Investigation of the Pyrolytic Conversion of Poly(silylenemethylene) to Silicon Carbide

Q. Liu,[†] H.-J. Wu,[‡] R. Lewis,[§] G. E. Maciel,[||] and L. V. Interrante*,[†]

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180, and Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Received November 13, 1998. Revised Manuscript Received May 20, 1999

The pyrolysis of poly(silylenemethylene) (PSE), $[SiH_2CH_2]_n$, a linear polycarbosilane with a regularly alternating Si−C backbone structure and a high-yield precursor to stoichiometric SiC, was investigated by using a combination of thermogravimetric analysis, evolved gas analysis, and solid-state NMR and IR spectroscopies. The observed evolution of D_2 from the deuterio-derivative of PSE, $[SiD_2CH_2]_n$, as the primary gaseous product in the range of ca. 250−400 °C, where cross-linking of the polymer occurs, suggests that loss of H_2 from the Si is a key step in the cross-linking process. A reaction pathway is postulated for the cross-linking and pyrolysis of PSE in which both 1,1-H_2 elimination and intramolecular H-transfer reactions lead to highly reactive silylene intermediates; these insert into Si−H bonds of neighboring polymer chains forming Si−Si bonds which rapidly rearrange to Si−C bonds at these temperatures to form Si−C interchain cross-links. The cross-links prevent extensive fragmentation of the polycarbosilane network as the temperature is increased further to the range (> ca. 420 °C) where homolytic bond cleavage occurs at an appreciable rate, leading to free radicals. These free radical processes are presumably the main mechanisms at higher temperatures (>475 °C) where extensive rearrangement of the Si/C network structure is evidenced by solid-state NMR spectroscopy. Further heating of the polymer to 1000 °C leads to the formation of silicon carbide (SiC) in high yield (ca. 85%).

Introduction

An understanding of the chemistry involved in the pyrolytic conversion of polymeric precursors to ceramic materials is critical to the intelligent design and use of such precursors. Although extensive research has been carried out on the preparation and application of polymeric precursors to SiC, few detailed studies of the chemistry occurring during the thermosetting and subsequent thermal decomposition of these materials have been reported.

Several groups studied the chemistry involved in the preparation and subsequent pyrolysis of the Yajima "polycarbosilane", a partially cross-linked, solid material derived from poly(dimethylsilane) by thermal treatment, usually in the presence of a "catalyst" such as polyborodiphenylsiloxane.[1−6] This "polycarbosilane", which has been employed as a precursor for the production of continuous "SiC" fiber, is known to have a complex structure and to give a C-rich SiC, which may also contain appreciable oxygen, on pyrolysis. The conversion from the Si−Si bonded polysilane, $[Si(CH_3)_2]_n$, to a largely Si−C bonded structure (usually represented as "$[Si(H)(CH_3)CH_2]_n$") occurs above 400 °C, or at somewhat lower temperatures in the presence of a borosiloxane or titanium alkoxide catalyst. Between 600 and 800 °C, free radical reactions that involve the cleavage of Si−H and C−H bonds are operative, leading to an amorphous, three-dimensional, "SiC_x" ($x > 1$) network structure, which still contains appreciable amounts of residual H (mainly on C) and, usually, oxygen in the form of Si−O−Si linkages.[7]

The pyrolysis of various other polysilanes, including a vinylic, methylpolysilane,[8] and poly(methylsilane) $[Si(CH_3)(H)]_n$,[9] has also been examined by solid-state NMR and other methods. As with the initial stage in the conversion of the polysilane starting material to the Yajima polycarbosilane, in these cases it is believed that the relatively weak intrachain Si−Si bond undergoes cleavage above ca. 400 °C leading to silyl radicals. These radicals then presumably induce cross-linking via olefin coupling or Si−Si/C−H bond rearrangement processes.

[†] Rensselaer Polytechnic Institute.

[‡] Current address: Allied Signal Inc., Advanced Microelectronic Materials, 1349 Moffett Park Drive, Sunnyvale, California 94089.

[§] Current address: Analytical Research, Elf Atochem, 900 First Ave., King of Prussia, Pennsylvania 19406.

[||] Colorado State University.

* To whom correspondence should be addressed.

(1) Hasegawa, Y.; Okamura, K. *J. Mater. Sci.* **1983**, *16*, 3633.

