Mechanism of Pyrolysis of Polycarbosilanes: Poly(silylethylene) and Poly(dimethylsilylethylene)

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The thermal degradation of linear polycarbosilanes, poly(silylethylene), $(Si(H_2)C_2H_4)_n$, and poly(dimethylsilylethylene), $(Si(Me_2)C_2H_4)_n$, having the same backbone an differing by the nature of the substituents of the silicon atoms, was investigated by means of thermogravimetric analysis coupled to mass spectrometry and solid-state NMR spectroscopy. Both fragmentation and cross-linking mechanisms appear strongly dependent on the substituents on the silicon atoms, as shown by the nature of the gases and volatile organosilicon compounds evolved and the pyrolysis yields. In the case of poly(dimethylsilylethylene), random chain scission via a simple free-radical mechanism explains the formation of the volatile products detected during the degradation. On the other hand, in the case of poly(silylethylene), the fast elimination of hydrogen at temperatures as low as 380 °C and the formation of SiH_2Et chain ends cannot be accounted for by a free-radical mechanism and suggests the formation of silylene species. Thus, the formation of silylenes by 1,1-elimination of H_2, followed by insertion and rearrangement reactions, would provide an efficient way of cross-linking, whereas the formation of silylenes by 1,1-cleavage of Si–C and Si–H bonds would account for the formation of SiH_2Et chain ends and the fragmentation of the polymer.

Introduction

Since the work of Yajima et al. led to the commercialization of SiC fibers obtained by pyrolysis of a polymeric precursor,[1] there have been many efforts aimed at the design of new silicon carbide precursors.[2] The conception of a good precursor is not an easy task, and one of the main obstacles is the requirement of high ceramic yields. Actually, in the pyrolysis of linear ceramic precursors, negligible ceramic yields are the rule,[3] due to the fragmentation of the polymer chains which leads to the loss of volatile organometallic species. Although the mechanisms of degradation of organosilicon polymers (except polysiloxanes) are not well-known, it was shown that a high cross-linking degree of the precursor hinders the splitting of volatile organosilicon compounds (which requires more bond ruptures) and markedly slows down the kinetics of fragmentation reactions,[3] thus leading to higher ceramic yields. However, the increase in the cross-linking degree of a polymer leads rapidly to an intractable, infusible and insoluble network. It is thus necessary to synthesize functional polymers, that may be cross-linked after the processing step.

For this purpose, a highly functional linear polycarbosilane, with two SiH functions per unit, was prepared in our laboratory: poly(silylethylene),[4] $(Si(H_2)C_2H_4)_n$, (also called poly(vinylsilane)). This precursor leads to exceptionally high ceramic yields for a linear polymer (around 30%). Recently, still higher ceramic yields (87%) were reported for poly(silylmethylene), $(Si(H_2)CH_2)_n$,[5] another linear polycarbosilane containing SiH_2 groups. As a comparison, linear poly(methylsilylmethylene), $(Si(MeH)CH_2)_n$,[6] or poly(dimethylsilylmethylene), $(Si(Me_2)CH_2)_n$,[7] give much lower ceramic yields, around 5%. This indicates that the presence of SiH_2 groups allows the occurrence of thermal cross-linking reactions, either simultaneously or at a lower temperature than the fragmentation reactions. It was suggested that this behavior might arise from the possibility of cross-linking reactions involving silylene intermediates.[4c,5]

In the present work, we compare the thermal degradation of two polycarbosilanes, possessing the same backbone and differing by the substituents on the silicon atoms, poly(dimethylsilylethylene), $(Si(Me_2)C_2H_4)_n$, and poly(silylethylene), $(Si(H_2)C_2H_4)_n$, (Scheme I) in order to evidence the influence of SiH_2 groups on the mechanisms of degradation.

Experimental Section

General Comments. All manipulations were carried out under argon, in oven-dried glassware; solvents were distilled from appropriate drying agents prior to use. Et_2SiH_2 and Me_2SiVi_2 (Vi = vinyl) were used as received from Petrarch. $Me_2SiViCl$ and $H_2PtCl_6{\cdot}6H_2O$ were kindly provided by Rhône-

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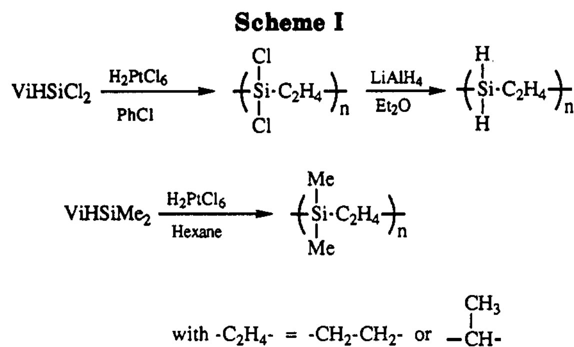

Table I. ^{29}Si Chemical Shifts in PSE and PDMSE (ppm from TMS)

sample	chemical shift	attribution
PSE	-21.9	$-CH_2CH_2-Si(H_2)-CH_2CH_2-$
	-19.8	$-CH_2CH_2-Si(H_2)-CH(CH_3)-$
	-19.7	$-CH(CH_3)-Si(H_2)-CH(CH_3)-$
	-55.0, -52.8	$-SiH_3$
	-31.8, -28.9	$-SiH_2Vi$
PDMSE	+6.0	$-CH_2CH_2-Si(Me_2)-CH_2CH_2-$
	+6.6	$-CH_2CH_2-Si(Me_2)-CH(CH_3)-$

Table II. ^{13}C Chemical Shifts in PSE and PDMSE (ppm from TMS)

sample	chemical shift	attribution
PSE	+3.5	$Si-CH_2CH_2-Si$
	-4.5	$Si-CH(CH_3)-Si$
	+12.6	$Si-CH(CH_3)-Si$
PDMSE	+7.0, +7.1	$Si-CH_2CH_2-Si-CH_2CH_2-Si$
	+6.6	$Si-CH_2CH_2-Si-CH(CH_3)-Si$
	+3.7	$CH_2CH_2-Si-CH(CH_3)-Si-CH_2CH_2$
	+10.1	$CH_2CH_2-Si-CH(CH_3)-Si-CH_2CH_2$
	-4.0	$CH_2CH_2-Si(CH_3)_2-CH_2CH_2$
	-3.0, -2.5	$CH_2CH_2-Si(CH_3)_2-CH(CH_3)$

Poulenc. Me_2SiViH was prepared according to ref 8. Elemental analyses were performed by the "Service Central d'Analyses" of CNRS (France).

Preparation of Poly(silylethylene). Poly(silylethylene) (PSE) was prepared according to a previously described procedure[4b] using chlorobenzene as a solvent (50% v/v) and 2.5 × 10^{-4} M H_2PtCl_6. M_n = 2600, M_w = 3960.

^{29}Si and ^{13}C NMR (Tables I and II) showed the presence of $Si(H_2)CH_2CH_2$ units (β units) and $Si(H_2)CH(CH_3)$ units (α units), arising from β- and α-hydrosilation modes, respectively. ^{1}H NMR integration indicated that 68% of β units and 32% of α units are formed.

Preparation of Poly(dimethylsilylethylene). In a three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel, 6.38 g (0.074 mol) of vinyldimethylsilane and 4.6 mL of hexane were mixed. H_2PtCl_6 (1.75 × 10^{-6} mol) diluted in 2.3 mL of hexane was introduced dropwise at room temperature by means of a syringe pump. The mixture was stirred 3 h at room temperature. Then the catalyst was removed by filtration over diatomaceous silica and the solvent is evaporated in vacuo, leading to 4.45 g of a viscous oil. Yield: 70%; M_n = 2740, M_w = 3710.

