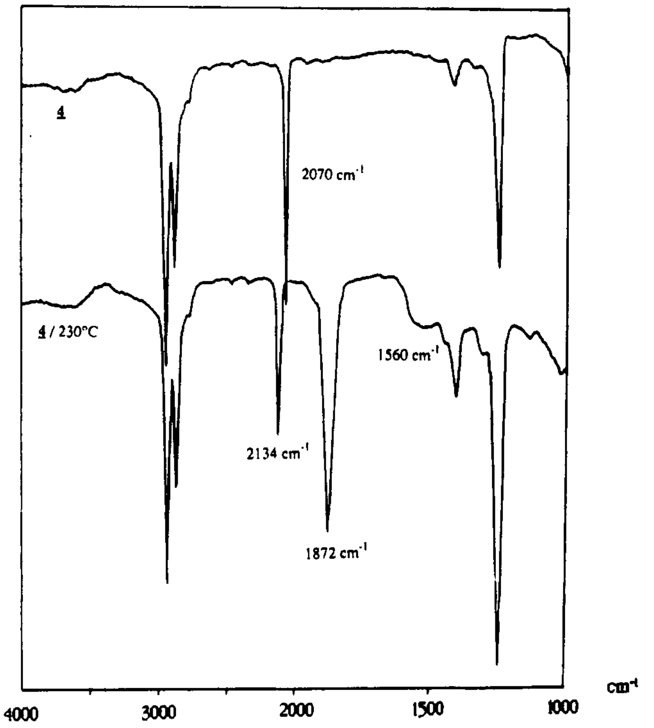


Figure 4. Infrared spectra of 4 at room temperature and at 230 °C for 30 days.

(4), used as a model. When a sample of 4 was heated to 230 °C, the reaction slowly led to oligomers (M_w = 1200; M_w/M_n = 1.24; degree of polymerization 6) soluble in the usual organic solvents. The low polydispersity value (1.24) observed for this oligomeric material allows us to exclude a 1,2-addition of the diacetylenes which would lead to a highly cross-linked network (Scheme II).

As shown in Figure 4, the absorption band characteristic of the diacetylene group at 2070 cm^{-1} has completely disappeared. The IR spectrum of the pyrolyzed sample exhibits three new absorptions at 2134, 1560, and 1872 cm^{-1}, attributed respectively to ene–yne and butatriene structures such as 5 and 6[10b,12] (Scheme II). The ^{13}C solution NMR spectrum also exhibits peaks indicative of ene–yne (140, 108 ppm) and triene (218, 103 ppm) groups[13] and, thus, of a 1,4-addition pathway.

The conversion of 2 was monitored by the changes in the infrared (Figure 5) and ^{13}C NMR spectra of the solid samples with increased pyrolysis temperature (Figure 6).

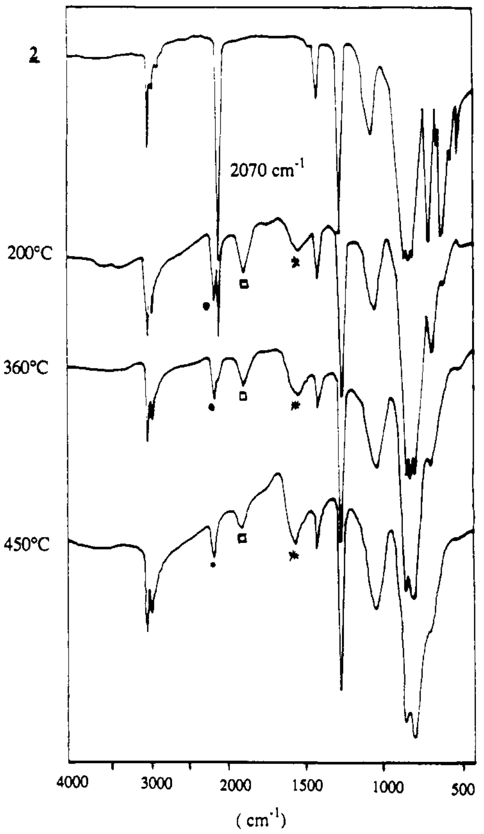


Figure 5. Infrared spectra of 2 at room temperature and at 200, 360 and 450 °C: (●) 2114 cm^{-1}; (□) 1872 cm^{-1}; (*) 1560 cm^{-1}.

