

JOM 23880

Organogermanium polymers: pyrolysis chemistry of poly[(germylene)diacetylenes]

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(Received March 21, 1993)

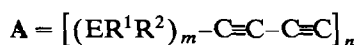
Abstract

The pyrolysis of poly[(germylene)diacetylenes] and poly[(germylene)diacetylene][(silylene)diacetylenes] was studied under argon. The ceramic residues were obtained in good yield (66–82%) due to cross-linking through the triple bonds at relatively low temperatures (150–250°C) which gave a carbon sp^2 matrix with disubstituted organogermyl and/or silyl groups. The ceramic residues contained a high amount of carbon (40–61%) and all the germanium was recovered as metallic germanium above 500°C. Pyrolysis of poly[(germylene)diacetylenes] under ammonia gave germanium nitride after cross-linking and nitridation between 400 and 600°C.

Key words: Germanium; Polymer; Diyne; Ceramic

1. Introduction

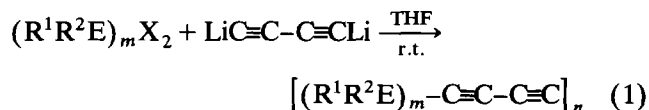
As a part of our studies of organosilicon and organogermanium polymers containing a π -electron system in the polymer backbone, we reported recently on the synthesis of polymers A in which a regular arrangement of a silylene or germylene unit alternate with a diacetylide group [1].



(E = Si, $m = 1$ or 2; E = Ge, $m = 1$;

$R^1, R^2 =$ alkyl, aryl)

These derivatives were obtained by condensation of a dilithium derivative with dihalogeno-silanes or -germanes, according to eqn. (1).



The above polymers exhibit conductivity values in the range 10^{-3} – 10^{-5} S cm^{-1} when doped with $FeCl_3$

[1]. These compounds are also interesting as ceramic precursors. Indeed, due to the easy cross-linking capability of the diacetylene unit, we observed high ceramic yields for the poly[(dialkyl- or diaryl-silylene)diacetylenes]. For instance, a weight loss of only 15% was observed after pyrolysis of the poly[(dimethylsilylene)diacetylene] to 1400°C, leading to a mixture of silicon carbide and carbon in the ratio SiC/4C [2]. Two successive steps were observed in the pyrolysis process: the first, between 200 and 400°C, corresponds to the thermal cross-linking of the acetylene units leading to a carbon sp^2 network; the second, above 500°C, occurred with weight loss and is related to the mineralization stage with evolution of CH_4 and H_2 . The amount of silicon in the polymer was completely retained in the final ceramic residue as SiC. The formation of the carbon matrix by cross-linking of the acetylene units allowed the transformation of isolated $SiMe_2$ groups into an SiC network.

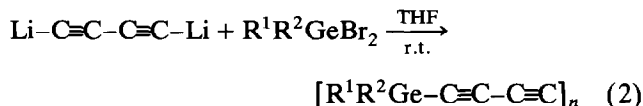
We have extended the above study using germanium as heteroelement in order to prepare germanium ceramic phases. We describe now the thermal behaviour of poly[(germylene)diacetylenes] and poly[(germylene)diacetylene][(silylene)diacetylenes] under inert and re-active atmospheres.

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2. Results and discussion

2.1. Synthesis of polymers A

The synthesis of the polymers of structure A has been described previously [1]. Equation (2) gives the reaction in the case of the germanium polymers.



- 1: $\text{R}^1 = \text{R}^2 = \text{Et}$
 2: $\text{R}^1 = \text{Me}; \text{R}^2 = \text{Ph}$
 3: $\text{R}^1 = \text{Et}; \text{R}^2 = \text{Ph}$
 4: $\text{R}^1 = \text{R}^2 = \text{Ph}$

The copolymers having both silylene diacetylene and germylene diacetylene units were prepared according to Scheme 1. Table 1 gives the characteristics of the copolymers 5 and 6. The polydispersities observed, 1.73 for 5 and 2.25 for 6, were consistent with a linear and regular alternation of a diacetylene unit and a group with a heteroelement. The molecular weights obtained by gel permeation chromatography (GPC) using polystyrene standards (1780 for 5 and 3040 for 6) indicated that these oligomers have, on average, seven units in the chain.

TABLE 1. $\text{Li-C}\equiv\text{C-C}\equiv\text{C-}[-\text{MePhGe-C}\equiv\text{C-C}\equiv\text{C}]_m\text{Li} + \text{RR}'\text{SiCl}_2 \rightarrow \text{Me-}[-\text{SiRR}'-\text{C}\equiv\text{C-C}\equiv\text{C-}(-\text{MePhGe-C}\equiv\text{C-C}\equiv\text{C-})_m]_n\text{SiRR}'\text{Me}$

Chlorosilane	MW ^a	MW/M _n ^a	DP _n	Yield (%)	Polymer
Me ₂ SiCl ₂	1780	1.73	7	92	5
MePhSiCl ₂	3040	2.25	7	88	6

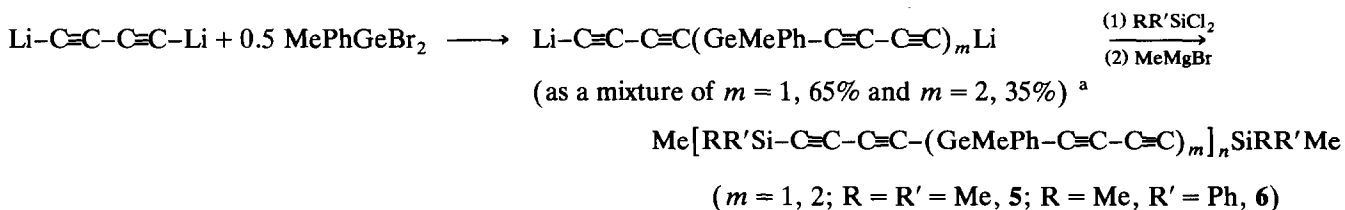
^a Molecular weights were determined relative to polystyrene standards.