IR spectroscopy (neat): cm^{-1} (assignment) 2951 (CH_3), 1406, 1133, 1058 (CH_2CH_2), 1465, 1105, 992 ($CH-CH_3$).

^{29}Si and ^{13}C NMR: see Tables I and II. As in the case of poly(silylethylene), two kinds of units are present: $Si(Me_2)CH_2CH_2$ and $Si(Me_2)CH(CH_3)$ units, arising from β- and α-hydrosilation modes, respectively. NMR integration indicated that 70% of β units and 30% of α units are formed.

Nuclear Magnetic Resonance Spectroscopy. NMR spectra were recorded using Bruker AC200, AC250, and AM300 spectrometers with $CDCl_3$ as a solvent and internal standard. Chemical shifts are given relative to TMS. Inverse-gated decoupling, power-gated decoupling and proton-coupled or -decoupled sequences were used.

Solid-state NMR experiments were carried out on a Bruker FT-AM300 spectrometer, applying proton decoupling and magic angle spinning (MAS). Cross-polarization (CP) from ^{1}H to ^{29}Si or ^{13}C was used with contact times of 2 and 5 ms, respectively, and with repetition times of 10 and 5 s, respectively.

Thermogravimetric Analysis Coupled with Mass Spectroscopy (TG/MS). Thermogravimetric analysis (TGA) was carried out by means of a Netzsch STA409 thermobalance. Typically, about 20 mg of sample was heated in an alumina crucible from room temperature to 1200 °C at 10 K min^{-1} in a stream of argon.

The thermogravimetric analyzer was coupled to an Anagaz 200 Delsi Nermag quadrupole mass spectrometer (ionization energy 75 eV). The volatile products evolved during pyrolysis were sampled above the crucible by a stainless steel capillary (internal diameter 0.25 mm) heated at 150 °C. The capillary is connected to the mass spectrometer through a 32-μm molecular leak. A scan from 2 to 150 amu was collected and stored every 30 s throughout the pyrolysis process. This apparatus permits the identification of the different gases evolved during pyrolysis; it is possible either to plot mass spectra obtained at selected temperatures or to plot the evolution of the signal of characteristic ions as a function of temperature. In the absence of standardization only qualitative information may be drawn from these curves. It should be noted that, due to the limited range of the mass spectrometer and to condensation in the cold parts of the apparatus, only low molecular weight compounds such as gases or volatile liquids are detected by TG/MS. Thus, a release of condensable compounds, such as oligomers, may not be detected by MS despite a noticeable weight loss in the TGA curve.

Thermal Treatments. Thermal treatments of PSE samples have been done under argon, either in the TGA apparatus ($T \leq$ 310 °C) or in a tube furnace equipped with a temperature controller ($T \geq$ 380 °C). The samples were heated at 10 K min^{-1} from 25 °C to the specified temperature with a 15-h hold at this temperature.

Gel Permeation Chromatography. Polymer molecular weights were determined by gel permeation chromatography (GPC) in tetrahydrofuran (flow rate 1 mL/min) using a Waters apparatus (Ultrastyragel columns, 100, 500, 1000, and 10 000 Å, pump EF410, refractive index detector) calibrated with polystyrene standards.

Results and Discussion

1. TG/MS Analysis of Poly(dimethylsilylethylene). The pyrolysis behavior of poly(dimethylsilylethylene), $(Si(Me)_2C_2H_4)_n$ (PDMSE), was investigated by TG/MS analysis (Figure 1). Two steps may be distinguished: (1) From 100 to ca. 400 °C, a continuous weight loss (10.6%) is observed, likely corresponding to the distillation of the lowest oligomers (not detected by MS). (2) Above 400 °C, a fast weight loss takes place, so that the percent residue is negligible at 520 °C. At the same time, a large escape of organosilicon compounds is detected, together with ethylene (*m/z* 26–28) and small amounts of hydrogen (*m/z* 2). A small escape of methane (*m/z* 14–16) is observed above 450 °C. The mass spectrum of the gases evolved around 480 °C is reported in Figure 2. From the mass spectra reported in Table III, the peaks observed may be attributed to the following organosilicon ions: *m/z* 58, Me_2Si^+; *m/z* 59, Me_2HSi^+; m/z 43, $MeSi^+$; *m/z* 45, MeH_2-

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Table III. Mass Spectral Data[a] for Some Organosilicon Compounds

compd	m/z (abundance, relative)	ref
SiH_4[b]	30 (100), 31 (78.2), 29 (23.4), 28 (23.0), 32 (0.3)	9a
$MeSiH_3$[b]	44 (100), 45 (66.8), 43 (43.4), 28 (24.9), 30 (21.5), 42 (17.6), 41 (11.9), 31 (11.3), 40 (2.1), 46 (0.6)	9a
Me_2SiH_2[b]	59 (100), 58 (75.0), 45 (70.2), 44 (57.6), 43 (54.9), 31 (24.5), 28 (24.3), 42 (19.3), 29 (15.5), 57 (10.9)	9a
Me_3SiH[b]	59 (100), 73 (54.6), 43 (23.8), 58 (21.6), 31 (14.1), 45 (13.5), 29 (8.4), 42 (6.5), 57 (5.2), 28 (5.0)	9a
Me_4Si[b]	73 (100), 45 (16.0), 43 (10.7), 44 (7.0), 29 (5.2), 31 (3.0), 59 (2.8), 42 (2.4), 53 (1.7), 28 (1.7)	9a
$EtSiH_3$	58 (100), 59 (55.2), 43 (42.0), 31 (34.4), 28 (22.4), 29 (17.6), 60 (19.2), 30 (13.6), 56 (8.0), 57 (8.0), 53 (7.2), 27 (6.8)	9b
Et_2SiH_2	59 (100), 58 (91.8), 43 (28.7), 87 (19.4), 86 (15.3), 57 (13.3), 60 (11.5), 88 (10.0), 55 (8.3)	9c
Et_2SiMe_2[c]	59 (100), 101 (52.3), 87 (45.1), 73 (40), 45 (12.3), 43 (10.7), 115 (7.0), 58 (5.6), 31 (4.5), 130 (3.2)	9d
Me_2SiViH	58 (100), 71 (52.5), 45 (50.2), 43 (45.1), 59 (45.0), 86 (14.1), 85 (12.1), 55 (13.9), 53 (11.1)	9c
Me_2SiVi_2	97 (100), 71 (45.2), 59 (34.3), 85 (26.8), 43 (18.9), 98 (13.1), 45 (10.9), 55 (9.4), 58 (8.1), 95 (7.0), 53 (6.2), 69 (6.1), 73 (5.4)	9c
$Me_3Si(CH_2)_2SiMe_3$[c]	73 (100), 86 (25.4), 85 (17.2), 159 (15.8), 174 (10.1), 131 (10.0), 45 (9.3), 58 (7.7), 59 (6.0), 43 (4.3)	9e

[a] All spectra recorded at 70 eV unless specified. [b] Monoisotopic mass spectrum. [c] Spectrum recorded at 50 eV.