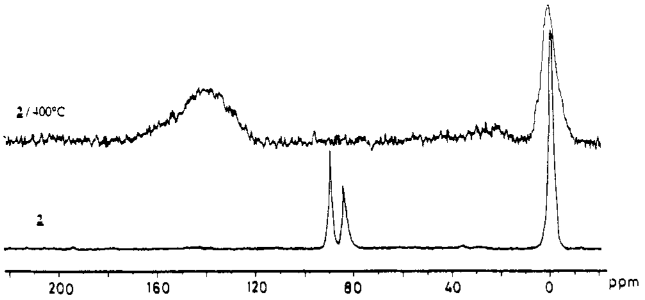


Figure 6. Solid-state ^{13}C NMR spectra of 2 at room temperature and at 400 °C for 2 h under argon.

The following observations can be made.

(1) When a sample is heated above 200 °C, the infrared spectrum, as observed with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, shows absorption bands characteristic of ene–yne and triene structures, i.e., respectively centered at 2114, 1872, and 1520 cm^{-1}, besides the peak at 2070 cm^{-1} indicative of the presence of unchanged diacetylene groups (Figure 5). In addition, ^{13}C NMR spectroscopy (Figure 6) suggests that the initial stages of the cross-linking process involve the conversion of the sp carbons into sp^2 carbons. Peaks occur at the expected resonance positions for the butatriene (195, 98 ppm) and ene–yne (140, 106 ppm) structures.

(2) Heating of a sample up to 400 °C led to the gradual disappearance of the above infrared absorptions (Figure 5). Furthermore, the solid-state ^{13}C NMR spectrum for a sample heated at 400 °C for 2 h reveals complete disappearance of the resonances at 83.96 and 89.19 ppm assigned to the diacetylenic carbons of the starting material. They are replaced by a broad envelope of signals in the 130–160 ppm region (Figure 6) indicative of sp^2 carbons. Moreover, an X-ray powder diffraction experiment suggests that the solid residue is amorphous.

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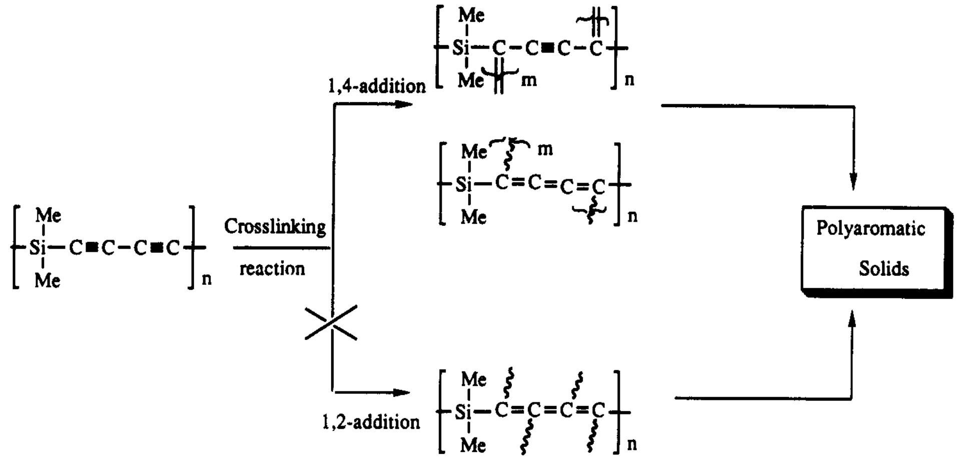
[12] (a) West, R.; Chwang, T. L. *J. Am. Chem. Soc.* **1973**, *95*, 3324. (b) Jaffe, F. *J. Organomet. Chem.* **1970**, *23*, 53.

[13] Kalinowski, H. O.; Berger, S.; Braun, S. In *Carbon-13 NMR Spectroscopy*; Wiley: New York, 1988.