2.2. Pyrolysis under argon

2.2.1. Bulk pyrolysis

The pyrolysis of the germanium polymers 1–4 and the silicon-germanium copolymers 5 and 6 were performed under argon at a heating rate of 10°C min⁻¹ up to 1400°C, where the temperature was held for 3 h. Tables 2 and 3 summarize the yields, elemental analyses and stoichiometries obtained. The residues were also analysed using X-ray powder diffraction spectroscopy and, in the case of 2, scanning electron microscopy (SEM).

We always observed high ceramic yields (66–82%). Elemental analyses indicated germanium and carbon (polymers 1–4) or silicon, germanium and carbon (polymers 5 and 6). The amount of carbon in the



Scheme 1. (a) The mixture was analysed as follows: the condensation of this dilithioderivative with Me₃SiCl gave a mixture of two compounds, $m = 1$ and $m = 2$. The derivative ($m = 1$) was prepared independently as described in the Experimental section and this allowed the determination of the composition of the mixture using ¹H NMR spectroscopy.

TABLE 2. Pyrolysis of $[\text{R}^1\text{R}^2\text{Ge-C}\equiv\text{C-C}\equiv\text{C}]_n$ under argon

Precursor	R ¹	R ²	Y% ^a	Analysis (%)			Stoichiometry of the residue
				C	Ge	O	
1	Et	Et	71.5	40.16	54.00	3.4	GeC _{4.5} O _{0.28}
2	Me	Ph	77	52.13	43.43	1.7	GeC _{7.26} O _{0.17}
3	Et	Ph	66	47.09	49.17	4.0	GeC _{5.8} O _{0.3}
4	Ph	Ph	67	60.03	36.74	1.47	GeC ₁₀ O _{0.18}

^a Ceramic yield. $\text{Y\%} = m/m_0 \times 100$; m = weight of the residue after pyrolysis; m_0 = weight of the precursor.

TABLE 3. Pyrolysis of $\text{Me-}[-\text{SiRR}'-\text{C}\equiv\text{C-C}\equiv\text{C-}(\text{GeMePh-C}\equiv\text{C-C}\equiv\text{C})_m]_n\text{SiRR}'\text{Me}$

Precursor	R	R'	Y% ^a	Analysis				Stoichiometry
				Ge	Si	C	O	
5	Me	Me	82	26.5	12.3	55.4	5.7	GeSi _{1.2} C _{12.8} O _{0.8}
6	Me	Ph	69	18.7	12.3	61.2	5.7	GeSi _{1.7} C _{19.8} O _{1.7}

^a Ceramic yield. $\text{Y\%} = m/m_0 \times 100$; m = weight of the residue after the pyrolysis; m_0 = weight of the precursor.

TABLE 4. Calculated and observed germanium percentages in the ceramics

Precursor	Ge _p ^a	Ge _c	
		Calc. ^b	Found ^a
1	40.7	56.9	54.0
2	31.15	40.4	43.4
3	32.3	48.9	49.2
4	27.6	41.2	36.7

^a Ge_p = wt% germanium content of the starting polymer; Ge_c = wt% germanium content of the ceramic. ^b Calculated Ge_c = (Ge_p × 100)/Y with Y = ceramic yield.

residue depended on the nature of the substituents at the germanium atom in the precursor: 60.0% for 4, 52.13% for 2 and 40.16% for 1. As observed with the silicon analogues [2], a phenyl group enhanced significantly the amount of carbon in the residue. A small amount of oxygen (1.5–4%) was always present in the residues.

The X-ray powder diffractograms of the pyrolysis residues of 1–4 corresponded to crystalline germanium; for 5 and 6, a mixture of β SiC and crystalline germanium was observed. In contrast to SiC, which is very stable, non-stoichiometric germanium carbides, Ge_xC_{1-x} (*x* between 0.2 and 0.7) are known to decompose near 500°C, leading to metallic germanium [3].

As with the silicon analogues [2], we did not observe any loss of germanium or silicon during pyrolysis of the polymers 1–6. Tables 4 and 5 give the calculated and observed percentages of germanium and silicon in the ceramic residues.

These values, based on elemental analyses, are in relatively good agreement and prove that all germanium and silicon of the starting polymers was recovered. Furthermore, the mixed oligomers 5 and 6 led to ceramics whose stoichiometries appear to be equal to the sum of the stoichiometries of the solid residues obtained from separate pyrolysis of the corresponding germanium and silicon polymers.

The SEM micrograph of pyrolysed 2 (Fig. 1) shows large germanium particles. Germanium melts at 937°C, so that during heating at 1400°C for 3 h, diffusion of the germanium in the ceramic residue to form aggregates which then crystallize on cooling may occur.

2.2.2. Thermal studies

The thermal analyses of polymers 1–4 were performed up to 1200°C at a heating rate of 10°C min⁻¹. The TGA curves and the gas analyses of the heated polymers 1 and 2 are shown in Figs. 2 and 3, respectively.