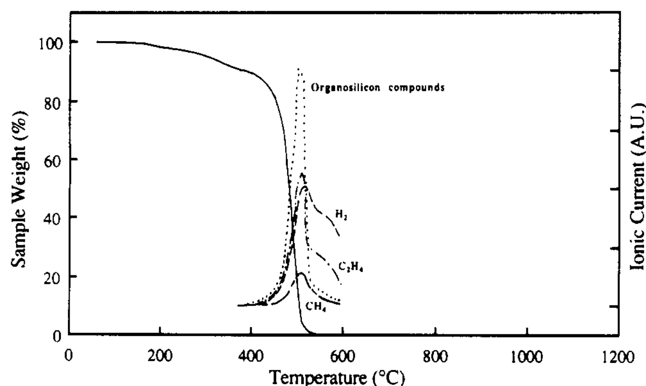


Figure 1. TG/MS analysis under argon of PDMSE: (—) TGA curve; ion signal at m/z 2 (- - -) arising from hydrogen; m/z 16 (– – –) arising from methane; m/z 28 (– · –) arising from ethylene; m/z 71 (···) corresponding to $MeSiHVi^+$, arising from Me_2SiViH and Me_2SiVi_2.

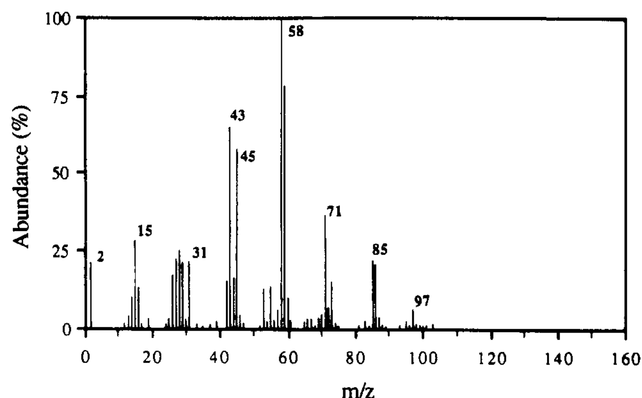


Figure 2. Mass spectrum of the gases evolved at 480 °C during the pyrolysis of PDMSE under argon. Attribution of the most significant peaks (see text): m/z 2, H_2^+; m/z 15, CH_3^+; m/z 28, $C_2H_4^+$ and Si^+; m/z 45, MeH_2Si^+; m/z 58, Me_2Si^+; m/z 59, Me_2HSi^+; m/z 71, $MeViHSi^+$; m/z 85, Me_2ViSi^+; m/z 97, $MeVi_2Si^+$.

Si^+; m/z 71, $MeViHSi^+$, m/z 85, Me_2ViSi^+; m/z 86, Me_2ViHSi^+; m/z 31, H_3Si^+; m/z 97, $MeVi_2Si^+$. These fragments are consistent with an escape of a mixture of dimethylsilane (Me_2SiH_2), vinyldimethylsilane ($ViMe_2SiH$), and divinyldimethylsilane (Vi_2Me_2Si). Higher molecular weight compounds are also evolved, as shown by the small peaks detected above m/z 100, and the ion at m/z 86, which is typical of compounds $R^1Me_2SiCH_2CH_2SiMe_2R^2$ (R = H, Me,...) (see Table III). The peak at m/z 73, corresponding to Me_3Si^+, shows that small amounts of silanes such as Me_3SiH, Me_4Si, or Me_3SiVi are probably formed. Organosilicon compounds, as well as ethylene, hydrogen, or

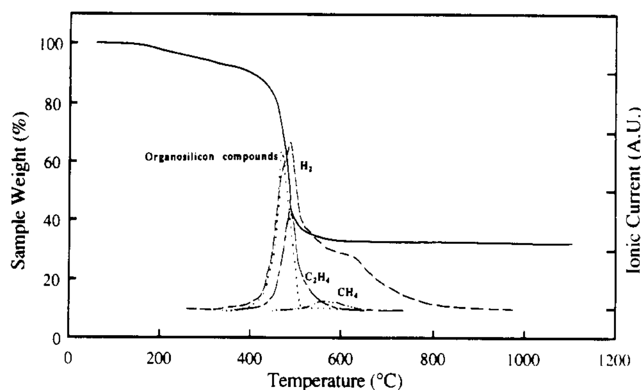


Figure 3. TG/MS analysis under argon of PSE: (—) TGA curve; ion signal at m/z 2 (- - -) arising from hydrogen; m/z 16 (– ·· –) arising from methane; m/z 28 (– – –) arising from ethylene; m/z 58 (···) corresponding to $SiEt_2^+$, arising from $EtSiH_3$ and Et_2SiH_2.

methane, are still detected above 525 °C, whereas the thermal degradation of the polymer is finished, as indicated by the TGA curve. This escape could be related to secondary decomposition of condensable primary degradation products, deposited in the cold parts of the oven.

From the nature of the organosilanes detected it may be concluded that the degradation of the polycarbosilane skeleton involves mainly the cleavage of Si–C bonds. The cleavage of C–C bonds also occurs, but to a lesser extent, as shown by the low intensity of the fragment at m/z 73 (Me_3Si^+). In addition, the cleavage of lateral $Si–CH_3$ bonds does not occur during the first steps of the polymer degradation, as shown by the fact that the escape of methane starts about 40 °C higher than the escape of organosilanes.

2. TG/MS Analysis of Poly(silylethylene). The TG/MS analysis under argon of poly(silylethylene), $(Si(H_2)C_2H_4)_n$, (PSE), is reported in Figure 3. Three steps may be distinguished in the pyrolysis process: (1) From 100 to 380 °C, a continuous weight loss (10%) is observed, which corresponds to the distillation of the lowest oligomers (not detected by MS). (2) From 380 to 500 °C, a large, fast weight loss (52%) is observed, together with a violent escape of hydrogen (m/z 2), ethylene (above 425 °C), and organosilicon fragments (the nature of which will be discussed below). This step clearly corresponds to the fragmentation of the polymer chains. No methane is evolved during this step; the main hydrocarbon detected is ethylene (m/z 26–28), from 425 to 590 °C. (3) Above 500 °C, a 6% weight loss is observed, which corresponds to the mineralization step, with a small loss of methane

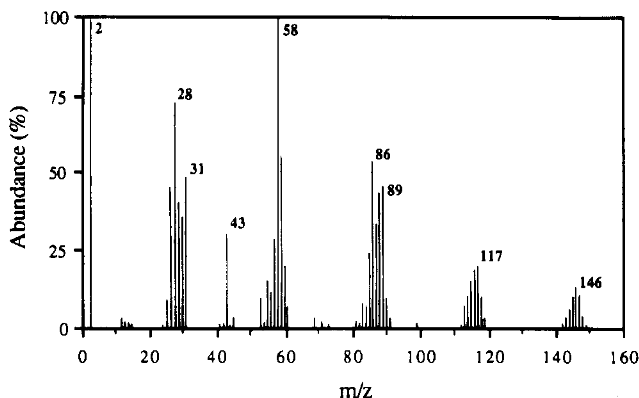


Figure 4. mass spectrum of the gases evolved at 470 °C during the pyrolysis of PSE under argon. Attribution of the most significant peaks (see text): m/z 2, H_2^+; m/z 28, $C_2H_4^+$ and Si^+; m/z 31, SiH_3^+; m/z 58, $EtHSi^+$; m/z 59, EtH_2Si^+; m/z 86, $(Et)_2Si^+$; m/z 89, $H_3Si–C_2H_4–SiH_2^+$; m/z 117, $EtH_2Si–C_2H_4–SiH_2^+$; m/z 146, $H_3Si–C_2H_4–Si(H_2)–C_2H_4–SiH^+$ and $EtH_2Si–C_2H_4–SiEtH_2^+$.

