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Pyrolysis of poly[(silylene)diacetylenes]: direct evidence between their morphology and thermal behavior

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Abstract

The pyrolysis of poly[(silylene)diacetylenes] under argon to 1400°C gives β-SiC-containing ceramics in high yields (63–87%). All the solid residues contain a large amount of free carbon depending upon the nature of the substituents at silicon, *i.e.*, saturated or unsaturated. Furthermore, the total amount of silicon present in the precursor remains in the final residue. The polymer-to-ceramic conversion has been studied by means of thermal analyses (TGA, TDA and DSC). The polymers primarily undergo low-temperature crosspolymerization through the triple bonds without weight loss which leads to a highly crosslinked carbon network. The mineralization occurs in the temperature range 450–800°C. The crosslinking step can be related to the morphology of the poly[(silylene)diacetylenes]. As shown clearly by X-ray powder diffraction and transmission electron microscopy studies, steric requirement of the side-groups bonded to silicon (methyl versus ethyl, phenyl and trimethylsilyl) greatly influences the degree of crystallinity of the above polymers. The relationship between this structural observation and the crosspolymerization rate is discussed.

1. Introduction

Recently, we have started studies that deal with a new type of organosilicon (germanium) polymers, **1**, in which a regular alternating arrangement of a silylene (or germylene) unit and a diacetylene group is found [1].

$$\mathbf{1} = \text{+}(MR^1R^2)_m{-}C{\equiv}C{-}C{\equiv}C\text{+}_n$$

($M = Si$ or Ge; R^1, R^2 = alkyl, aryl or vinyl;
$m = 1$ or 2)

They are readily prepared by coupling reactions involving the use of the dilithiobutadiyne (or the corresponding di-Grignard reagent) and a wide variety of dihalogenosilanes (or germanes) [1,2].

Besides their charge-transport properties consistent with a delocalization of the π-electron density along the main chain, we have also been interested in the thermal properties of polymers **1** and their evaluation as preceramic polymers [3]. Numerous publications have been devoted to the thermal conversion of organosilicon polymers whose pyrolysis gives SiC-containing ceramic materials [4]. High ceramic yields are related to a high degree of branching of the polymeric chains [5,6]. Thus, the presence of appropriate reactive (or potentially reactive) functionalities whose reactivity will result in substantial crosslinking during the initial stages of the pyrolysis, is one of the factors that determine the yield of ceramic residue. Polymers of the $\text{+}X{-}C{\equiv}C{-}C{\equiv}C\text{+}_n$ type with X being either $\text{+}CH_2\text{+}_n$ ($n = 3$, 5 or 8) [7], an aromatic group [8] or polyester and polyurethane units [9] have been reported to undergo thermally induced crosspolymerization at relatively low temperature. A similar process occurs with

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poly[silylene (or germylene)diacetylenes], as a result of the reactive triple bonds, and may greatly influence their thermal behavior.

In a base-line study, we have previously shown that the pyrolysis of $\left[\mathrm{Si(CH_3)_2{-}C{\equiv}C{-}C{\equiv}C} \right]_n$ in an argon atmosphere to 1400°C affords a β-SiC-containing ceramic in high yield (84%) [3]. Crosslinking through the diacetylene groups proceeds at about 300°C below the mineralization stage. They are thermally converted into an amorphous carbon network where the organometallic–inorganic transition and the formation of SiC take place. All the silicon contained in the dimethylsilyl groups is quantitatively present in the final ceramic as SiC. The latter results from silicon units that contain no functional groups at silicon and which are separated from one another inside the carbon matrix. This is illustrative of a ceramic formation process which is different from the usual one, such as occurs for instance in the case of polycarbosilanes. The latter contain reactive Si–H groups which are known to determine the crosslinking of the polymer and the subsequent mineralization stage.

Expanding upon our previous report, we now describe additional data obtained by studying analogous poly[(silylene)diacetylenes] with various side-groups at silicon,

$$\left[(\mathrm{SiR^1R^2})_m{-}\mathrm{C{\equiv}C{-}C{\equiv}C} \right]_n$$

$(R^1 = R^2 = \mathrm{Me},\ m = 1,$ **2**;
$R^1 = R^2 = \mathrm{Et},\ m = 1,$ **3**;
$R^1 = R^2 = \mathrm{Me},\ m = 2,$ **4**;
$R^1 = \mathrm{Me},\ R^2 = \mathrm{Ph},\ m = 1,$ **5**;
$R^1 = R^2 = \mathrm{Ph},\ m = 1,$ **6**;
$R^1 = R^2 = \mathrm{SiMe_3},\ m = 1,$ **7**$)$

The main objectives of this investigation were: (1) to compare the general thermal stabilities of these organometallic precursors; (2) to find relationships between their structure and thermal behavior.