The DSC analyses of polymers 1–4 were performed under argon up to 500°C at a heating rate of 10°C

TABLE 5. Calculated and observed germanium and silicon percentages in the ceramics

Pre-cursor	Si _p ^a (%)	Si _c (%)		Ge _p ^a (%)	Ge _c (%)	
		Calcd ^b	Found ^a		Calcd ^b	Found ^a
5	10.10	12.3	12.3	21.3	26.0	26.5
6	8.8	12.75	12.3	13.9	20.1	18.7

^a Obtained by elemental analysis. ^b Calculated using E_c = (E_p × 100)/Y with E = Si, Ge; E_c = wt% Si or Ge in the ceramic; E_p = wt% Si or Ge in the precursor.

min⁻¹. Figure 4 gives the DSC curve obtained with polymer 2.

As observed previously in the case of poly[(silylene)-diacetylenes] [2], thermal analysis indicated two steps. The first corresponds to an exothermic transformation without weight loss at *ca.* 200°C. The DSC analysis confirms this result: no melting point, but a strong exotherm was observed between 100 and 250°C depending on the substituents at germanium. The second step occurs mainly between 400 and 600°C and corresponds to the ceramization of the samples with weight loss. For polymer 1 (Fig. 2), ethylene evolution started near 350°C and continued up to 500°C. Hydrogen was detected mainly from 350 to 600°C. Methane and propene, which may originate from ethylene decomposition [4], were also observed. In the case of polymer 2 (Fig. 3), benzene evolved between 400 and 600°C and then methane in the temperature range 450–600°C. Hydrogen was detected mainly in the range 500–800°C. Some toluene, characterized as the tropylium cation in the mass spectrum, was also present.

Both steps were also followed using infrared and NMR spectroscopy.

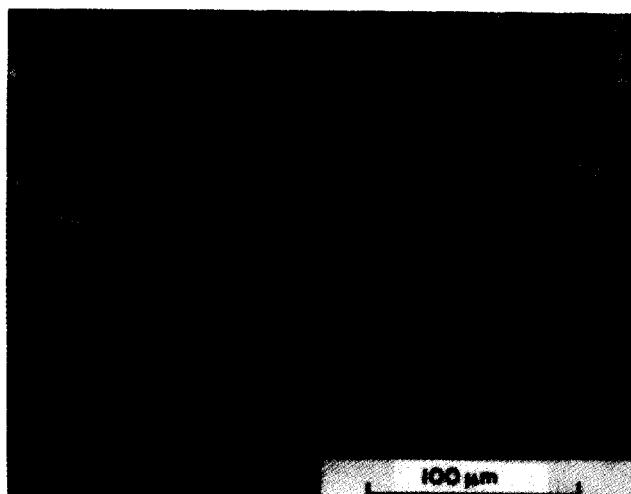


Fig. 1. SEM microphotograph of the ceramic obtained from the pyrolysis of 2 under argon.

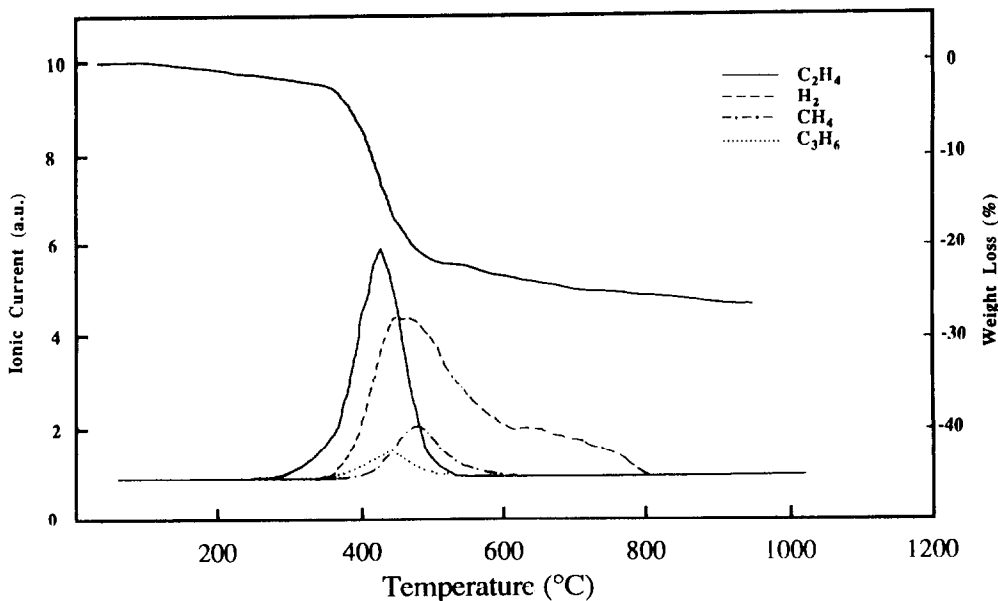


Fig. 2. Pyrolysis of **1** under argon followed by TGA. Analysis of the volatiles by mass spectrometry.

2.2.2.1. Thermal cross-polymerization. $\text{Et}_3\text{Ge}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{GeEt}_3$ (**7**) was chosen as a model for diacetylene polymerization studies. The DSC curve of **7** indicated an exotherm between 190 and 250°C, in the same temperature range as for the poly[(germylene)diacetylene] derivatives. Compound **7** was also heated in a sealed tube under vacuum at 230°C for 120 h. A red-brown liquid soluble in organic solvents, such as Et_2O and CH_2Cl_2 , was obtained. A GPC analysis gave an average molecular weight $\text{MW} = 1180$ and a poly-

dispersity of 1.2. This latter value indicated a linear oligomeric structure. The infrared spectrum of the red-brown liquid showed no absorption band at 2060 cm^{-1} characteristic of the diacetylene unit, and two new bands at 2130 and 1880 cm^{-1} which are attributed to an ene-yne structure [5] and a butatriene unit [6], respectively. The ^{13}C NMR spectrum of the red-brown oil confirmed the presence of both moieties [7].