(m/z 14–16) (up to 680 °C), ethylene (up to 590 °C), and hydrogen (up to 1000 °C).

The spectrum of the gases evolved at 470 °C is displayed in Figure 4. As in the previous case, intense peaks at m/z 58 and 59 are observed, which could correspond either to $SiMe_2^+$ and $SiMe_2H^+$, respectively, or $EtHSi^+$ and EtH_2Si^+. Starting from the structure of PSE, $SiMe_2^+$ and $SiMe_2H^+$ could only arise from Me_2SiH_2, which would be formed by the cleavage of C–C bonds. However, the absence of a significant peak at m/z 45 ($SiMeH_2^+$) shows that Me_2SiH_2 is not formed. Thus, according to this reasoning, the main peaks observed may be ascribed to the following organosilicon ions: m/z 30, SiH_2^+; m/z 31, SiH_3^+; m/z 43, $MeSi^+$; m/z 58, $EtHSi^+$; m/z 59, EtH_2Si^+; m/z 86, $(Et)_2Si^+$. From the mass spectral data reported in Table III, it may be concluded that these ions arise from a mixture of diethylsilane (Et_2SiH_2), ethylsilane ($EtSiH_3$), and possibly silane (SiH_4). Oligomers with two or three silicon atoms are also present, as shown by the peaks at higher m/z values, such as m/z 89 ($H_3Si–C_2H_4–SiH_2^+$), m/z 117 ($EtH_2Si–C_2H_4–SiH_2^+$), m/z 146 ($H_3Si–C_2H_4–Si(H_2)–C_2H_4–SiH^+$ and $EtH_2Si–C_2H_4–SiEtH_2^+$) for instance. These fragments are consistent with an escape of linear oligomers, SiH_3 and/or SiH_2Et terminated, $R^1H_2SiC_2H_4(Si(H_2)C_2H_4)_nSiH_2R^2$ (R = Et or H).

Contrary to the previous case, the escape of vinyl compounds, such as $ViSiH_3$ and Vi_2SiH_2, which would give intense peaks at m/z 56 ($ViSiH^+$), m/z 82 (Vi_2Si^+), and m/z 83 (Vi_2SiH^+), is negliglible. The organosilanes detected also show that the degradation of the backbone of PSE involves only the cleavage of Si–C bonds. The cleavage of C–C bonds would lead to the formation of methylsilanes, such as $MeSiH_3$, Me_2SiH_2, $MeViSiH_2$, or $MeEtSiH_2$, and intense peaks at m/z 44 ($MeSiH^+$), m/z 45 ($MeSiH_2^+$), m/z 71 ($MeViSiH^+$), or m/z 73 ($MeEtSiH^+$) should be observed. In addition, the large escape of hydrogen above 380 °C indicates an extensive cleavage of the Si–H bonds during the degradation of the chains.

3. Evolution of the Residue during the Pyrolysis of Poly(silylethylene). The structural evolution of the residue with temperature was followed by elemental analysis and solid-state NMR spectroscopy. The ^{29}Si NMR data available in the literature concern mainly methylsilanes, poly(silylmethylenes) $(Si(R^1R^2)CH_2)_n$, and

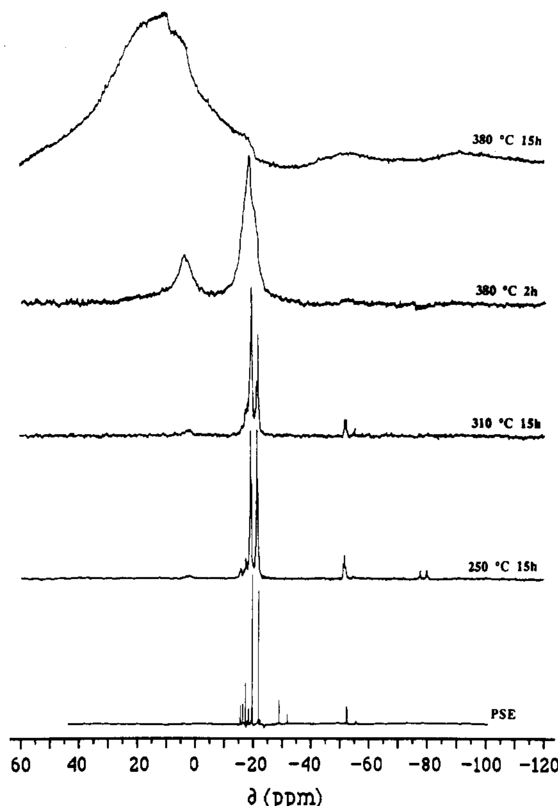


Figure 5. ^{29}Si NMR of PSE (bottom) and solid-state ^{29}Si NMR (CP-MAS) of PSE heated under argon (second from bottom to top): 15 h at 250 °C; 15 h at 310 °C; 2 h at 380 °C; 15 h at 380 °C.

Table IV. ^{29}Si Chemical Shifts in Alkylsilanes and Polycarbosilanes (ppm from TMS)

tetrahedral sites	model	chemical shift
$SiCH_3$	PSE (chain ends)	−52.8, −55.0
	$MeSiH_3$	−65.2
SiC_2H_2	PSE	−17.8 to −21.8
	Me_2SiH_2	−37.7
	Et_2SiH_2	−22.5
SiC_3H	PMSM[a]	−15.5 (Du)[6a]
	Me_3SiH	−15.5
	Et_3SiH	+0.15
SiC_4	PDMSE	+6.0, +6.6
	PDMSM[b]	+0.5[6c]
	Me_4Si	0
	Me_2SiEt_2	+4.6
	Et_4Si	+7.1

[a] Poly(methylsilylmethylene). [b] Poly(dimethylsilylmethylene).

PCS, but their chemical shifts happen to be quite different from those observed for our poly(silylethylenes), $(Si(R^1R^2)C_2H_4)_n$ (Table IV). On the other hand, ethylsilanes appear as much better NMR models.[10]

Evolution of the Residue below 380 °C. At ambient temperature, PSE is a viscous liquid; annealing at 250 or 310 °C for 15 h leads to the formation of an elastic solid, indicating the occurrence of some cross-linking reaction. Elemental analysis indicates that annealing PSE at these temperatures does not modify its composition. On the other hand, solid-state NMR spectra are slightly modified: at 250 °C, the ^{29}Si spectrum (Figure 5) shows the disappearance of the resonance around -30 ppm, corresponding to $SiCViH_2$ sites (i.e. silicon atoms bonded to one saturated carbon group, one vinyl group, and two

(10) Marsmann, H. In *NMR basic principles and progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1981.