Scheme III. Cross-Linking of Poly[(dimethylsilyl)diacetylene]



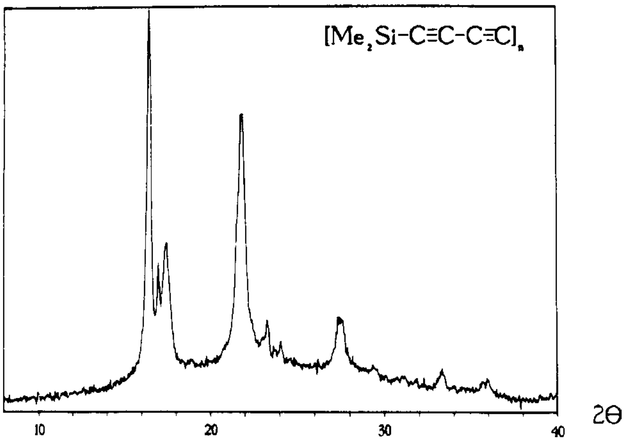
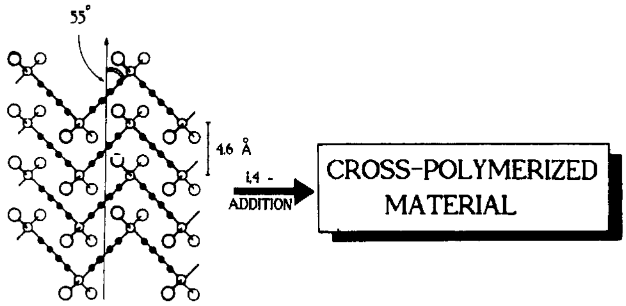


Figure 7. X-ray powder diffraction pattern for **2**.

Scheme IV



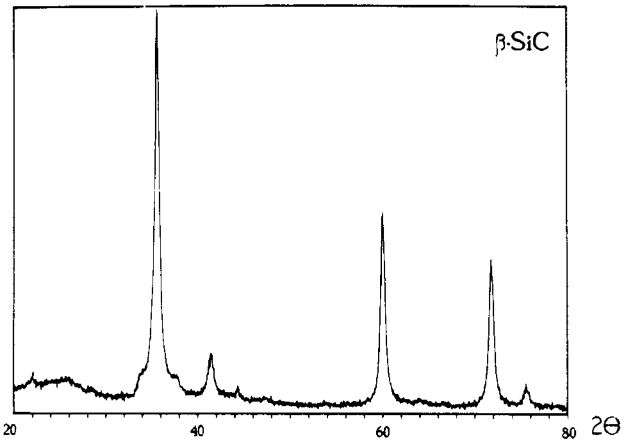


Figure 8. X-ray powder diffraction pattern for the ceramic obtained by pyrolysis of **2**.