(2) Poupeau, J. J.; Abbe, D.; Jamet, J. *Mater. Sci. Res.* **1984**, *17*, 287.

(3) Ishikawa, T.; Shibuya, M.; Yamamura, T. *J. Mater. Sci.* **1990**, *25*, 2809.

(4) Soraru̇, G. D.; Babonneau, F.; Mackenzie, J. D. *J. Mater. Sci.* **1990**, *25*, 3886.

(5) Bouillon, E.; Langlais, F.; Pailler, R.; Naslain, R.; Cruege, F.; Sarthou, J. C.; Delpuech, A.; Laffon, C.; Lagarde, P.; Monthioux, M.; Oberlin, A. *J. Mater. Sci.* **1991**, *26*, 1333.

(6) Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **1992**, *4*, 711.

(7) Laffon, C.; Flank, A. M.; Lagarde, P.; Laridjani, M.; Hagege, R.; Olry, P.; Cotteret, J.; Dixmier, J.; Miquel, J. L.; Hommel, H.; Legrand, A. P. *J. Mater. Sci.* **1989**, *24*, 1503.

(8) Schmidt, W. R.; Interrante, L. V.; Doremus, R. H.; Marchetti, P.; Maciel, G. *Chem. Mater.* **1991**, *3*, 257.

(9) Zhang, Z.-F.; Babonneau, F.; Laine, R. M.; Mu, Y.; Harrod, J. F.; Rahn, J. A. *J. Am. Ceram. Soc.* **1991**, *74* (3), 670.

10.1021/cm981067c CCC: $18.00

Most of these previous studies focused on branched or highly cross-linked polymers. Linear polymers generally are not considered to be good ceramic precursors because of thermally induced "chain-unzipping" processes that lead to volatile, low molecular weight fragments, giving poor ceramic yield.[10] For example, the linear polycarbosilane, poly(silabutylene) (PSB), $[Si(CH_3)_2CH_2]_n$, while resisting decomposition under an inert atmosphere to almost 500 °C, yields negligible ceramic residue on further heating to 1000 °C.[11]

On the other hand, it is recognized that the presence of Si−H bonds, and in particular SiH_2 units, in the polymer chain can considerably enhance cross-linking during the initial stages of pyrolysis, thus resulting in an improved ceramic yield.[11−13] Corriu et al. used thermogravimetric analysis (TGA)−MS and solid-state NMR spectroscopy to study the pyrolysis of $[SiH_2C_2H_4]_n$ and $[Si(Me)_2C_2H_4]_n$ and found that both fragmentation and cross-linking mechanisms were strongly dependent on the substituents on Si; the rapid evolution of H_2 at low temperatures suggested silylene formation by 1,1-H_2 elimination from the SiH_2 groups, thus providing an efficient mechanism for cross-linking.[12] Our previous studies of the decomposition of polysilapropylene (PSP), $[Si(H)(CH_3)CH_2]_n$,[11] and our preliminary work on polysilaethylene (PSE), $[-SiH_2CH_2-]_n$,[13] and its hyperbranched analogue "HPCS", $[H_3SiCH_2-]_x[-H_2SiCH_2-]_y[=HSiCH_2-]_z[\equiv SiCH_2-]_m$,[13,14] also suggested that Si−H_x ($x > 1$) groups were effective in suppressing fragmentation of the linear polycarbosilanes in the temperature range of 400−600 °C to form volatile byproducts; thus, the ceramic yield from PSP was improved compared to that for the all-methyl-substituted polycarbosilane, PSB, and PSE gives an almost quantitative yield of SiC.[15,16]

Poly(silylenemethylene) is notable for both its near-quantitative conversion to SiC on pyrolysis and also as the monosilicon analogue of the important organic polymer, polyethylene.[17−19] Unlike most other examples of linear polycarbosilanes, which fragment on pyrolysis to yield volatile organosilanes with little or no ceramic residue, this polymer gives H_2 as the main volatile byproduct on pyrolysis and converts to stoichiometric SiC. The simplicity of the structure of linear poly(silaethylene) provides an unique opportunity to observe the structural changes occurring during pyrolysis, which has not been the case in most of the previous studies because of the complex structure of the precursors employed.