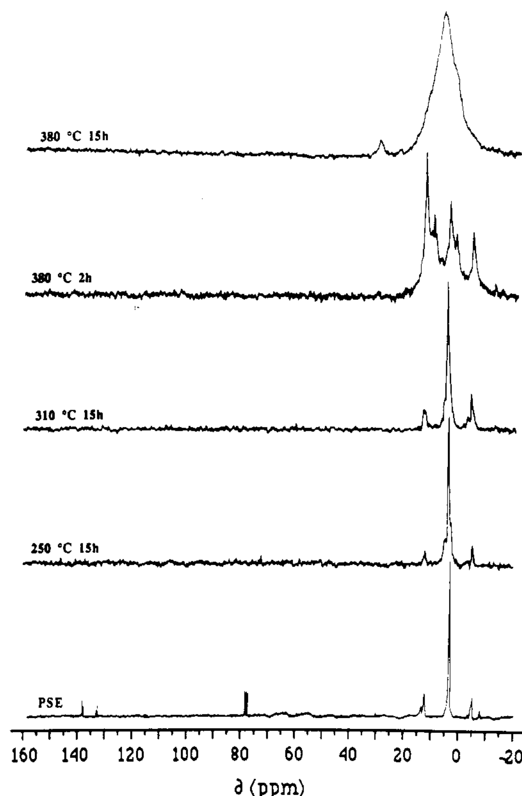
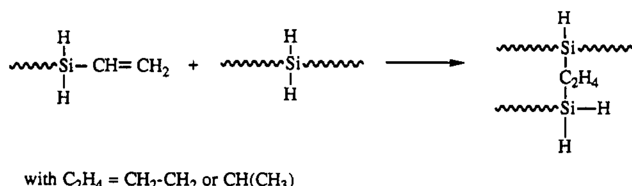


Figure 6. ^{13}C NMR of PSE (1, bottom) and solid-state ^{13}C NMR (CP-MAS) of PSE heated under argon (second from bottom to top): 15 h at 250 °C (2); 15 h at 310 °C (3); 2 h at 380 °C (4); 15 h at 380 °C (5).

Scheme II



hydrogen atoms), arising from the $SiViH_2$ chain ends; in addition a small resonance around 2 ppm is detected, which may be ascribed to the formation of $\mathit{Si}C_3H$ tetrahedra, by comparison with Et_3SiH (Table IV). The disappearance of vinyl groups is confirmed by the disappearance of the resonances at -131 and -136 ppm in the ^{13}C spectrum (Figure 6). After 15 h at 310 °C, the ^{29}Si and ^{13}C spectra remain unchanged; more particularly, the small peak around 2 ppm does not increase.

Both disappearance of vinyl groups and formation of $\mathit{Si}C_3\mathit{H}$ tetrahedra may be ascribed to the thermal hydrosilation of Si–H on vinyl end groups[4a,4c,11,12] (Scheme II), which leads to a weakly cross-linked polymer (ca. 3% of branched silicon atoms, as estimated from NMR integration, which is consistent with the polymerization degree of the starting polymer, around 30).

Another cross-linking reaction must be considered: it is the partial oxidation of the Si–H bonds by traces of oxygen, leading to silanol groups which further condense on heating with Si–H groups to give siloxane bridges and hydrogen (Scheme III).[13]

Scheme III

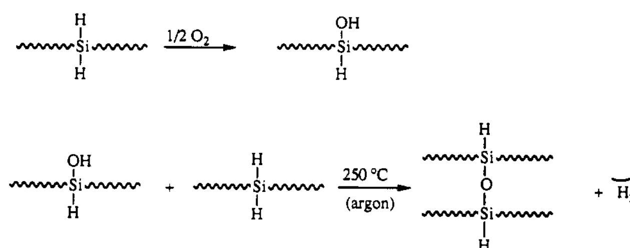


Table V. Elemental Analyses of PSE after Heating 15 h at the Specified Temperature (°C)

temp	wt % Si	wt % C	wt % H	wt % O	total %
not treated	43.10	41.19	10.76		95.05
250	47.70	41.82	11.40	0.22	101.27
310	48.20	41.22	11.03	0.26	100.91
380	50.10	38.41	7.08	1.88	97.47
430	52.35	29.66	5.47	6.65	94.13
480	59.70	28.08	3.14	6.31	97.23
580	56.20	30.17	1.61	3.75	91.73
1000	65.55	30.39	<0.1	3.76	99.70
1200	62.20	32.14	0.16	3.46	97.96
1400	66.20	33.39	<0.1	0.59	100.18

Indeed, TG/MS analysis on PSE samples stored without precautions showed a large, poorly reproducible escape of hydrogen in the range 250–380 °C, and ceramic yields as high as 60% were observed,[4e] indicating that extensive oxidation occurred on ageing in air. However, in the present case, samples have been handled and stored under argon; furthermore, the heat treatments at 250 and 310 °C have been done in the TGA apparatus, and the very low oxygen content of the annealed samples (Table V) indicates that oxidation is negligible, with less than 1 oxygen atom for 100 silicon atoms.

Evolution of the Residue at 380 °C. Drastic changes in the structure of the residue take place during the fragmentation of the polymer; thus, ^{29}Si NMR (Figure 5) shows that, after only 2 h at 380 °C, a large resonance at −2.5 ppm appears; this resonance is ascribed to the formation of $\mathit{Si}C_3H$ and possibly $\mathit{Si}C_4$ sites (Table IV). Simultaneously, the line width increases, which is indicative of a significant cross-linking of the silicon atoms in the polymer. The presence of $\mathit{Si}C_2HSi$ sites, which would correspond to a cross-linking of the chains with elimination of hydrogen, cannot be discarded: indeed, the chemical shifts of $\mathit{Si}C_2HSi$ sites and $\mathit{Si}C_2H_2$ sites are too close to be distinguished in our case ($Me_3Si–\mathit{Si}Me_2H$, −39.1 ppm; $Me_2\mathit{Si}H_2$, −37.7 ppm).[10]

The ^{13}C spectrum (Figure 6) also is strongly modified, with an apparent increase of the peaks around +13 and −4 ppm, and new resonances around +10 and +2 ppm. The increase of the peaks around +13 and −4 ppm could be tentatively ascribed to an increase of $\mathit{C}H_3C$ sites and, to a lesser extent, of $\mathit{C}HCSi_2$ sites in the sample (Table III); however, second-neighbor effects due to changes in the substitution of the silicon atoms would lead to variations in the chemical shifts of the same order of magnitude, and additional NMR experiments are necessary to give an unambiguous explanation.

Longer annealing times at 380 °C lead to further transformations in the ^{29}Si spectrum: thus, after 15 h at 380 °C, all the signals around −20 ppm ($\mathit{Si}C_2H_2$ and possibly

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(12) Schmidt, W. R.; Interrante, L. V.; Doremus, R. H.; Trout, T. K.; Marchetti, P. S.; Maciel, G. E. *Chem. Mater.* **1991**, *3*, 257.
(13) Ichikawa, H.; Machino, F.; Teranishi, H.; Ishikawa, T. In *Silicon-Based Polymer Science. A Comprehensive Resource*; Zeigler, J. M., Fearon, F. W., Eds.; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1990; Vol. 224, p 619.

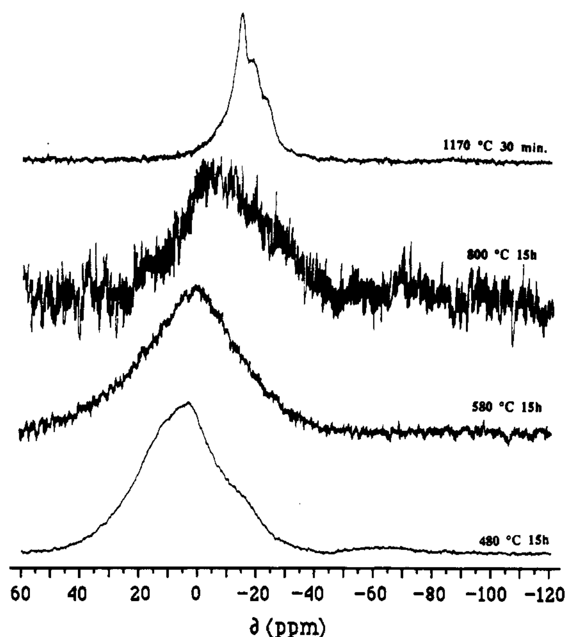

Figure 7. Solid-state ^{29}Si NMR (CP-MAS) of PSE heated under argon (bottom to top): (1) 15 h at 480 °C; (2) 15 h at 580 °C; (3) 15 h at 800 °C; (4) 30 min at 1170 °C.