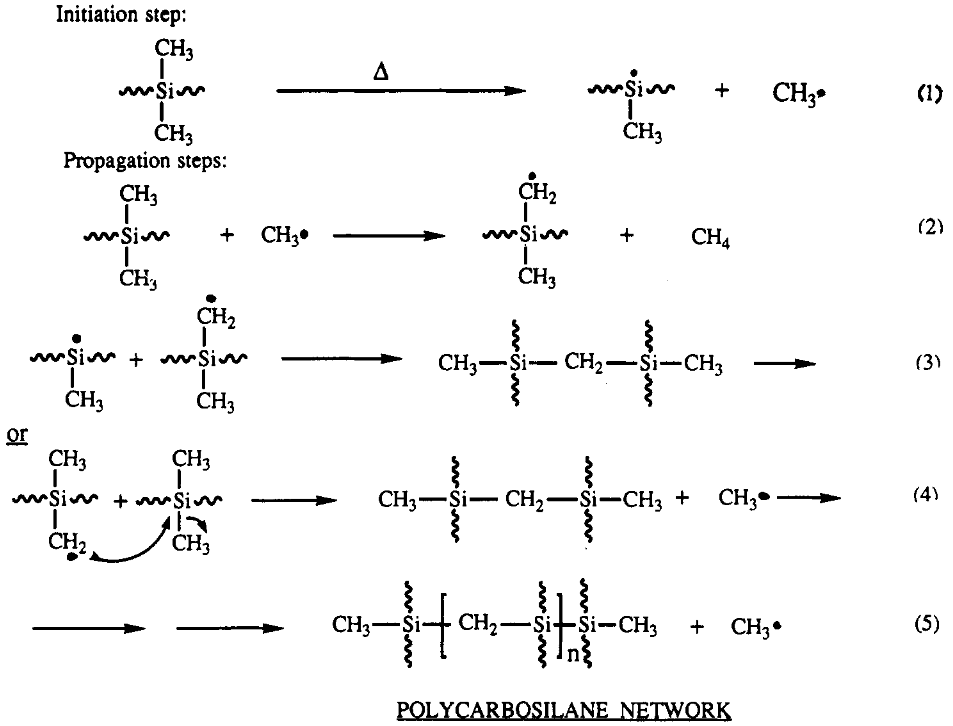
From a mechanistic point of view, it seems clear that the observed cross-polymerization of the diacetylene groups occurs via a 1,4-addition process. Both butatriene and ene–yne structures have been produced in the initial stages of the pyrolysis (Scheme III). In addition, the X-ray powder diffraction pattern of the starting material **2** (Figure 7) is indicative of a partially crystalline structure. Four peaks are observed at 2θ = 16.6, 17.6, 20.9, and 27.4°. The repeat distance of the diacetylene backbone inside these regions was measured to be 4.6 Å and is of the same order of magnitude as that observed with fully chain-aligned monomer single crystals[9] or with macromonomer poly(diacetylenes)[6] (Figure 7). Therefore, on the principle of least motion, we can assert that the initial polymerization reaction of the acetylenic groups will start at about 200 °C in these crystalline parts in which the optimal arrangement of the diacetylene units is present (Scheme IV). Subsequent thermal treatment up to 400 °C will lead to additional cross-linking reactions in the whole mass of the polymer and form a stabilized sp^2-ultrastructure network system. Moreover, the cross-linking reaction occurs at about 300 °C below the mineralization stage. Thus, the formation of SiC will occur inside the amorphous carbon matrix.

The Organometallic–Inorganic Transition. Poly[(dimethylsilylene)methylene] and poly(silapropylene) have been shown to undergo depolymerization on pyrolysis,[5a,h–i] which leads to very low ceramic yields (5–10%). In this context, poly[(dimethylsilylene)diacetylene] (**2**) would be of interest as a suitable model in order to explore the mechanisms of the thermal conversion of silicon-containing polymers into silicon carbide. As discussed above, a low-temperature cross-linking through the diacetylene groups occurs at about 300 °C below the mineralization stage. Thus, the formation of SiC will take place inside an amorphous carbon matrix and involve only dimethylsilyl units that contain no Si–H or functional groups and which are separated from one another.

In a typical experiment, a sample of **2** (M_w = 4063 relative to polystyrene standards, M_w/M_n = 1.24)[2] was heated to 1400 °C under a stream of argon. It was maintained at 1400 °C for 12 h, and a black ceramic-type residue was obtained in high yield (84%). Examination of this material by X-ray powder diffraction showed the presence of crystalline β-SiC (Figure 8).

Elemental microanalysis of the pyrolysis product gave 33.1% Si, 65.9% C, and a small amount of oxygen (1.3%). These data suggest that the material formed at 1400 °C contained a large excess of free carbon (compare SiC:

Scheme V



calculated 70% Si, 30% C). Similar observations have been previously made by others[14] in the case of analogous silylene–acetylene polymers. The analytical composition corresponds to a hypothetical stoichiometry of $SiC_{4.65}O_{0.06}$, and the ceramic blend may be represented as $(SiC)(C)_4$ on a molar basis. It suggests that besides the four carbon atoms arising from the diyne units, only one carbon atom of the two methyl groups was involved in the formation of SiC. The other one is eliminated as CH_4.