2. Results and discussion

2.1. Bulk pyrolysis: elemental analysis and ceramic yields

Table 1 shows the ceramic yields and compositions of pyrolyzed poly[(silylene)diacetylenes] after heating to 1400°C for 12 h under argon. In all cases, a black ceramic-type residue was recovered in high yields (63–87%). Examination of these materials by X-ray powder diffraction shows the formation of crystalline β-SiC. Elemental analyses indicate carbon and silicon as the only elemental components of the chars and prompt the following remarks:

(1) All the solid residues at 1400°C contain a large amount of free carbon. Similar observations have been made previously by others in the case of analogous silylene-acetylene polymers [10]. The effect of the R groups on the ceramic char composition is also quite clear. As outlined previously by others [11], the substituents at silicon can be divided into two groups, saturated and unsaturated. Alkyl groups, *i.e.*, methyl or ethyl, gave ceramic chars containing 37.5–54.5 wt% carbon (Table 1, runs 1–3). In contrast, phenyl substitution (Table 1, runs 4, 5) produced the greatest amount of carbon (73.0–78.3 wt%).

(2) The loss of silicon during the pyrolysis, $\Delta \mathrm{Si} = \mathrm{Si_p} - \mathrm{YSi_c}$, may be estimated on the basis of the elemental analysis values, *i.e.*, $\mathrm{Si_p}$ (wt% silicon content of the starting polymer) and $\mathrm{Si_c}$ (wt% silicon content of the final ceramic), and the ceramic yields Y (Table 1). In this respect, two different behaviors may be pointed out:

(i) Polymers with silicon included in the main chain (Table 1, runs 1–5) exhibit quite close values. All the silicon contained in the organosilyl groups of the starting precursor was quantitatively recovered at the end of the pyrolysis.

(ii) A polymer where silicon is also present in the pendant groups as trimethylsilyl substituents (Table 1, run 6) leads to a signifi-

TABLE 1. Pyrolysis of the poly[(silylene)diacetylenes]: ceramic yields and chemical composition of the ceramic residues

Run	Precursor (no.) [a]			Ceramic yield [b]	Elemental analysis		Stoichiometry of the ceramic	Free C%	$\mathrm{Si_p}$ [b]	$\mathrm{YSi_c}$ [b]
	R^1	R^2	*m*		Si%	C%				
1	Me	Me	1 (**2**)	84	33.10	65.90	SiC–4C	54.5	26.41	27.80
2	Et	Et	1 (**3**)	72	29.10	68.19	SiC–4C	54.5	20.89	20.95
3	Me	Me	2 (**4**)	72	40.31	55.51	2(SiC)–4C	37.5	34.14	29.02
4	Me	Ph	1 (**5**)	87	18.30	77.92	SiC–9C	73.0	15.80	16.01
5	Ph	Ph	1 (**6**)	83	15.00	82.84	SiC–12C	78.3	11.70	12.52
6	$\mathrm{Me_3Si}$	$\mathrm{Me_3Si}$	1 (**7**)	63	38.80	58.02	2(SiC)–5C	42.8	37.84	24.44

[a] Precursor: $\left[(\mathrm{SiR^1R^2})_m{-}\mathrm{C{\equiv}C{-}C{\equiv}C} \right]_n$; **2**, MW = 4060; **3**, MW = 6070; **4**, MW = 3540; **5**, MW = 3070; **6**, MW = 1830; **7**, MW = 7310.

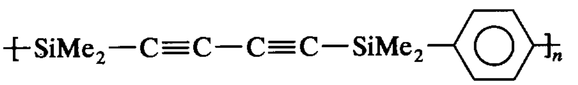
[b] Ceramic yield: (weight pyrolysis residue × 100)/(weight pyrolysis charge); $\mathrm{Si_p}$ = wt% silicon content of the starting polymer; Y, ceramic yield, $\mathrm{Si_c}$, wt% silicon content of the final ceramic, $\mathrm{YSi_c}$, silicon amount in the solid residue afforded by the pyrolysis of 100 g of precursor.

cantly higher weight loss. Ceramic yield obtained for **7** was 63% and the analytical composition of the ceramic product corresponds to a hypothetical stoichiometry of 2(SiC)-5C. Only two of the three silicon atoms of the precursor are present in the final residue.