Experimental Section

Preparation of Polymeric Precursors. PSE and DPSE ($[SiD_2CH_2]_n$) were synthesized by ring-opening polymerization of 1,1,3,3-tetrachloro-1,3-disilacyclobutane, followed by reduction with $LiAlH_4$ or $LiAlD_4$, respectively, in a manner similar to that described previously.[15,20,21] The resultant polymers are viscous, pale yellow, liquids. Although no change in weight or IR spectrum was observed after a 24 h exposure of the neat polymer to air at room temperature, as a precaution against possible atmospheric oxidation, the samples used in these measurements were stored under a dry N_2 atmosphere and, except for brief exposures during transfers, were handled in an inert atmosphere glovebox.

Preparation of a Mixed PSE/DPSE Polymer Sample. In a N_2-filled glovebox, 1.0 g of PSE and 1.1 g of DPSE (ca. 1:1 molar ratio) were weighed into a flask fitted with magnetic stirrer and a few milliliters of benzene was added to dissolve the polymers. After the clear solution was stirred under N_2 for several hours, the solvent was removed under vacuum to give a viscous, light yellow, liquid polymer mixture.

Measurements. Elemental analyses were performed by Galbraith Laboratories Inc. TGA studies were carried out on a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 °C/min under N_2. IR spectra were obtained by using a Perkin-Elmer 1800 Fourier transform infrared spectrometer. The solid samples were first ground in a glovebox to a fine powder using a mortar and pestle, mixed with KBr, and then pressed into pellets for transmission studies. Liquid samples were examined as a thin film between KBr plates. ^1H solid-state NMR analyses were performed at Colorado State University at a proton frequency of 187 MHz on a system built in house from a Nicolet NT-200 spectrometer. Either single pulse/magic angle spinning (SP/MAS) or the combined rotation and multiple pulse spectroscopy (CRAMPS) were used with a 90° pulse width of 1.30 μs, a rotor frequency of 1.3 kHz, and 100 acquisitions. Appropriate recycle delays were determined for each sample via progressive saturation.[22] ^{13}C solid-state NMR spectra were obtained either on a Chemagnetic CMX-360 solid-state NMR spectrometer at Rensselaer (these measurements were performed by Donna Narsavage at Rensselaer Polytechnic Institute) via SP/MAS with and without ^1H decoupling with a 90° pulse width of 3.5 μs and delay of 5 s, or by the cross-polarization/magic angle spinning technique (CP/MAS) on a 100 MHz system built in house at Colorado State University with 90° pulse of 6 μs and delay of 10 s. ^{29}Si solid-state NMR spectra were obtained at Colorado State University via SP/MAS with and without ^1H decoupling and CP/MAS with ^1H decoupling. Appropriate recycle delays were determined by measuring either ^{29}Si or ^1H T_1 values via saturation recovery.[23]

Bulk Pyrolysis of PSE. Pyrolysis experiments were performed by placing weighed amounts (ca. 0.5 g) of PSE into a molybdenum foil boat, which was then placed into a gastight quartz furnace tube. The polymer was then pyrolyzed to various temperatures in a CM 1000 Series programmable high-temperature furnace under flowing, purified, N_2 at 5 °C/min. After the quartz tube containing the sample was heated to the desired temperature, followed by a 5 min soak period, the tube was removed from the furnace and cooled with a fan to room

---

(10) Wynne, K. T.; Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 297.

(11) Wu, H.-J.; Interrante, L. V. *Chem. Mater.* **1989**, *1*, 564.

(12) Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Planeix, J. M.; Vioux, A.; *Organometallics* **1993**, *12*, 454.

(13) Interrante, L. V.; Whitmarsh, C. W.; Sherwood, W.; Wu, H.-J.; Lewis, R.; Maciel, G. In *Applications of Organometallic Chemistry in the Preparation and Processing of Advanced Materials*, *NATO ASI Series E*; Harrod, J. F., Laine, R. M., Eds.; Kluwer Academic Publishers: Norwell, MA, 1995; Vol. 297, p 173.

(14) (a) Whitmarsh, C.; Interrante, L. V. *Organometallics* **1991**, *10*, 1336. (b) Whitmarsh, C. W.; Interrante, L. V. U.S. Patent 5,153,295, Carbosilane Polymer Precursors to Silicon Carbide Ceramics. Oct 6, 1992. (c) Yang, C.-Y.; Interrante, L. V. *Polym. Preprints* **1992**, *33* (2), 152. (d) Interrante, L. V.; Whitmarsh, C. W.; Sherwood, W.; Wu, H.-J.; Lewis R.; Maciel, G. E. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 593.