Polymer **2** showed similar properties. IR spectra of samples heated at room temperature, and at 190, 280,

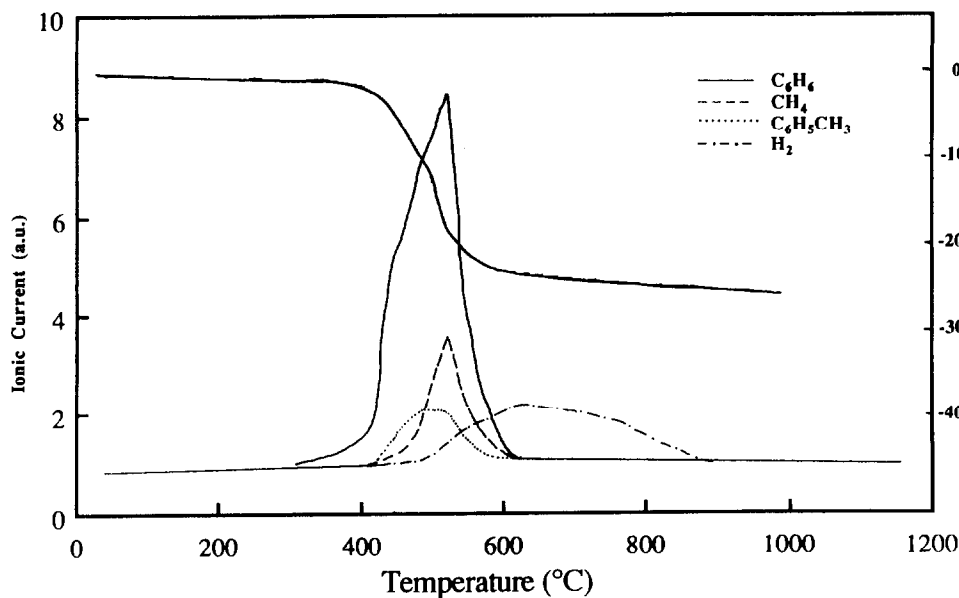


Fig. 3. Pyrolysis of **2** under argon followed by TGA. Analysis of the volatiles by mass spectrometry.

and 400°C (Fig. 5) indicated the progressive disappearance of the diacetylene band at 2070 cm⁻¹ and the appearance of the two bands at 2125 and 1870 cm⁻¹ attributed to the ene-yne and triene units. At 400°C, the ene-yne and triene bands diminished and a new band appeared at 1630 cm⁻¹, corresponding to conjugated carbon double bonds. This last structure is confirmed by solid state ¹³C NMR spectrum which gave a broad signal centred at 130 ppm.

Solid-state polymerization of diacetylene monomers, R-C≡C-C≡C-R, has been studied extensively [8]. The reaction proceeds *via* 1,4-addition of the diacetylene units in the crystal lattice to give ene-yne and triene structures. A similar polymerization process was detected in the case of Et₃Ge-C≡C-C≡C-GeEt₃ (7) and can be extended to the pyrolysis of poly(germylene)diacetylenes. Cross-polymerization occurs through 1,4-addition of the triple bonds, leading to a carbon sp² matrix (with GeR₂ groups isolated in the matrix). These results parallel those obtained in the case of the silicon analogues [2]. Furthermore, the dominant influence of cross-polymerization through the diacetylene units on the ceramic yield is confirmed by the following example. The reduction of the triple bonds of 2 using H₂ with palladium dispersed in carbon led to the saturated polymer [GeMePh(CH₂)_n]. Pyrolysis of the latter at 1100°C gave only 9% of solid residue.

2.2.2.2. Organometallic-inorganic transition. The second step of the pyrolysis occurred in the temperature range 400–600°C with weight loss. It corresponds to the transformation of isolated GeR₂ in a carbon matrix into metallic germanium. The IR spectra of polymer 2 pyrolyzed at 450, 500, and 565°C (Fig. 6) showed that the vibrations arising from GeMe and GePh at 1230 and 1082 cm⁻¹ [9] diminished, and