Ceramic yields and combustion analyses of the chars also show considerable control of the nature of the polymeric skeleton. Model compounds **8**, **9**, **10** [1,3] have been prepared and thermally converted.

$$8 = \left[\mathrm{SiMe_2{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_2{-}(CH_2)_4}\right]_n$$

$$9 = \left[\mathrm{SiMe_2{-}(CH_2)_4}\right]_n$$

10 =


When the reactive diacetylene groups are progressively replaced by the tetramethylene units (polymer **8**), a dramatic decrease in the ceramic yield (32%) was observed. Polymer **8** lost a considerable amount of mass and, in particular, about one-third of the silicon initially present in the polymer was recovered at the end of the pyrolysis. As an extreme example, the pyrolysis of **9** left no solid residue [3]. Due to its pure linear structure and the lack of reactive centers, the polymeric chain fragments during the pyrolysis and leads to low molecular weight species. Finally, the introduction of a phenylene group in the main chain of **10** again resulted in a high ceramic yield (84%). Conservation of silicon in the final residue from **10** was found and the composition of the ceramic corresponds to a SiC–5C stoichiometry. As a comparison, note that $\left[\mathrm{(SiMePh){-}C{\equiv}C{-}C{\equiv}C}\right]_n$ where the phenyl is a pendant group at silicon, leads to a SiC–9C stoichiometry and, thus, to a higher free carbon content. These results emphasize the role of the latent reactive diacetylene centers in the pyrolysis step. They can undergo relatively facile thermally induced crosspolymerization and lead to a crosslinked structure prior to chain scission.

Finally, the degree of polymerization seems to have a minor effect on the ceramic yield. Silylene-diacetylene polymers of higher weight average molecular weights ($10^4 < \mathrm{MW} < 2 \times 10^4$) reported by Barton *et al.* [2] led to quite similar ceramic yields compared to those summarized in Table 1.

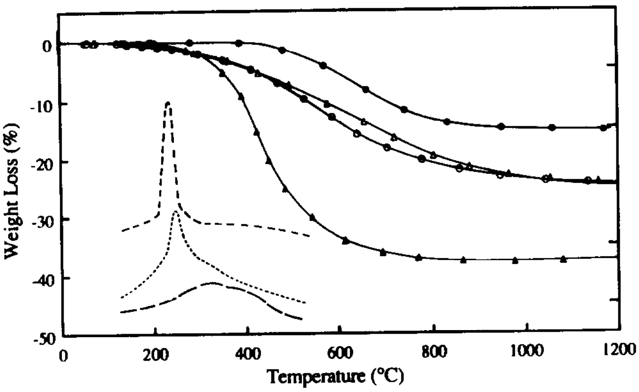


Fig. 1. Thermogravimetric and thermal differential analyses of poly[(silylene)diacetylenes] **2**, **5**, **6** and **7** (TGA traces: ●, **2**; ○, **5**; △, **6**; ▲, **7**. TDA curves: - - - - - -, **2**; · · · · · ·, **6**; ———, **7**).

2.2. *Thermal analysis: thermogravimetric (TG), thermal differential (TD) analyses and results from differential scanning calorimetry (DSC)*

To guide the examination of the pyrolysis of poly[(silylene)diacetylenes], thermogravimetric and thermal differential analyses under an inert gas (argon) were obtained. Typical thermograms are shown in Fig. 1 for samples of **2** [3], **5**, **6** and **7**. Whatever the nature of the R groups bonded to silicon, pyrolyses of the various poly[(silylene)diacetylene] precursors proceed in an identical fashion. The thermograms clearly show that two different steps take place successively when the temperature of a sample is progressively increased up to 1200°C. The following remarks can be made:

(1) The TGA traces (Fig. 1) reveal that the poly[(silylene)diacetylenes] are thermally stable to almost 400°C. At this point, decomposition starts and the major weight loss (13–37%) is complete below 800°C.

(2) The TDA curves (Fig. 1) show in each case a strong exotherm in the temperature range 200–400°C without weight loss. Diacetylene materials are known to be thermally reactive and the observed exothermic areas have been ascribed to the crosspolymerization of the poly[(silylene)diacetylene] derivatives through the triple bonds. This first step irreversibly modifies the backbone of the starting polymer and as we have shown in the case of the poly[(dimethylsilylene)diacetylene] **2**, it leads to a stabilized sp^2-ultrastructure network system [3]. Furthermore, a sharp exotherm centered at 200°C, indicative of a fast process, was obtained with **2**. In contrast, the presence of bulky trimethylsilyl groups bonded to silicon results in a broad exothermic area in the temperature range 250–450°C. This suggests a close relationship between the molecular environment of the diacetylene groups and the crosspolymerization rate.