(15) Wu, H.-J.; Interrante, L. V. *Polym. Prepr.* **1991**, *32* (3), 588.

(16) Wu, H.-J. Ph.D. Thesis, Rensselear Polytechnic Institute, Troy, NY, 1993.

(17) Wu, H.-J.; Interrante, L. V. *Macromolecules* **1992**, *25*, 1840; *Polym. Prepr.* **1992**, *33* (2), 210.

(18) Interrante, L. V.; Wu, H.-J.; Apple, T.; Shen Q.; Ziemann, B.; Narsavage, D. M.; Smith, K. J. *J. Am. Chem. Soc.* **1994**, *116*, 12085.

(19) Tsao, M.-W.; Pfeifer, K.-H.; Rabolt, J. F.; Holt, D. B.; Farmer, B. L.; Interrante, L. V.; Shen, Q. *Macromolecules* **1996**, *29*, 7130.

(20) Shen, Q.; Interrante, L. V. Preprints of 35th IUPAC International Symposium on Macromolecules, Akron, OH, 345, 1994; *Polym. Prepr.* **1995**, *36* (2), 378.

(21) Shen, Q.; Interrante, L. V. *Macromolecules* **1996**, *29*, 5788.

(22) Freeman, R.; Hill, H. D. W. *J. Chem Phys.* **1971**, *54*, 3367.

(23) Markley, J. L.; Horsley, W. J.; Klein, M. P. *J. Chem. Phys.* **1971**, *55*, 3604.

temperature while the sample was still under flowing N_2. The pyrolyzed products isolated were then stored under N_2 in a glovebox for future elemental analysis, NMR, and IR studies.

MS Analysis of the PSE Pyrolysis. A Hiden analytical quadrupole mass spectrometer (200 amu range) with an electron multiplier detector was used to detect the gaseous species produced during the pyrolysis. The sample (ca. 0.3 g) was placed into a 1 in. diameter quartz tube, which was connected through glass and stainless steel tubing to a diffusion-pumped vacuum system. A T-connector placed between the quartz tube and the vacuum line led to a mass spectrometer. A needle valve was used to control the amount of gaseous species introduced into the probe of the mass spectrometer. After the system was pumped and baked out for several days, a tube furnace was used to heat the sample from room temperature to 1000 °C at 3 °C/min under vacuum. The heating rate was controlled by a CN8600 Series process controller (OMEGA Engineering, Inc.). Three scans through the region of the molecular ion peak were collected for each species monitored at various temperatures throughout the pyrolysis process. At least two pyrolysis runs were performed on each sample; no significant differences in the individual gas product evolution curves were observed between these separate runs.

Two different platinum complexes, hexachloroplatinic acid hydrate ($H_2PtCl_6{\cdot}6H_2O$) and a divinylsiloxane platinum(0) complex (Karsted's catalyst, as a solution (5 wt % Pt) in xylene), were used to investigate the effect of added catalyst on the pyrolysis of PSE. PSE (ca. 0.3 g) and the platinum complex were weighed out into a quartz tube such that the molar ratio of Pt relative to PSE was ca. 1%. The solvent was removed under vacuum for the Pt(0) complex solution. The same procedure described above for the mass spectrometric study was followed for the pyrolysis of these samples. The H_2 evolution was monitored as a function of temperature.

GC Analysis of the PSE Pyrolysis. PSE (0.3 g) was placed in a quartz tube that was connected via a rubber septum and cannula tube to a silicon oil bubbler under nitrogen. A syringe needle was used to flush the quartz tube with N_2. The bottom of the tube containing the sample was then heated from room temperature to 1000 °C at 3 °C/min. Gaseous products were collected every 20−30 °C through the septum by using a gastight syringe. The gas samples were then introduced into a Shimadzu GC-9A gas chromatograph with an Alltech VZ-10 packed column and a Hewlett-Packard HP 3396A integrator. A flame ionization detector (FID) was used as the detector. After the collection of the gaseous products, the tube was flushed immediately with N_2 for 3 min before it was heated to a new temperature and the next gas sample was collected.

Quantitative GC analysis of the PSE pyrolysis was carried out on a Carle CGC 500 gas chromatograph equipped with an auto injection mode; therefore, a constant injected sample amount could be achieved. About 0.3 g of PSE was placed inside a quartz tube and He was used as the carrier gas during the pyrolysis. The He flow rate was 20 mL/min and was controlled by a mass flow controller. The sample was heated from room temperature to 1000 °C at 5 °C/min. The calibration of the response factors for H_2, CH_4, C_2H_4, C_2H_6, and C_2H_2 was carried out by using a tank of a standard mixture of the above gases.