SiC_2HSi sites) have disappeared, and only a very broad resonance centered around +10 ppm is observed, corresponding to SiC_3H and SiC_4 sites. The ^{13}C spectrum is no more resolved and displays a peak at 8.5 ppm, with a shoulder at 5 ppm. These shifts are comparable to those observed in the case of Yajima's PCS treated under argon at 500 °C (δ = +4.7 ppm) or 600 °C (δ = +10 ppm).[14]

The loss of silicon ΔSi during the heat treatment is given by

$$\Delta Si = Si_0 - YSi_r$$

where Y is the yield of residue and Si_0 and Si_r are the weight percentage of silicon in the starting polymer and in the residue, respectively.

After 15 h at 380 °C, the relative loss of silicon, $\Delta Si/Si_0$ = 58%, is equal to the loss of silicon after pyrolysis at 1100 °C. Thus, the loss of organosilicon species by depolymerization is complete after 15 h at 380 °C. The atomic composition of the residue, $SiC_{1.79}H_{3.94}O_{0.07}$, is significantly different from the theoretical composition of the starting PSE, SiC_2H_6. The low hydrogen content of the residue has to be related with the large hydrogen escape observed and the disappearance of the starting SiC_2H_2 sites.

Evolution of the Residue above 380 °C. Infrared spectroscopy indicates that most of the Si–H groups are consumed after 15 h at 480 °C; thus, the broad resonances observed in the ^{29}Si NMR spectra at 480, 580, and 800 °C (Figure 7) may be ascribed to SiC_4 sites. From 480 to 800 °C, the residue gradually converts to amorphous silicon carbide in the same way as Yajima's PCS; for instance,[15a] the broad ^{29}Si resonance gradually shifts upfield, from +2 to −8 ppm. The ^{13}C NMR peaks (Figure 8) shift downfield and broaden, indicating a significant cross-linking of carbon atoms.

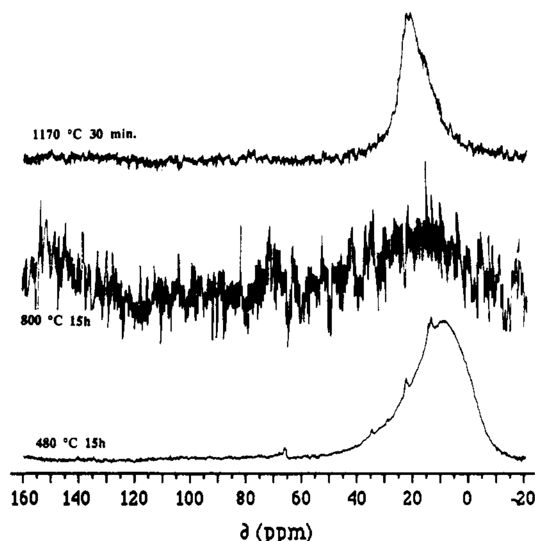

Figure 8. Solid-state ^{13}C NMR (CP-MAS) of PSE heated under argon (bottom to top): (1) 15 h at 480 °C; (2) 15 h at 800 °C; (3) 30 min at 1170 °C.

After 30 min at 1170 °C, partial crystallization to β SiC occurred, as indicated by the X-ray diffraction pattern, which exhibits two broad peaks around 2θ = 35° and 2θ = 60°. Simultaneously, the NMR line width decreases. The ^{29}Si NMR spectrum shows a sharp peak at −15 ppm, with shoulders at −18 and −23 ppm; the ^{13}C NMR spectrum indicates a resonance at +22 ppm, comparable to the chemical shift observed in silicon carbide[15b] or in ceramic fibers prepared by pyrolysis of PCS.[15c] In addition a large resonance centered around 125 ppm is observed, which indicates the presence of unsaturated excess carbon atoms.[15c] At 1170 °C, the composition of the final ceramic is $SiC_{1.21}O_{0.1}$. According to Soraru et al.,[15a] the composition of the ceramic obtained by pyrolysis of Yajima's PCS at 1200 °C under argon is $SiC_{1.44}$ (oxygen content not given). The excess of carbon in the case of PSE, estimated at 7.1 wt % according to the rule of mixture calculations,[16] is significantly lower.

4. Mechanisms of Degradation. The thermal depolymerization of polycarbosilanes was much less studied than that of polysiloxanes. It is well-known that linear, trimethylsilyl-terminated polysiloxanes decompose via intramolecular redistribution reactions involving the exchange of silicon–oxygen bonds.[17] However, in the case of polycarbosilanes, such a low-energy reaction path is quite unlikely,[18] as the exchange of silicon–carbon bonds is much more difficult than Si–O bond exchange.[19] The thermal depolymerization of PCS[20] and poly(dimethyl-*p*-silylphenylene), $(Si(Me_2)\text{-}p\text{-}C_6H_4)_n$,[21] has been reported to occur via random scission of Si–C bonds in the polycarbosilane skeleton, followed by hydrogen abstraction.

As the first step in the free-radical degradation of a polymer is the thermal dissociation of a covalent bond

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(16) Lipowitz, J.; Freeman, H. A.; Chen, R. T.; Prack, E. R. *Adv. Ceram. Mater.* **1987**, *2*, 121.
(17) (a) Thomas, T. H.; Kendrick, T. C. *J. Polym. Sci. A2* **1969**, *7*, 537. (b) For a review see for example: Montaudo, G.; Puglisi, C. In *Developments in Polymer Degradation*; Grassie, N., Ed.; Elsevier Applied Science: London, New York, 1987; pp 66–80.
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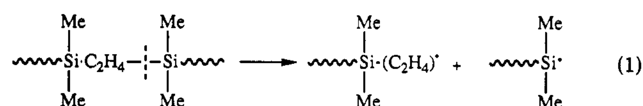
(21) Zelei, B.; Blazso, M., Dobos, S. *Eur. Polym. J.* **1981**, *17*, 503.

into two radicals, the degradation should be mainly governed by the bond dissociation energies.[22] Taking into account the effect of the substitution of silicon and carbon atoms and α or β stabilization of the alkyl radicals by silicon, the dissociation energy of the various bonds present in our poly(silylethylenes) have been evaluated from the data given by Walsh.[23] One finds that Si–C and C–C bonds in the skeleton should have the lower dissociation energies, around 83 kcal·mol^{-1}; lateral bonds, Si–Me bonds in PDMSE and Si–H bonds in PSE, should have higher dissociation energies, around 89 kcal·mol^{-1}. Finally, C–H bonds have the highest dissociation energies, ranging from 92 kcal·mol^{-1} (in CH_2–CH_2 bridges) to 99 kcal·mol^{-1} (Me groups in PDMSE).