Results from differential scanning calorimetry (DSC) are also quite clear. Studies have been carried out only with polymers **2**, **3**, **6** and **7** where both pendant R^1 and R^2 groups are identical in order to avoid the effects of tacticity. Data are summarized in Figs. 2–4. The two main features are:

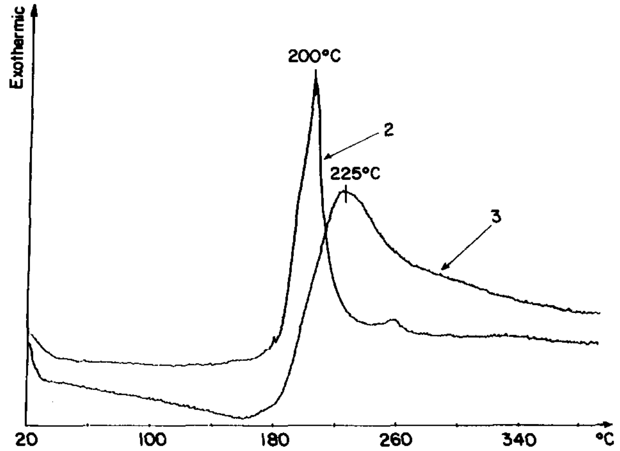


Fig. 2. A comparison of the DSC plots of **2** and **3**.

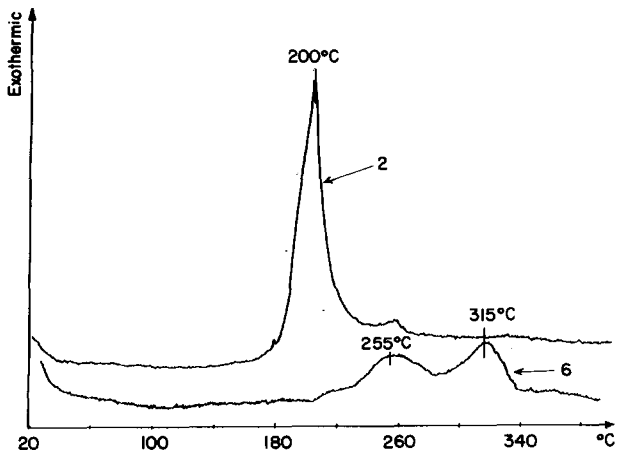


Fig. 3. A comparison of the DSC plots of **2** and **6**.

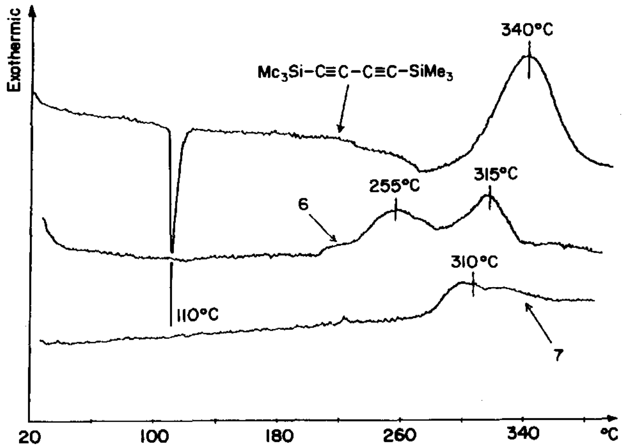


Fig. 4. A comparison of the DSC plots of **6**, **7** and bis(trimethylsilyl) butadiyne.

(1) No distinct melting endotherms in the DSC traces can be observed. This means that the thermal induced diacetylene polymerization takes place in the solid state prior to melting.