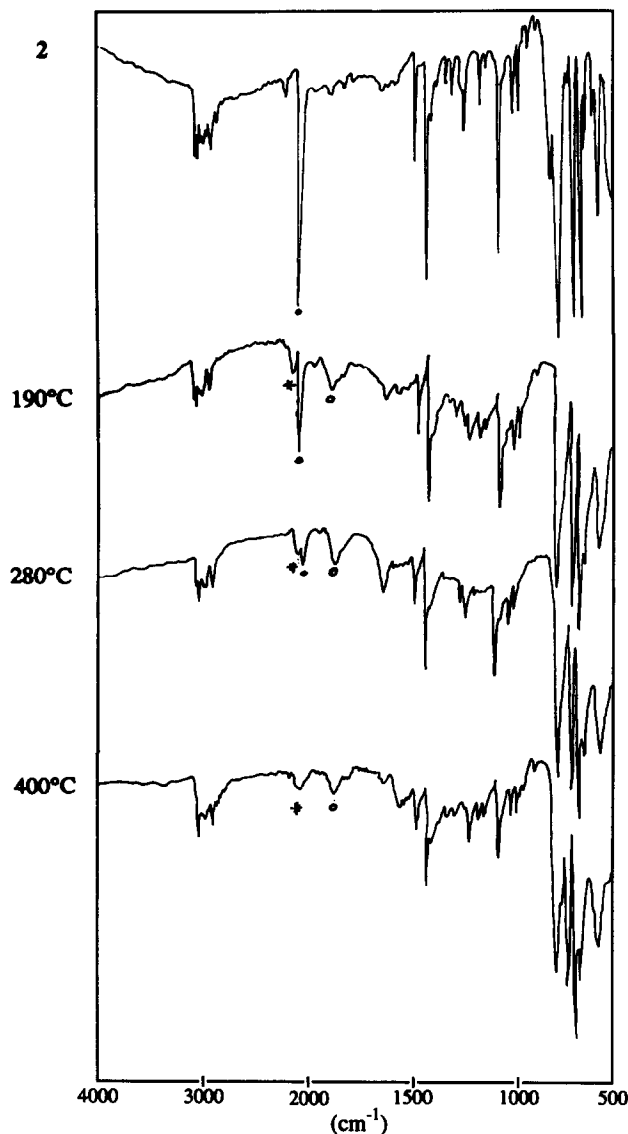


Fig. 5. IR spectra of 2 at room temperature and after heating at 190, 280, and 400°C under argon (●, 2070 cm⁻¹; *, 2125 cm⁻¹; ○, 1870 cm⁻¹).

disappeared above 565°C. The same observation was made for $\nu(\text{Ge}-\text{C})$ at 580 cm⁻¹.

These results are consistent with the evolution of benzene and methane (Fig. 3). Furthermore, a sample of 2 heated at 550°C for 3 h gave a solid ¹³C NMR spectrum with a broad peak at 125 ppm characteristic of sp² carbon atoms. No NMR signal was observed in the Ge-alkyl region. The X-ray powder diffractogram indicated the presence of germanium metal only. The SEM micrograph of 2 heated at 600°C showed that germanium was randomly dispersed in the carbon matrix (Fig. 1). Similar data were obtained for the poly[(diethylgermylene)diacetylene] (1). Pyrolyzed at 350°C, 1 gave an IR spectrum with carbon-hydrogen

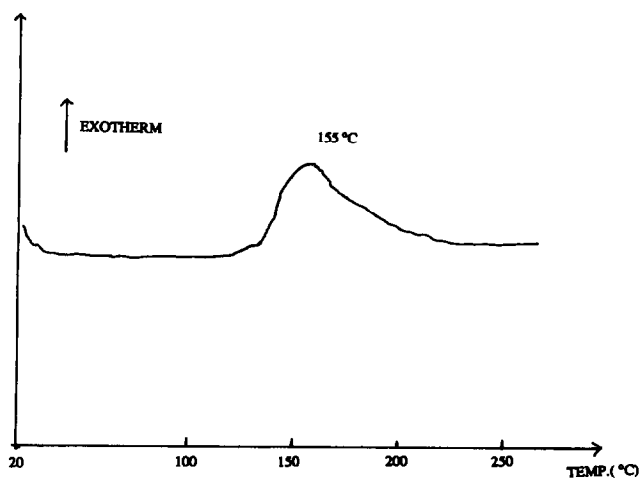


Fig. 4. DSC curve of 2.

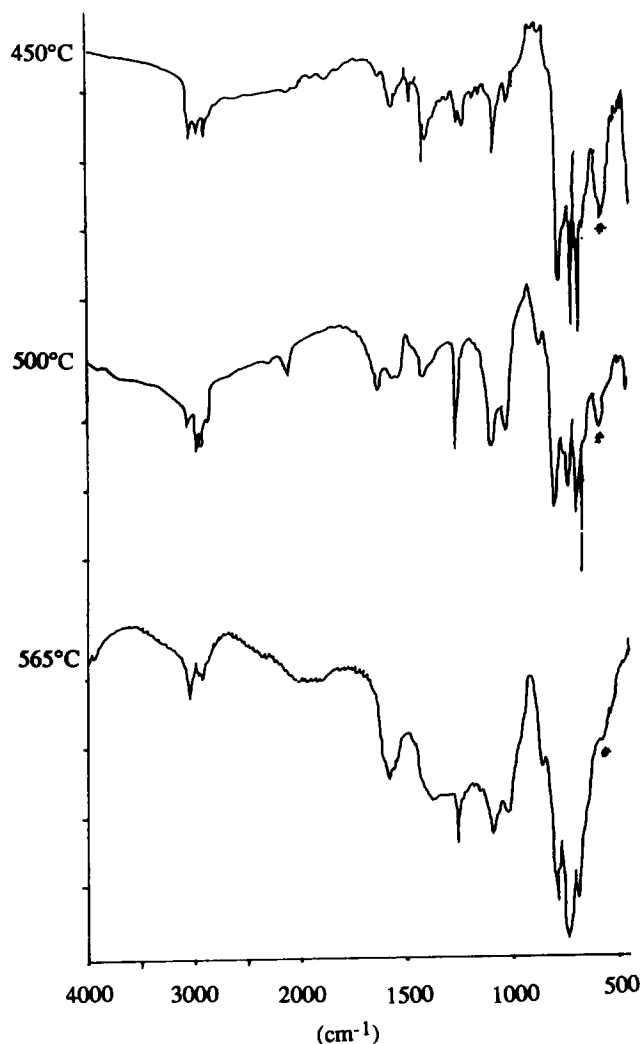


Fig. 6. IR spectra of **2** after heating at 450, 500 and 565°C under argon (*, 580 cm⁻¹).

stretches at 2384 and 2960 cm⁻¹. These absorptions, and $\nu(\text{Ge}-\text{C})$ at 580 cm⁻¹ also disappeared completely after heating at 480°C. This result is consistent with the weight loss detected between 350 and 500°C, corresponding to ethylene evolution.