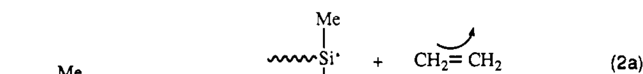
Experimentally, it is known that the thermal degradation of compounds such as $MeR_2SiCH_2CH_2SiMeR_2$ (R = Me, Ph, $PhCH_2$, C_5H_{11})[24a,24b] and $Me_3SiCH_2CH_2Si(NH)_{1.5}$[24c] involves mainly the cleavage of Si–C bonds and, to a lesser extent, the cleavage of the C–C bonds in the CH_2–CH_2 bridges, leading to the formation of silanes, vinylsilanes, and ethylene via a free-radical mechanism rather than a concerted mechanism.[24c]

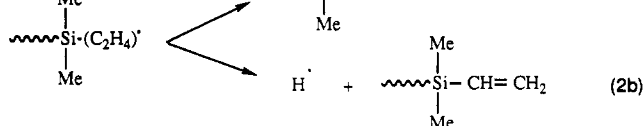
Degradation of PDMSE. In the case of PDMSE, the formation of the volatile compounds detected during the degradation, Me_2SiH_2, Me_2SiViH, and Me_2SiVi_2, may easily be accounted for by simple radical reactions. The first step mainly involves the homolytic cleavage of the Si–C bonds of the skeleton:



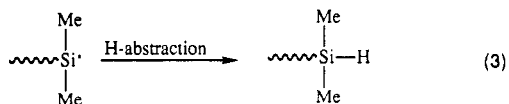
where C_2H_4 = CH_2CH_2 or $CH(CH_3)$

The formation of ethylene and $SiMe_2Vi$ chain ends is readily explained by the evolution of the $SiMe_2(C_2H_4)^\bullet$ radicals formed in reaction 1:





The silyl radicals may then abstract hydrogen from C–H bonds, leading to $SiMe_2H$ chain ends:



Further evolution of the $SiMe_2H$ and $SiMe_2Vi$ chain ends leads to the formation of the low molecular weight silanes detected, Me_2SiH_2, Me_2SiViH, and Me_2SiVi_2 (Scheme IV). The fact that no ethyl groups are formed indicates

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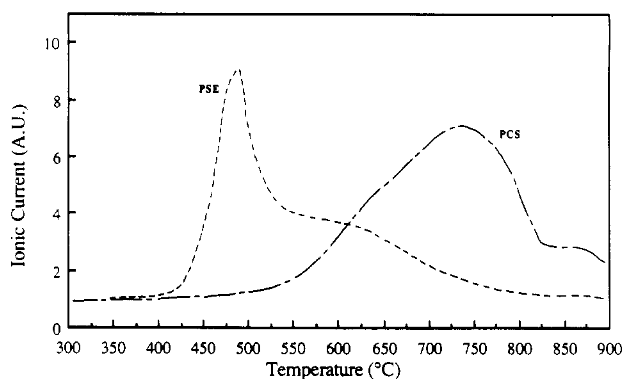
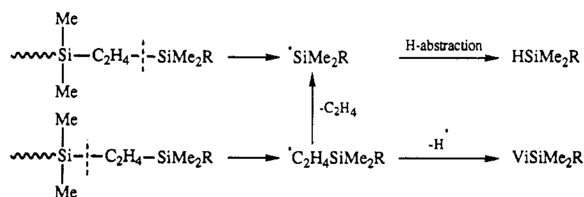
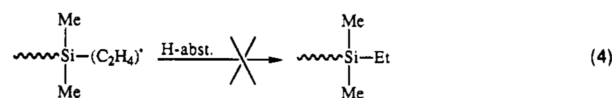


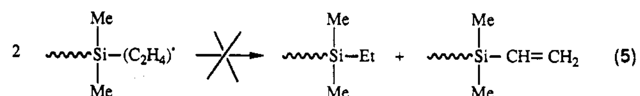
Figure 9. Comparison of the hydrogen escape during the pyrolysis under argon (heating rate 10 °C/min) of PSE (- - -) and PCS (– – –).

Scheme IV. R = H or Vi

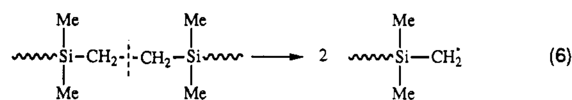


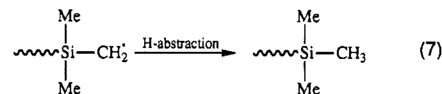
that hydrogen abstraction (eq 4) or dismutation (eq 5) are





much less favorable. The cleavage of C–C bonds in Si–CH_2CH_2–Si bridges also occurs to a small extent, as in the case of $Me_3SiCH_2CH_2SiMe_3$,[24a] leading after hydrogen abstraction to $SiMe_3$ chain ends, which account for the $SiMe_3^+$ ions detected:





Degradation of PSE. In the case of PSE, a mechanism of depolymerization involving free radicals cannot account either for the formation of ethylsilanes or for the violent escape of hydrogen at a temperature as low as 380 °C; thus, the formation of silylene intermediates has to be considered.

Indeed, although the dissociation energies of Si–H bonds in PSE and in PCS[20] must be very close, the escape of hydrogen, in the same conditions, is completely different (Figure 9). In the case of PSE, the dehydrogenation starts at a lower temperature and, above all, with a much higher rate. In the same way, although the dissociation energy of Si–H bonds in PSE and the one of Si–Me bonds in PDMSE should be very close, the scission of Si–Me bonds is negligible below 450 °C, as shown by the escape of methane.

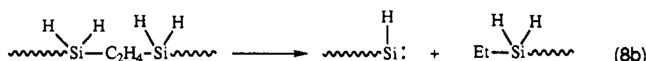
In a previous paper,[20] we suggested that the primary processes in the thermal degradation of polycarbosilanes should be the same as those evidenced in the gas-phase thermal decomposition of the corresponding alkylsilanes. Indeed, in the case of the thermal degradation of a polymer, the first reactions occur in the liquid phase, where, at least for free-radical reactions, reactions should be fairly similar to that occurring in the gas phase.[25] However, the rate of formation and of evolution of the reactive species should be strongly influenced by the high concentration and viscosity of the polymer melt, as well as the possibility of intramolecular reactions;[22] in addition, as the degradation goes on, the increase in the cross-linking of the polymer may lead to the formation of a solid residue, and the last steps of the degradation should involve more complicated heterogeneous mechanisms.

It is now well established that primary dissociation reactions for methylsilane and dimethylsilane[26] produce silylenes (or their silene isomers), whereas free radicals are formed in the case of trimethylsilane and tetramethylsilane.[27] In the case of dimethylsilane, the formation of dimethylsilylene, Me_2Si:, by elimination of hydrogen, as well as the formation of methylsilylene, MeHSi:, by elimination of methane, requires a significantly lower activation energy than the formation of free radicals; according to O'Neal and Ring,[26b] free-radical production is negligible below 1000 K.

Thus, in the thermal degradation of PSE, the more likely primary process should correspond to the formation of silylenes. Two processes may be involved: (i) First, silylenes may be formed without chain cleavage, by elimination of hydrogen:

(8a)

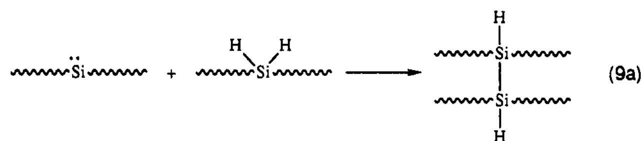
The occurrence of this reaction accounts for the rapid escape of hydrogen in the range 400–500 °C. (ii) The second possibility is the formation of silylenes by cleavage of the Si–C bonds and hydrogen transfer from the silicon atom to the adjacent carbon atom:



(8b)

This reaction, which is comparable to the formation of methylsilylene with elimination of methane in the case of dimethylsilane, should also involve a low activation energy and then compete with reaction 8a. In addition, reaction 8b provides the best explanation for the large escape of ethylsilanes, such as $EtSiH_3$ or Et_2SiH_2, instead of vinylsilanes as in the case of PDMSE. Indeed, the exclusive formation of ethyl groups via a free-radical mechanism is quite unlikely, even taking into account the possibility of hydrogen abstraction from Si–H bonds in PSE.