(2) Steric requirements due to the R groups attached at silicon, *i.e.*, methyl *versus* ethyl, phenyl or trimethylsilyl substituents, result in a significant effect on the DSC curves. $\left[SiMe_2{-}C{\equiv}C{-}C{\equiv}C \right]_n$ displays only a sharp and strong exothermic peak centered at 200°C (Fig. 2). Integration of this exothermic area corresponds to 181 cal g^{-1}. In the case of the poly[(diethylsilylene)diacetylene] **3**, the crosspolymerization exotherm shifts to higher temperatures (Fig. 2). The replacement of the methyl side groups by ethyl substituents is sufficient to increase the T_{exo} by about 25°C. The phenyl groups likewise exert a stronger effect. Figure 3 shows a comparison between the DSC plots of **2** and $\left[SiPh_2{-}C{\equiv}C{-}C{\equiv}C \right]_n$ **6**. In the latter, phenyl substituents provide a more unfavorable environment for the diacetylene polymerization. Crosslinking occurs at about 250°C, *i.e.*, 50°C above the temperature observed for **2**. Moreover, an additional peak appeared at 315°C (Fig. 4). As the thermal degradation of the polymer **6** takes place above 450°C (Fig. 1), it is clear that this second exotherm is related to the reaction of the diacetylene groups. Polymer **7** is also of interest (Fig. 4). The thermal conversion occurs at a higher temperature range above 300°C. Significant broadening of the exothermic area, indicative of a slow reaction, was observed. Integration of the DSC curve reflects a lower exothermic process (70 cal g^{-1}). Note that the DSC traces of **7** and of 1,4-bis(trimethylsilyl)-butadiyne show some similarities (Fig. 4). The latter melts at 110°C and thus undergoes thermal polymerization through the triple bonds in a highly disordered amorphous state. As observed for **7**, $Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3$ displays a broad exotherm in the temperature range 270–400°C (Fig. 4).

2.3. The crosspolymerization: influence of the chemical environment of the diacetylene groups

The above data demonstrate the feasibility of using poly[(silylene)diacetylenes] to produce β-SiC-containing materials in high yields. In general, their pyrolysis proceeds in an identical fashion. The first step likely corresponds to a low-temperature crosslinking through the triple bonds without weight loss. The organometallic-to-inorganic transformation leading to the ceramic residue occurs at higher temperatures between 450 and 800°C. Mechanisms have previously been proposed for both the crosslinking and the mineralization of the poly[(dimethylsilylene)diacetylene] mainly on the basis of infrared and solid-state ^{13}C NMR spectroscopies [3]. As outlined by the above data, varying the nature of the R groups attached at silicon provided dramatic changes in the crosslinking process and we now discuss their mechanistic implications.

Solid-state free-radical polymerization of crystalline diacetylene monomers, $R{-}C{\equiv}C{-}C{\equiv}C{-}R$, has been well documented in the literature [12]. The reaction proceeds *via* a 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 [12,13]. Moreover, it was shown that the polymerization in the macromonomers $\left[C{\equiv}C{-}C{\equiv}C{-}X\right]_n$ results in crosslinking within the crystalline regions [7–9].

We have previously shown that the poly[(dimethylsilylene)diacetylene] behaves in a similar manner [3]. When a sample is heated above 200°C, the infrared spectrum indicates that the peak at 2070 cm^{-1} characteristic of the presence of the diacetylene groups is progressively replaced by the absorption bands of an ene–yne or triene structure, centered at 2114, 1520 and 1872 cm^{-1}, respectively. ^{13}C NMR spectroscopy also suggests that the initial stages of the crosslinking process involve the conversion of the sp carbons into sp^2 carbons.

Results from differential scanning calorimetry give evidence of the dominant influence of the environment of the triple bonds on their polymerization rate. Such influence can be readily understood from the X-ray powder diffraction patterns of polymers, **2**, **3**, **6** and **7** (Figs. 5 and 6), and the following comments can be made:

(1) The poly[(dimethylsilylene)diacetylene] **2** displays four diffraction peaks at defined angles $2\theta = 16.6$, 17.6, 20.9 and 27.4°, indicative of a highly crystalline structure (Fig. 5). The repeat distance of the diacetylene backbone inside the crystalline regions was measured to be 4.6 Å [14] and is of the same order of magnitude as that observed with fully chain-aligned monomer single crystals or with macromonomers. The DSC plot of **2** exhibits a sharp and strong exothermic peak centered at 200°C (*vide supra*), indicative of a fast crosspolymerization reaction.