In summary, germanium-carbon bond cleavage occurred between 350 and 600°C leading to germanium, carbon matrix, and volatiles. The volatiles are mainly ethylene and hydrogen with polymer **1**, and benzene, toluene, methane, and hydrogen in the case of **2**. At 600°C, the X-ray powder analysis indicated only metallic germanium.

2.2.3. Mechanism of the ceramization

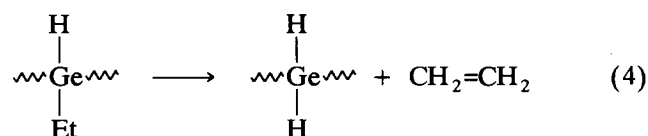
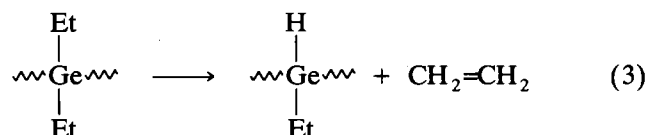
The main results of the mineralization of poly-[(germylene)diacetylenes] **1** and **2** are the following. Weight loss occurred between 350 and 550°C, at lower

temperatures and in a narrower range than in the case of poly[(silylene)diacetylenes] (400–700°C) [2]. The ceramic residues were obtained in good yields (71.5% for **1** and 77% in the case of **2**). As observed for silicon with poly[(silylene)diacetylenes], no germanium was lost during the pyrolysis. The amount of carbon in the ceramic residues depends on the substituents at germanium: Ge, 4.5C with **1**, Ge, 7.2C with **2**. The main difference is the formation of germanium metal in the carbon matrix above 500°C instead of the carbide in the case of the silicon polymers.

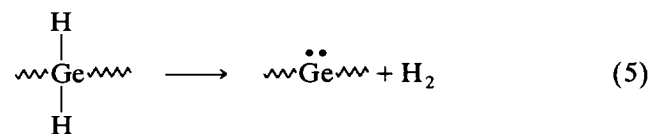
2.2.3.1. Mineralization of $[-\text{GeEt}_2-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-]_n-$

The pyrolysis of tetraethylgermanium has been studied [3,10] and the mechanism proposed is a homolytic scission of a Ge-Et bond followed by the decomposition of the ethyl radical into ethylene and a hydrogen radical, which led to H₂.

During the ceramization of **1**, we observed elimination of C₂H₄ starting at 300°C, and followed by hydrogen evolution above 350°C (Fig. 2). These observations are consistent with a cleavage of the Ge-Et bond involving a β -elimination mechanism and leading to an ethyl hydridogermanium moiety (eqn. (3)) and thence to a dihydrogermanium moiety in a second step (eqn. (4)).



The next step is the formation of a germylene species (eqn. (5)) and it can be related to the important evolution of H₂ which takes place up to 550–600°C. Germylenes can react by insertion into the Ge-H bonds leading to Ge-Ge units. Indeed, such a route is followed in the pyrolysis of poly(silethylene) [11]. Thus, germylene formation and subsequent insertion reactions would progressively lead to a polygermane backbone (eqn. (6)). Reaction of two germylenes giving polygermanes is a second possible process.



tal analysis gave less than 0.1% of carbon in the residue. Complete elimination of carbon as HCN [2,13,14] was explained by reactions in the carbon matrix of the radicals formed by the decomposition of ammonia at temperatures above 750°C.

We studied the reaction of ammonia and poly[(germylene)diacetylenes] in order to prepare germanium nitride, which is known to be stable only up to 760°C under an ammonia atmosphere [15,16]. The germanium polymers were pyrolysed under ammonia at a heating rate of 10°C min⁻¹ up to 750°C, and then held there for 3 h. In the case of poly[(methylphenylgermylene)diacetylene] (**2**), the ceramic yield was 71%. Elemental analysis (N, 7.8; C, 30.97; Ge, 50.4; O, 10.8%) corresponds to GeN_{1.3}C_{3.6}O_{0.9}. The contamination of the ceramic residue with oxygen is certainly due to the high affinity of the product for oxygen and moisture of the NH₃ stream and also to the small volume of the sample submitted to pyrolysis compared to the volume of the furnace [17]. Nevertheless, the amount of germanium found in the final residue (50.4%) was close to the expected value (54%), were no germanium lost during the pyrolysis. Carbon involved in the cross-polymerization of the triple bonds, four atoms per Ge, was recovered nearly quantitatively at the end of the experiment.

The X-ray diffractogram of the grey solid (Fig. 7) showed crystalline Ge₃N₄ and germanium. The presence of free germanium may be due to the partial thermal decomposition of Ge₃N₄ as was observed previously [16] (eqn. (12)).