The silylenes formed may then insert into the various bonds present in the polymer. Theoretical, as well as experimental, studies indicate that the insertion of silylenes into Si–H bonds occurs with no barrier. On the other hand, the activation energies found for the insertion into Si–C, C–H, or C–C bonds are much higher, from 20 to 58 kcal·mol^{-1}.[28a] In our case, although steric effects of the chains would certainly lower the insertion rate of the "macrosilylenes" relative to "molecular" silylenes such as Me_2Si: or H_2Si:, the insertion into Si–H bonds should still be the more favorable. Insertions of the silylenes arising from reactions 8 into the Si–H bonds of PSE should lead to the formation of Si–Si cross-links (reactions 9). However, our attempts to evidence the formation of Si–Si bonds, either by NMR or Raman spectroscopy, were unsuccessful. Actually, even if the formation at 380 °C of Si–Si bonds cannot be eliminated on the basis of the ^{29}Si NMR spectra, they are not present above this temperature. In fact, Si–Si bonds are not stable at high temperature. Thus, hexamethyldisilane rearranges thermally[29] according to



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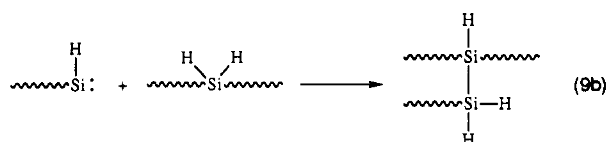
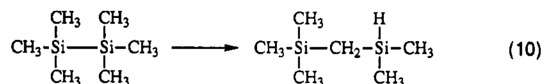


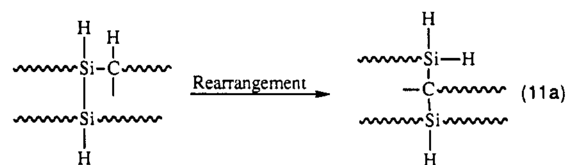
(9b)



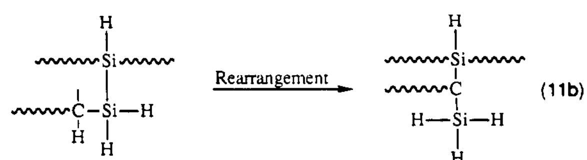
(10)

The low thermal stability of Si–Si bonds is also well illustrated by the thermal conversion of polysilanes to polycarbosilanes[1,12] or the very low proportion (3%) of Si–Si-containing compounds in the pyrolysis products of dimethylsilane.[26] In all cases, Si–Si bonds rearrange rapidly to more stable Si–C–Si bridges. This rearrangement involves either free-radical species, as in the pyrolysis of hexamethyldisilane,[28] or silylene intermediates, as in the pyrolysis of Me_2SiH_2.[26]

Thus, in our case, the Si–Si cross-links will also rearrange to Si–C–Si cross-links, as schematized in reactions 11. This rearrangement leads to silicon atoms surrounded by three carbon atoms and one hydrogen, corresponding to the SiC_3H sites evidenced by NMR at 380 °C.



(11a)



(11b)

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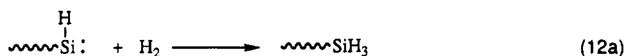
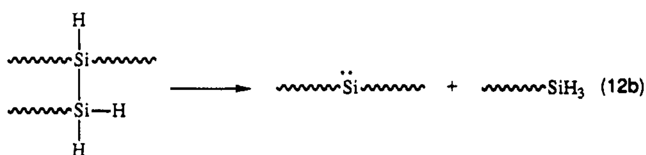
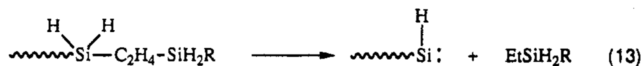
The formation of SiC_4 sites may be explained by similar reactions involving silylene formation, insertion into Si–H bonds, and rearrangement. However, as the temperature increases, free-radical reactions should become predominant;[26a] in addition, the concentration of Si–H bonds decreases rapidly, and therefore the formation of silylenes is hindered.

The early cross-linking of PSE via silylene intermediates explains the relatively high ceramic yield given by this polymer. However, about 57% of the silicon atoms are lost as volatile organosilicon species. The analysis of the evolved gases indicated an escape of linear oligomers, SiH_3 or SiH_2Et terminated. As mentioned above, the formation of the SiH_2Et chain ends corresponds to the formation of the silylene with chain cleavage (reaction 8b). The SiH_3 chain ends may be formed from the silylene chain ends (arising from reaction 8b) by insertion into H–H bonds (reaction 12a), which should require a very low activation



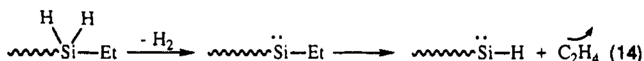


energy;[27b] another possibility is the insertion into Si–H bonds (reaction 9b), followed by the elimination of a middle-chain silylene (reaction 12b). Further evolution of the SiH_2Et and SiH chain ends leads to the formation of the low molecular weight silanes detected, such as Et_2SiH_2 and $EtSiH_3$:

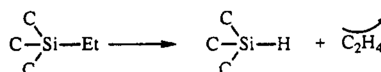


where R= Et, H

The escape of ethylene above 430 °C starts roughly at the same temperature as in the case of PDMSE and might arise from the same free-radical reactions. However, no significant escape of vinylsilanes is detected up to 500 °C, which does not correlate with this explanation. Ring et al.[26b] reported that ethylsilylene, EtHSi:, could convert to silylene, H_2Si:, by generating ethylene; a similar reaction involving the SiH_2Et chain ends might account for the escape of ethylene in the case of PSE:



The third possibility would be the decomposition of Si–Et groups (possibly via a free-radical mechanism) at the surface of the cross-linked solid residue, as observed for Si–Et species adsorbed on silicon surfaces:[29]



Conclusion

The mechanisms of the thermal degradation of polycarbosilanes appear strongly dependent on the substitution of the silicon atoms, as shown by the nature of the gases and organosilicon compounds evolved and the pyrolysis yields. When only $SiMe_2$ groups are present, a simple free-radical mechanism explains the formation of the volatile products detected using the degradation. The competition between depolymerization and cross-linking reactions (via free-radicals combinations) leads to negligible ceramic yields. On the other hand, when SiH_2 groups are present, as in the case of poly(silylethylene), the rapid elimination of hydrogen and the formation of SiH_2Et chain ends cannot be accounted for by a free-radical mechanism and suggests the formation of silylene species. Thus, the formation of silylenes by 1,1-cleavage of Si–C and Si–H bonds would lead to a fragmentation of the polycarbosilane chains; conversely, the formation of silylenes by 1,1-elimination of H_2, followed by insertion and rearrangement reactions, would provide an efficient way of cross-linking, which may favorably compete with fragmentation, thus explaining the high ceramic yields observed.

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