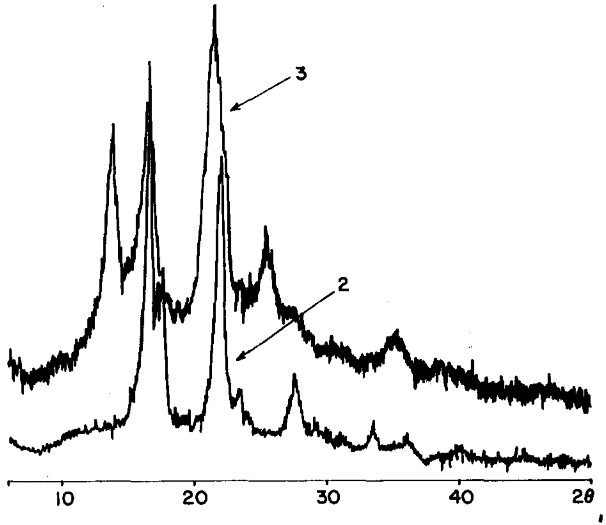


Fig. 5. A comparison of the X-ray powder diffraction patterns of 2 and 3.

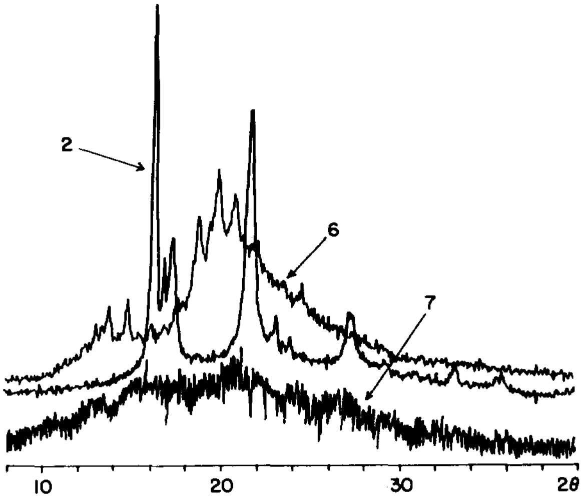


Fig. 6. A comparison of the X-ray powder diffraction patterns of 2, 6 and 7.

(2) Progressively increasing the steric requirement around silicon results in a parallel decrease in the degree of crystallinity. For instance, the diethyl polymer **3** compared to **2** (Fig. 5) shows a higher amorphous contribution and a greatly broadened X-ray diffraction pattern. Likewise, the diphenyl derivative **6** (Fig. 6) exhibits a much lower degree of crystallinity and a larger stacking distance which has been estimated to be about 6 Å [14]. Finally, the case of **7** is more significant. The presence of the very bulky trimethylsilyl groups resulted in a completely disordered amorphous structure possessing a liquid-like short-range order (Fig. 6). In both cases, data from differential scanning calorimetry reveal a general shift of the corresponding exotherms to higher temperatures (*vide supra*) and a parallel reduced exothermic activity as shown in Figs. 2, 3 and 4. Moreover, **6** and **7** which exhibit less defined structures, have thermal behaviors (*vide supra*) that are partly similar to that of the 1,4-bis(trimethylsilyl)butadiyne which polymerizes after melting, *i.e.*, in a completely amorphous state. Besides a first exotherm centered at about 255°C, **6** shows a second exothermic area at 315°C which can be related to a crosslinking reaction through the diacetylene units present in the amorphous phase. Similarly, **7** shows

Fig. 7. TEM image of a $+\mathrm{SiMe_2{-}C{\equiv}C{-}C{\equiv}C}+_n$ sample deposited on a grid recovered with a collodion film.

only a broad exotherm at about 350°C, *i.e.*, essentially in the same range of temperature as the 1,4-bis(trimethylsilyl)butadiyne which crosslinks in an amorphous molten state.

Direct evidence for the morphology of **2** was obtained by transmission electron microscopy (TEM). An image of a thin film (< 0.1 μm) of **2** (MW = 2941, $n_w = 1.4$, relative to polystyrene standards) deposited on a sample grid from a THF solution is shown in Fig. 7. Clearly, this representative sample contains large amounts of defined diamond-shaped structure having particle sizes mostly in the range of 1–2 μm. These crystalline domains are dispersed in the whole mass of the material and their presence is in good agreement with the X-ray powder diffraction pattern obtained for **2** (Fig. 5). This again gives strong evidence of the high degree of crystallinity of the poly[(dimethylsilyl)diacetylene].