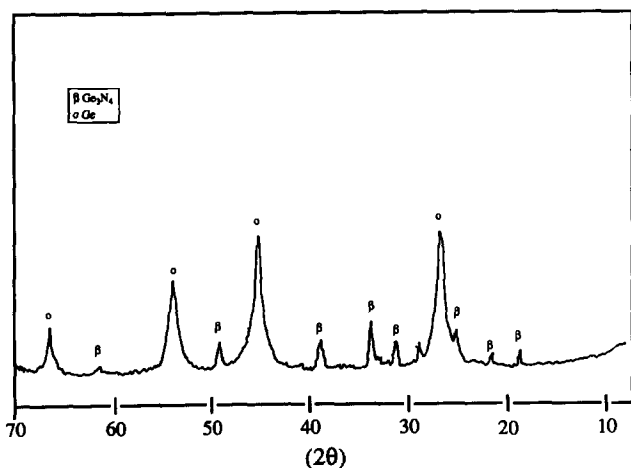
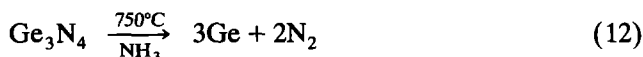


Fig. 7. X-Ray diffractogram of the ceramic obtained from the pyrolysis of **2** under NH₃.

The pyrolysis of **2** under ammonia was also followed by TGA and DTA. The DTA curve showed an exotherm at 160°C corresponding to a reticulation process as observed in the reaction under argon. The TGA curve gave a weight loss of 29% between 400 and 600°C, below the decomposition temperature of ammonia (750°C). In order to gain more information on the incorporation of nitrogen into the matrix, **2** was heated under ammonia to 420°C for 2 h. Elemental analysis of the residue (N, 6.05; C, 43.9; Ge, 45.6; O, 6.63%) indicated a product stoichiometry GeN_{0.7}C_{5.9}O_{0.6}. The IR spectrum of the sample showed a large absorption band at 766 cm⁻¹ corresponding to ν(Ge-N) [16]. This result is consistent with the formation of germanium-nitrogen bonds.

The pyrolysis of polymer **4** under ammonia confirms the results obtained with **2**. A weight loss of 46% was observed between 350 and 600°C. The residue has the same stoichiometry as the residue obtained from polymer **2**. This confirms the cleavage of all the substituents from the germanium and nitrogen incorporation. The mechanism of the reaction must involve a nucleophilic displacement of the methyl and phenyl substituents at germanium by ammonia (eqn. (13)).



In conclusion, the pyrolysis of poly[(germylene)diacetylenes] gave high yields of ceramic residues (66–82%). The efficient reticulation through the triple bonds at low temperature (150–250°C) avoids depolymerization side-reactions and affords a carbon matrix with disubstituted germanium groups. At the end of the pyrolysis, all the germanium was recovered as crystalline clusters, together with a large amount of free carbon (40–61%).

As observed in the case of the silicon analogues, the reticulation process proceeds *via* formation of ene-yne and triene units which evolved further on heating to give a highly conjugated carbon system. The mineralization step can be explained by a radical mechanism leading to organic volatiles and metallic germanium included in a free carbon network after successive radical and germylene formation and recombination.

The pyrolysis under an atmosphere of ammonia afforded germanium nitride. The cross-linking was followed by nitridation and ceramization of the precursor between 400 and 600°C with elimination of the substituents bonded to germanium.

3. Experimental section

All reactions were carried out under argon or dinitrogen using a vacuum line and Schlenk tubes. Solvents were dried and distilled before use. Tetrahydrofuran

(THF) was distilled over calcium hydride and then over sodium benzophenone.

Trimethylchlorosilane, dimethyldichlorosilane, and methylphenyldichlorosilane were purchased from Janssen, Aldrich, or Lancaster, and distilled over magnesium before use. 1,4-Dilithio-1,3-butadiyne and 1,4-bis(triethylgermyl)-1,3-butadiyne were prepared according to published methods [1,18]. Methylphenyldibromogermane was prepared from germanium tetrachloride using the general procedure of Brook and Peddle [19]. The synthesis of the poly[(germylene)diacetylenes] was described previously [1].

Gel permeation chromatography (GPC) was performed using a Waters 410 instrument with UV and refractive index detection. The solvent was THF and the porosities of the columns used were 100, 500, 10^3 and 10^4 Å. The elution rate was 0.9 ml min^{-1} . Argon ($\text{O}_2 < 5 \text{ ppm}$; $\text{H}_2\text{O} < 5 \text{ ppm}$) 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 K α radiation with a Philips diffractometer, modified by Professor R. Fourcade (Université Montpellier II).

Simultaneous TGA/DTA analyses were performed under flowing argon (50 ml min^{-1}) 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 $10^\circ\text{C min}^{-1}$.

DSC experiments were performed on a Mettler 30 instrument under argon at a heating rate of $10^\circ\text{C min}^{-1}$.

All NMR spectra were obtained at ambient temperature. ^1H spectra were acquired by using a Bruker AW 80 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.

Scanning electron microscopy (SEM) was performed on a Jeol T 300 instrument, operating at 20 kV.

The pyrolysis experiments were performed by pouring weighed portions (0.1–1 g) of the polymer into an

aluminium oxide boat ($80 \times 10 \times 10 \text{ mm}^3$) which was placed into a gas-tight aluminium 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 at *ca.* 50 ml min^{-1} . Pyrolyses were performed with a Eurotherm or Carbolite furnace, using a temperature programme of 10 K min^{-1} up to 1673 K with a 3 h hold at that temperature. In the case of ammonia (50 ml min^{-1}), a hold of 3 h at 1023 K was used. Ammonia was dried over KOH (60 cm column) and a 50:50 mixture of 3 Å molecular sieves and silica gel (30 cm column).