Elemental analyses and a 84% ceramic yield indicate that all the silicon contained in the dimethylsilyl groups of the starting polymer was quantitatively present in the ceramic as SiC.[15] The weight decrease arises only from loss of H_2, CH_4, and a small amount of ethylene (Figure 1). A detailed analysis of the TGA experiment and of the off-gases of the pyrolysis suggests that the mineralization takes place in two distinct steps. The primary detected volatile species is CH_4, which is evolved in the temperature range 450–750 °C. Elimination of hydrogen started only above 500 °C (Figure 1).

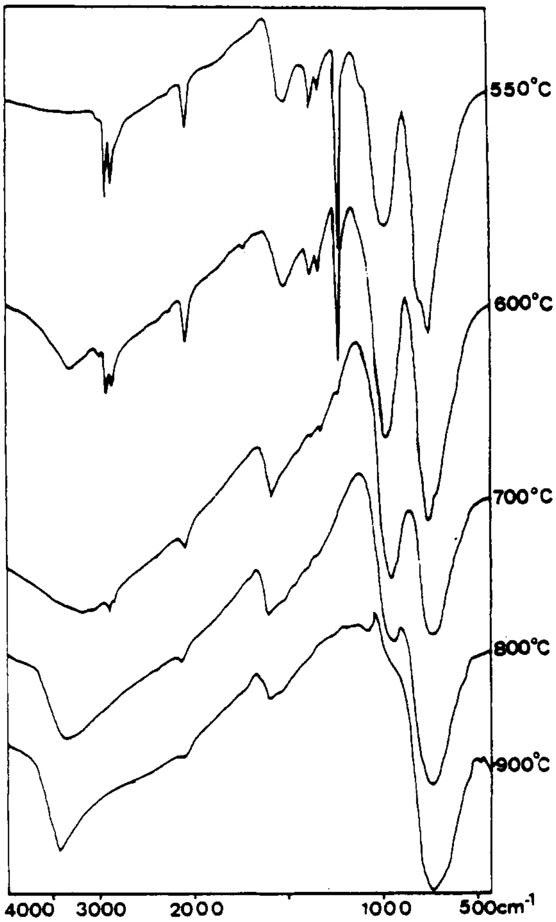


Figure 9. Infrared spectra of 2 pyrolyzed at 550, 600, 700, 800, and 900 °C.

Infrared analysis of samples heated at temperatures between 550 and 900 °C (Figure 9) are in qualitative agreement with the above TGA results. In the temperature range 550–620 °C, which corresponds to the evolution of CH_4 as the major pyrolysis off-gas, there is a significant decrease in the intensity of the $Si–CH_3$ deformation (1407, 1250 cm^{-1}) and stretching bands (2950, 2888 cm^{-1}). At the same time, the IR spectra exhibit a new absorption at 1350 cm^{-1}, assigned to a $Si–CH_2–Si$ group ($\delta_s(CH_2)$).[16] Finally,

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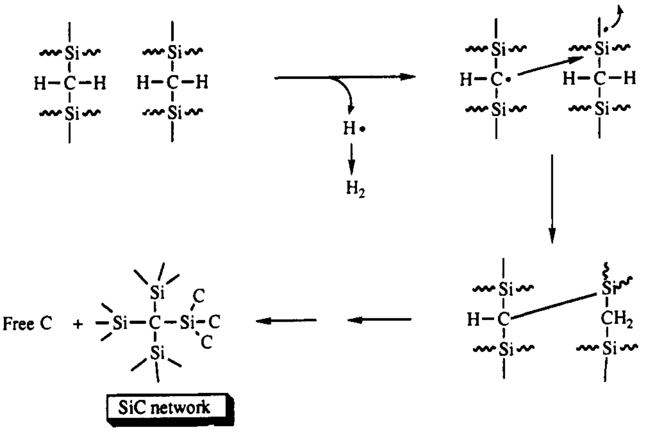
[15] Elemental analysis of the initial polymer 2 gave 26.41 wt % silicon. On the basis of elemental analysis and of an 84% ceramic yield, the silicon amount in a residue obtained from the pyrolysis of 100 g of 2 can be evaluated to be 27.80 g (Si amount in the residue is equal to (Si wt % in the residue) × 0.84). Both values are very close (26.41 versus 27.80 g). This result suggests that all the silicon contained in the dimethyl groups of 2 was quantitatively present in the final material.