The above data, together with results from thermal analyses, suggest a close relationship between the rate of the crosspolymerization reactions of the poly[(silylene)diacetylenes] and the structural environment of the triple bonds, as summarized below,

Degree of cristallinity (↘)	2 (Me) >	3 (Et) >	6 (Ph) >	7 ($\mathrm{SiMe_3}$)
T_{exo} (°C) (↗)	200 <	225 <	225, 315 <	350 (broad)
Exothermic activity (↘) (ΔH cal $\mathrm{g^{-1}}$)	181	–	125	70

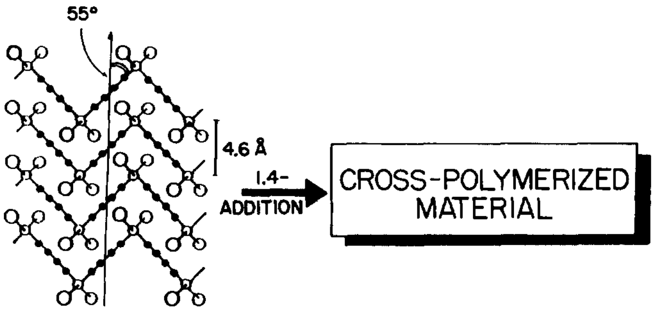


Fig. 8. Schematic representation of the poly[(dimethylsilylene)diacetylene] microstructures: optimal arrangement of the diacetylene units in the well-ordered crystalline regions.

Although the diacetylene content is essentially constant in each of the above polymers, it means that the number of triple bonds capable of undergoing solid-state crosspolymerization is considerably reduced when going from **2** to **7**. Clearly, the presence of the bulky trimethylsilyl groups disfavors the aggregation of the diacetylene units and disrupts the formation of structurally ordered crystalline domains. Thus, we can assert that on the principle of least motion, the initial polymerization reaction of the acetylenic groups starts in the crystalline parts in which the optimal arrangement of the diacetylene units is present (Fig. 8). Subsequent thermal treatment up to 400°C leads to additional crosslinking reactions in the whole mass of the polymer, as indicated for instance by the presence of a

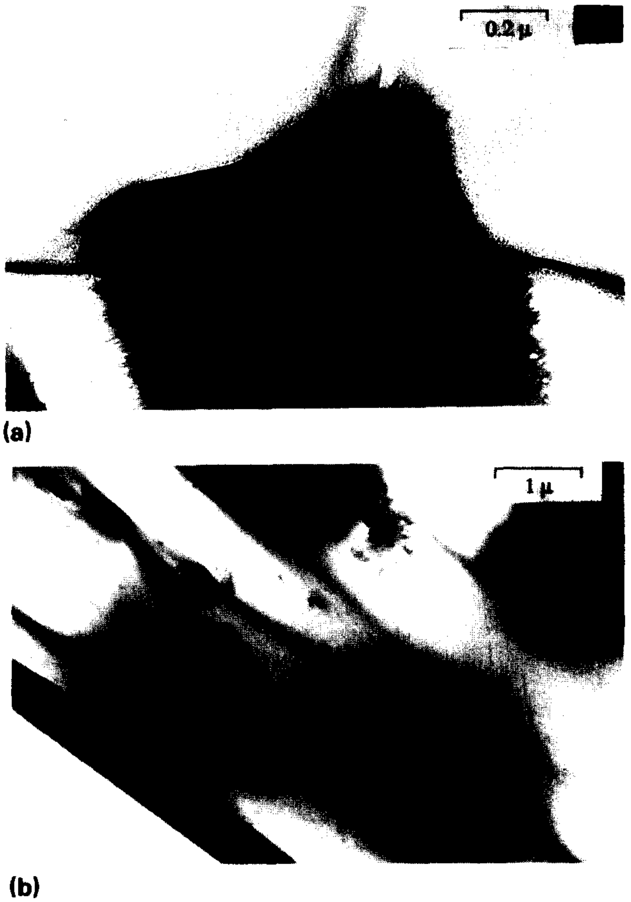
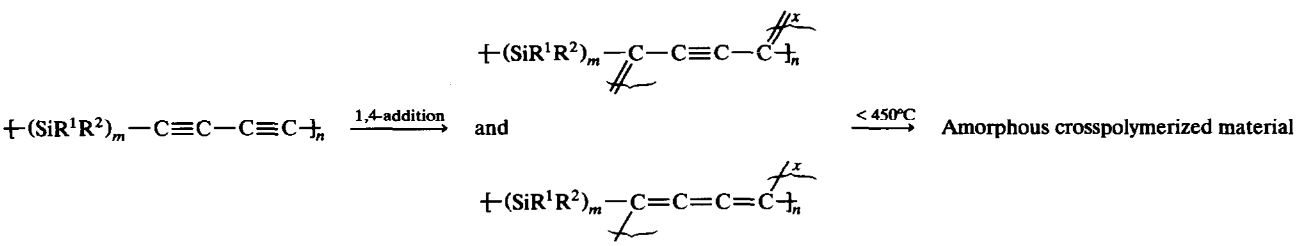


Fig. 9. TEM micrographs of **2** undergoing crosslinking due to the electron beam: (a) close to a crystalline domain, (b) in the whole mass of the polymer.