3.1. Poly{[(methylphenylgermylene)diacetylene] [(dimethylsilylene)diacetylene]} (5)

A solution of methylphenyldibromogermane (0.0125 mol) in THF was added dropwise to a slurry of 1,4-dilithio-1,3-butadiyne (0.025 mol) in the same solvent. The reaction mixture was stirred for 3 h at room temperature and dimethyldichlorosilane (0.015 mol) was added dropwise. After 3 h stirring, the polymer was stopped using MeMgBr (0.005 mol). After hydrolysis ($\text{H}_2\text{O-NH}_4\text{Cl}$) and extraction with pentane, the solution was dried over MgSO_4 and concentrated under vacuum. The oil was washed several times with pentane giving 3.6 g, 92% yield, of the title compound. IR (CCl_4): $\nu(\text{C}\equiv\text{C})$ 2072 cm^{-1} . ^1H NMR (CCl_4): δ 0.17 (s, SiMe $_3$); 0.41 (s, SiMe); 0.63 (s, GeMe) ppm [20*], 7.0–7.6 (m, Ph) ppm. ^{13}C NMR (CDCl_3): δ -0.1, 0.1 (CH $_3$); 80.5, 82.0 (Si-C \equiv C-, Ge-C \equiv C-), 89.3 (Ge-C \equiv C-, Si-C \equiv C-); 133.5, 130.7, 129.1 (Ph) ppm. ^{29}Si (CDCl_3): δ -37.0 (SiMe $_2$); -17.7 (SiMe $_3$) ppm. Anal. Found: C, 60.05; H, 5.26; Si 10.10; Ge 21.30; O, 3.30%. ($\text{C}_{17}\text{H}_{14}\text{GeSi}$) $_n$ calc.: C, 64.00; H, 4.39; Si 8.78; Ge, 22.78%.

3.2. Poly{[(methylphenylgermylene)diacetylene] [(methylphenylsilylene)diacetylene]} (6)

The same procedure as for 5 was used. The title compound was obtained as a brown powder with 88% yield. IR (CCl_4): 2072 cm^{-1} . ^1H NMR (CCl_4): δ 0.3 (s, SiMe $_2$); 0.5 (s, SiMe); 0.8 (s, GeMe) [20*] 7.0–7.8 (m, Ph) ppm. ^{13}C NMR (CDCl_3): -0.6, 0.1, 1.4 (Me); 82.2, 81.6, 80.5 and 79.9 (Si-C \equiv C and Ge-C \equiv C); 89.4 and 90.6 (Si-C \equiv C- and Ge-C \equiv C); 128.2 (br); 128.7, 129.1, 130.8, 131.2, 133.5, 133.8 (br), 134.5 (Ph) ppm. ^{29}Si NMR (CDCl_3): δ -42.2. Anal. Found: C, 67.93; H, 4.21; Si, 8.8; Ge 13.9; O, 3.4. ($\text{C}_{22}\text{H}_{15}\text{GeSi}$) $_n$ calcd.: C, 69.3; H, 4.20; Si, 7.35; Ge, 19.07%.

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

3.3. Bis(1-trimethylsilyl-1,3-butadiynyl)methylphenylgermane

A solution of methylphenyldibromogermane (3 g, 0.013 mol) in diethylether was added to a solution of 1-lithio-4-trimethylsilyl-1,3-butadiyne, prepared according to the Zweifel procedure in the same solvent. The mixture was stirred for 2 h at room temperature, hydrolyzed and extracted with pentane. The pentane solution was dried over MgSO_4 , concentrated under vacuum and chromatographed over a short column of silica gel. The title compounds (3 g) was obtained with 63% yield. IR (CCl_4): $\nu(\text{C}\equiv\text{C})$ 2069 cm^{-1} . ^1H NMR (CCl_4): δ 0.05 (s, 18H, SiCH_3); 0.0 (s, 3H, GeCH_3); 7.0–7.8 (m, 5H, GePh) ppm. ^{13}C NMR (CDCl_3): δ -0.17 (GeCH_3 , SiCH_3); 128.7, 129.0, 129.6, 130.6, 133.5 (GePh); 79.8, 86.9 ($\text{Ge}-\text{C}\equiv\text{C}$, $\text{Si}-\text{C}\equiv\text{C}$); 88.07, 89.6 ($\text{Ge}-\text{C}\equiv\text{C}$, $\text{Si}-\text{C}\equiv\text{C}$) ppm. ^{29}Si NMR (CDCl_3): δ -15.6 ppm. Anal. Found: C, 62.15; H, 6.13; Ge, 17.52; Si, 13.68. $\text{C}_{21}\text{H}_{26}\text{GeSi}_2$ calcd.: C, 61.97; H, 6.39; Ge, 17.85; Si, 13.77%.

3.4. Hydrogenation of 2 on Pd/C

Pd/C (0.010 g) was added to a solution of 0.68 g (0.0032 mol) of 2 in a mixture of THF (20 ml) and pentane (30 ml). The medium was evacuated and put under hydrogen. The reaction was followed by IR spectroscopy. After 10 days, the mixture was filtered and the solvents were removed under vacuum to leave a red-brown oil in quantitative yield. GPC: MW = 1092, $I = 1.70$. IR (CCl_4): no $\text{C}\equiv\text{C}$ vibration. ^1H NMR (CCl_4): δ 7.2 (5H, Ph); 0.8–2.6 (11 H, broad multiplet, CH_2 and CH_3) ppm.

Acknowledgements

The authors thank Dr Seigneurin (Rhône-Poulenc, Salindres, France) for SEM measurements and Pr Fourcade (Université Montpellier II) for X-ray facilities and fruitful discussions.

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