Scheme VI



above 620 °C, the bands due to C–H bonds almost disappeared.

At this stage, the data are insufficient to completely define the pyrolysis mechanism. Nevertheless, both the thermal analysis and infrared results are consistent with a homolytic cleavage of the Si–CH_3 bond in the initial stages of the mineralization to form reactive methyl radicals (Scheme V; step 1). Step 2 (Scheme V) would create silylmethylene radicals by an intermolecular hydrogen abstraction from Si–CH_3 fragments. The concomitant formation of methane as the primary off-gas is experimentally observed during the pyrolysis. Subsequent condensation of the silyl radical with the Si–CH_2 moiety would give rise to a methylene bridge (step 3). An alternative process, with certainly less weight, would be direct attack of the methylene radical at silicon with release of a methyl radical (step 4). In other words, such reactions (step 3 or 4) would lead to the stepwise conversion of the isolated dimethylsilyl groups into a –$(SiCH_2)_n$– polycarbosilane backbone inside the carbon matrix (steps 3 and 5). In the last stages between 620 and 900 °C, the major component of the volatile species becomes H_2. At that time, the material is progressively converted into an inorganic structure. These changes will include (i) the homolysis of the remaining C–H bonds, cross-linking by radical recombinations, and, thus, consolidation of the "Si–C" network and (ii) the scission of the Si–carbon matrix bonds with the formation of free carbon. Partial crystallization of the ceramic product takes place at higher temperatures (Scheme VI). In the infrared spectrum of a sample heated at 900 °C, the presence of a strong band centered near 800 cm^{-1} (Figure 9), characteristic of the Si–C stretch (SiC_4 tetrahedral species), provides further evidence for the formation of ceramic SiC.[17]

Pyrolysis under Ammonia. Due to the high carbon content (65.9% C) of the ceramic-type residue obtained by the thermal decomposition of **2** under argon, the pyrolysis chemistry was examined under ammonia.

The bulk pyrolysis to 1400 °C under a stream of ammonia (rather than argon) leaves a white ceramic residue in 20% yield. X-ray diffraction showed the presence of α- and β-Si_3N_4. Elemental analysis of the pyrolysis product gave 38.24% N, 55.17% Si, 8.7% O, and only a slight amount of carbon (0.10%). As observed previously by others,[14a,18] essentially all carbon is lost. Since the initial polymer **2** contained less than 3 wt % oxygen (61.31% Si, 5.91% H, 22.90% Si, 2.47% O), it seems that the contamination by oxygen (8.7% in the final ceramic) occurred during the pyrolysis itself.[5g] This contamination is certainly due to the high affinity of the product for oxygen and moisture afforded by the NH_3 stream and also to the small volume of the samples submitted to pyrolysis with respect to the furnace.[5g]

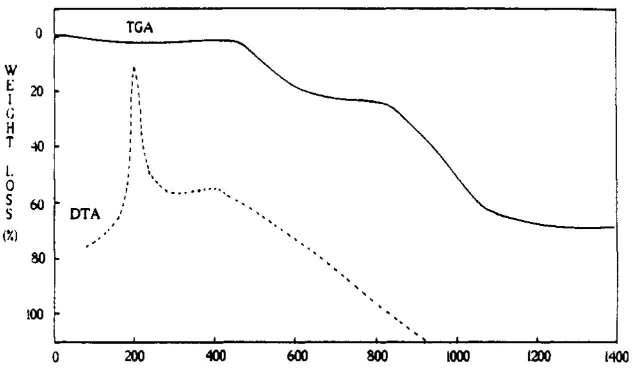


Figure 10. Pyrolysis of **2** under ammonia: TGA and DTA traces.