Scheme 1. Crosslinking of poly[(silylene)diacetylenes].

second exothermic area in the DSC trace of **6**. This is also well illustrated when **2** undergoes crosslinking induced by the electron beam during TEM experiments, as shown in Fig. 9. As the polymerization proceeds, we observed the formation of additional black hard domains starting from the crystalline structures (Fig. 9(a)) and the phenomenon readily extends to the whole film, generating cracks and leading to the disintegration of the sample.

The overall process results in the formation of a stabilized sp^2-ultrastructure network system, as summarized in Scheme 1. The formation of SiC occurs inside this amorphous carbon matrix and involves, as outlined previously, organosilyl units which are separated from one another. Greatest amounts of free carbon are obtained with unsaturated aryl substituents at silicon. Further studies are now in progress to establish a relationship between the nature of the pendant groups at silicon and the elemental composition of the final ceramic.

In conclusion, we have given a general picture of the pyrolysis of various poly[(silylene)diacetylenes]. The relationship between the structure of the starting precursor and its thermal behavior has been pointed out. Of particular interest are their ability to be converted into a highly crosslinked structure at relatively low temperature and the possibility of modulating the carbon content of the final ceramic residue in a large range of compositions. We are now taking advantage of both these properties in the carboreduction of metal oxide powders M_xO_y to multiphase ceramic powders $Si_mM_nC_p$ [15].

3. Experimental section

The synthesis of the poly[(silylene)diacetylenes] **2**–**7** and **9** was described previously [1,3], and 1,4-bis(trimethylsilyl)butadiyne was prepared according to the Zweifel procedure [16]. Polymers **8** and **10** were obtained in a similar fashion by reaction of the dilithiobutadiyne with 1,4-bis(chlorodimethylsilyl)butane and 1,4-bis(chlorodimethylsilyl)benzene, respectively.

8: 90% yield. MW = 4400, $I = 1.53$. ^1H NMR (CCl_4) δ −0.03 (s, 6H, $SiCH_3$); 0.47 (m, 4H, $SiCH_2$-CH_2); 1.26 (m, 4H, $SiCH_2$-CH_2) ppm. ^{29}Si NMR ($CDCl_3$) δ −14.15 ppm. Anal. Found: C, 62.03; H, 9.71; Si, 25.02. ($C_{12}H_{20}Si_2$) calcd.: C, 65.45; H, 9.09; Si, 25.45%.

10: 93% yield. MW = 9091, $I = 1.65$. ^1H NMR ($CDCl_3$) δ 0.3 (s, 6H, $SiCH_3$); 7.48 (s, 4H, Ar) ppm. ^{29}Si NMR ($CDCl_3$) δ −20.23 ppm. Anal. Found: C, 68.37; H, 4.36; Si, 21.90. ($C_{14}H_{16}Si_2$) calcd.: C, 70.00; H, 6.66; Si, 23.33%.

Argon ($O_2 < 5$ ppm; $H_2O < 5$ ppm) was used as the inert gas for the TGA experiments and the thermal decomposition reactions. Elemental analyses of the ceramic materials were performed by the Service Central de Microanalyse du CNRS, Vernaison, France. X-Ray diffraction measurements were obtained using Cu Kα radiation with a Philips diffractometer modified by Professor Fourcade [17].

The pyrolysis experiments were performed by pouring weighed portions (0.1–1 g) of the polymer into an aluminium oxide boat (80 × 10 × 10 mm) which was placed into a gastight aluminium oxide tube (1 m, i.d. 30 mm) fitted with glass taps to allow connection to a vacuum-line. During the pyrolysis, the argon flow was maintained around 50 ml/min. Pyrolyses were carried out with a Eurotherm or Carbolite furnace, using a temperature program of 10 K/min up to 1673 K with a 3 h hold at this temperature.

Simultaneous TGA/TDA measurements were performed under flowing argon (50 ml/min) with a Netzsch STA 409 thermobalance. The typical heating rate was 10°C/min.

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

TEM micrographs were obtained using a JEOL 200 CX transmission electron microscope operated at 200 kV. Polymers were deposited as a thin film (< 0.1 μm) by slow evaporation of a THF solution on copper grids recovered with a collodion film.

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