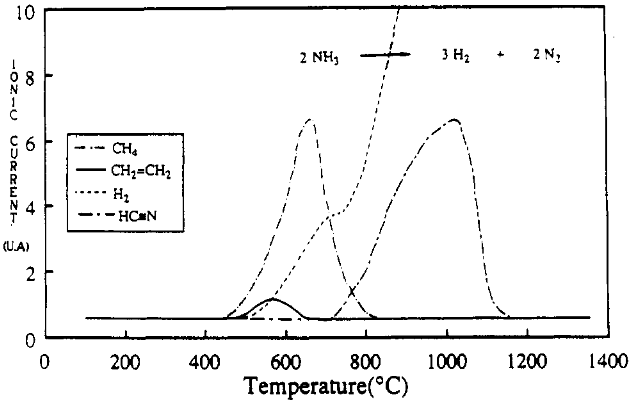


Figure 11. Pyrolysis of **2** under ammonia: mass spectroscopy analysis of the volatiles.

Thermogravimetric and thermal differential analyses were obtained (Figure 10). The TDA curve again exhibits a strong exotherm at about 200 °C without weight loss as observed under argon. This transformation is related to the thermally induced cross-polymerization of **2** through the triple bonds (vide supra). The TGA trace shows that the weight loss was 62%. The decomposition starts at about 400 °C and ends at 1200 °C. Furthermore, two main regions can be identified in the weight loss curve:

(1) The first region is 400–750 °C, where a 21% weight loss is observed. The latter is associated with evolution of methane and hydrogen as the major off-gases (Figure 11).

(2) The second region is 750–1200 °C, where extensive degradation of the sample and major weight loss (41%) occur. The only volatile species is HCN (Figure 11).

Between these two distinct regions, the thermal decomposition of NH_3 into N_2 and H_2 is taking place and, as a

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consequence, a dramatic increase of the hydrogen content among the volatiles is observed in the mass spectrum.

The evolution of H_2 and CH_4 in the temperature range 400–750 °C is indicative of the mineralization stage of the organometallic precursor. Elemental analysis of a sample heated at 750 °C, i.e., just below the decomposition temperature of NH_3, gave 21.50% Si, 45.32% C, 24.31% N, and 3.33% H. The analytical composition corresponds to a stoichiometry of $SiC_5N_{2.18}H_{4.3}$ and reveals an appreciable amount of nitrogen. Furthermore, the ^{29}Si NMR spectrum exhibits a broad signal centered at −42.83 ppm, which can be assigned to SiN_4 units.[19] The data clearly indicate that the nitrogen incorporation occurs at 400–750 °C. Thus, the first step of the organometallic–inorganic transformation involves the thermal decomposition of the cross-polymerized material, the reaction with ammonia, and the formation of the Si_3N_4 network.

During the second step (750–1200 °C), HCN was the only detected off-gas. The weight loss is 41% and is close to the carbon content of a sample heated at 750 °C (45% C). The final pyrolysis residue contains a slight amount of C (0.10% C). Thus, the second weight loss can be related to the consumption of the carbon matrix. We propose that reactive radicals such as NH_2, NH, and H, which can be present in the reactive pyrolysis atmosphere above the decomposition temperature of NH_3, lead to the conversion of the free carbon and the formation of HCN.[20]

Conclusion

The above data demonstrate the feasibility of using poly[(silylene)diacetylenes] to produce β-SiC-containing materials in high yields. The following features should be pointed out.

(i) Cross-linking through the diacetylene groups occurs at about 300 °C below the mineralization stage, leading to a stabilized sp^2-ultrastructure network system. Thus, the formation of SiC takes place inside this 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 CH_4, H_2, and a small amount of C_2H_4. SiC is formed from silicon units that contain no functional groups at silicon and which are separated from one another inside a carbon network. This is illustrative of a ceramic formation process which is different from the usual one, such as occurs for instance in the case of poly(carbosilanes). The latter contain reactive Si–H groups which are known to determine the cross-linking of the polymer and the subsequent mineralization stage.

(iii) Pyrolysis under ammonia leads to Si_3N_4. The data are consistent with a two-step process, i.e., (1) an organometallic–inorganic transformation which involves both the thermal decomposition of the cross-polymerized material and the reaction with ammonia affording a Si_3N_4 network, and (2) the consumption of the carbon matrix with the formation of HCN.

Experimental Section

The synthesis of poly[(dimethylsilylene)diacetylene] was described previously,[2b] and 1,4-bis(trimethyl)-1,3-butadiyne was prepared according to the Zweifel procedure.[11] Poly[1-(dimethylsilylene)-4-butylene] was prepared as follows: poly[(dimethylsilylene)diacetylene] (0.5 g, M_n = 2564, I = 1.55) was dissolved in a hexane/THF mixture (80/20; 20 mL), and a small amount of Pd/C was added under nitrogen. The mixture was put under an atmosphere of hydrogen and was stirred at room temperature for 6 days. Filtration on Celite gave a liquid which was concentrated under vacuum and led to a colorless oil (0.54 g, quantitative yield; M_n = 1063; I = 1.39). ^1H NMR (CCl_4; δ, ppm): 0.0 (s, 6 H, $SiCH_3$), 0.45 (m, 4 H, $SiCH_2$), 1,2 (m, 4 H, CH_2). ^{13}C NMR ($CDCl_3$; δ, ppm; main peaks): 2.94 ($SiCH_3$), 15.47 ($SiCH_2$), 28.37 (CH_2). ^{29}Si NMR (C_6D_6; δ, ppm): 2.21. IR (CCl_4; cm^{-1}): ν(CH) 2960, 2910; δ($SiCH_3$) 1407, 1256; δ($SiCH_2$) 1445, 1340, 1180, 1142. Anal. Calcd for $(C_6H_{14}Si)_n$: C, 63.15; H, 12.28; Si, 24.56. Found: C, 62.20; H, 11.46; Si, 23.65.

Argon (O_2 <5 ppm; H_2O <5 ppm) was used as the inert gas for the TGA experiments and the thermal decomposition reactions. Transmission infrared spectra were recorded with a Perkin-Elmer 1600 FT IR spectrophotometer operating at 4-cm^{-1} resolution. Solid IR samples were prepared under a normal atmosphere as KBr pellets. Elemental analyses of the ceramic materials were performed by the "Centre de Microanalyse du CNRS". X-ray diffraction measurements were obtained using Cu Kα radiation with a Philips diffractometer, modified by the method of Professor Fourcade.

Simultaneous TGA/DTA analyses were performed under flowing argon (50 mL/min) with a Netzsch STA 409 thermobalance interfaced with an Anagas 200 Delsi-Nermag mass spectrometer through a capillary tube and a molecular leak. The typical heating rate was 10 °C/min.

DSC experiments were performed on a Mettler 30 instrument, under argon, at a heating rate of 5 °C/min.

All NMR measurements were obtained at ambient temperature. ^1H spectra were acquired by using a Bruker AW 60 instrument and ^{13}C and ^{29}Si solution spectra with a Bruker WP 200 SY or WP 250 AC spectrometer. Chemical shift data were referenced to tetramethylsilane (TMS).

Solid-state ^{13}C and ^{29}Si cross-polarization magic-angle spinning (CP MAS) NMR spectra were obtained in natural abundance on a Bruker WP 300 AM spectrometer working at 75.47 and 59.62 MHz for carbon and silicon, respectively. A ZrO_2 cylindrical rotor was used in all cases.

The pyrolysis experiments were performed by pouring weighed portions (0.1–1 g) of the polymer into an aluminum oxide boat (80 × 10 × 10 mm) which was placed into a gastight aluminum oxide tube (1 m, i.d. 30 mm) fitted with glass taps to allow connection to a vacuum line. During pyrolysis the argon flow was maintained around 50 mL/min. Pyrolyses were performed with a Eurotherm or Carbolite furnace, using a temperature program of 10 K/min up to 1673 K with a 3-h hold at that temperature. In the case of ammonia (50 mL/min) a hold of 6 h at 1673 K was used. Ammonia was dried over KOH (60-cm-length column) and a 50/50 mixture of 3A molecular sieves and silica gel (30-cm-length column).

1,4-Bis(trimethylsilyl)butadiyne was pyrolyzed at 230 °C in a sealed glass tube, under vacuum, for 30 days. The reaction was monitored by IR spectroscopy, following the disappearance of the butadiyne band at 2070 cm^{-1}. ^{13}C NMR spectroscopy was performed in C_6D_6 as solvent; the ene–yne and triene carbons (140, 108 and 218, 103 ppm) gave very broad signals and needed long accumulation times (130 000 scans).

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