Results and Discussion

The detailed characterization of PSE by NMR spectroscopy and other physical methods was reported previously.[15,17,18,20] This polymer was shown to have a regular, linear $[SiH_2CH_2]_n$ structure and a degree of polymerization of about 250, whose (^1H decoupled) ^{29}Si and ^{13}C NMR spectra consist essentially of a single line, corresponding to, respectively, a "$\mathit{Si}H_2C_2$" and a "$\mathit{C}H_2$-Si_2" environment.

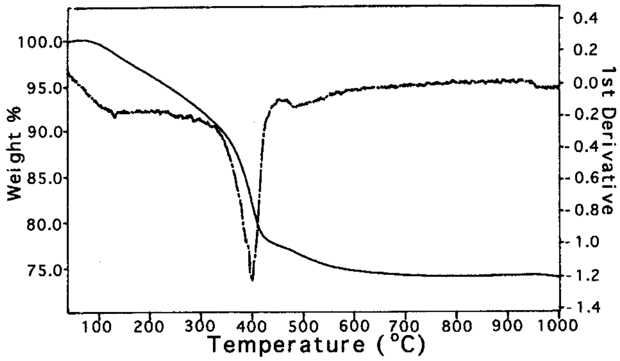


Figure 1. TGA plot for PSE under N_2.

Bulk Pyrolysis of PSE. The TGA plot for a sample of PSE having a relatively broad molecular weight distribution ($M_w/M_n = 3.5$, $M_n = 8300$ by gel permeation chromatography) is shown in Figure 1. With the aid of the first derivative, five main regions can be identified in the weight loss curve: in the range (1) 100−325 °C, there is a progressive, gradual weight loss of about 10%; (2) 325−400 °C, the weight loss rate increases (the total weight loss in this region is about 8%); (3) 400−500 °C, the rate of weight loss decreases and a total weight loss of 5% occurs; (4) 500−700 °C, the rate of weight loss continues to decrease, with a total weight loss of 2%; (5) above 700 °C, there is virtually no further weight loss. The final char yield of the ceramic product is ca. 75%. This is lower than the 91% calculated ceramic yield that would be expected for the loss of only H_2 from PSE. This can be attributed mainly to the evolution of volatile fractions in the polymer below 300 °C. After fractionation by precipitation from benzene with methanol, the high molecular weight fraction of PSE exhibits a total weight loss of around 15%, starting at ca. 200 °C, leading to an improved (85%) ceramic yield because of the removal of volatile oligomers.[13] Analyses of the gaseous byproducts of pyrolysis by mass spectrometry and GC indicate that H_2 is by far the major component along with traces of methane, C_2 hydrocarbons, and methylsilanes.

The elemental analysis of the sample obtained from the pyrolysis of PSE at 1000 °C under N_2 is Si, 69.07; C, 29.69; H, 0.86. This suggests a composition of $SiC_{1.003}H_{0.349}$, indicating that the 1:1 Si:C ratio of the initial $[SiH_2CH_2]_n$ polymer is retained on conversion to a ceramic product. Although oxygen was not directly analyzed in these samples, the observed values of C, H, and Si suggest that the wt % of oxygen is also quite low (0.38% by difference from 100%, which amounts to about 0.01 O/Si atom). Interestingly, the X-ray diffraction (XRD) pattern for this sample, while broad, shows distinct peaks at the appropriate positions for crystalline SiC,[8,24] suggesting that partial crystallization occurred even at this relatively low temperature.

NMR and IR Spectral Study of the Structural Evolution of the Solid Products during the Pyrolysis. The conversion of PSE to "SiC" was studied by analyzing both the solid and volatile products of pyrolysis at various stages in the conversion process. Solid-state NMR as well as FTIR spectra were obtained on

---

(24) Bishop, B. A.; Spotz, M. S.; Rhine, W. E.; Bowen, H. K.; Fox, J. R. In *Ceramic Transactions*; Messing, G. L., Fuller, E. R., Jr., Hausner, H., Eds.; The American Ceramic Society: Westerville, OH, 1988; Vol. 1, Part B, p 856.

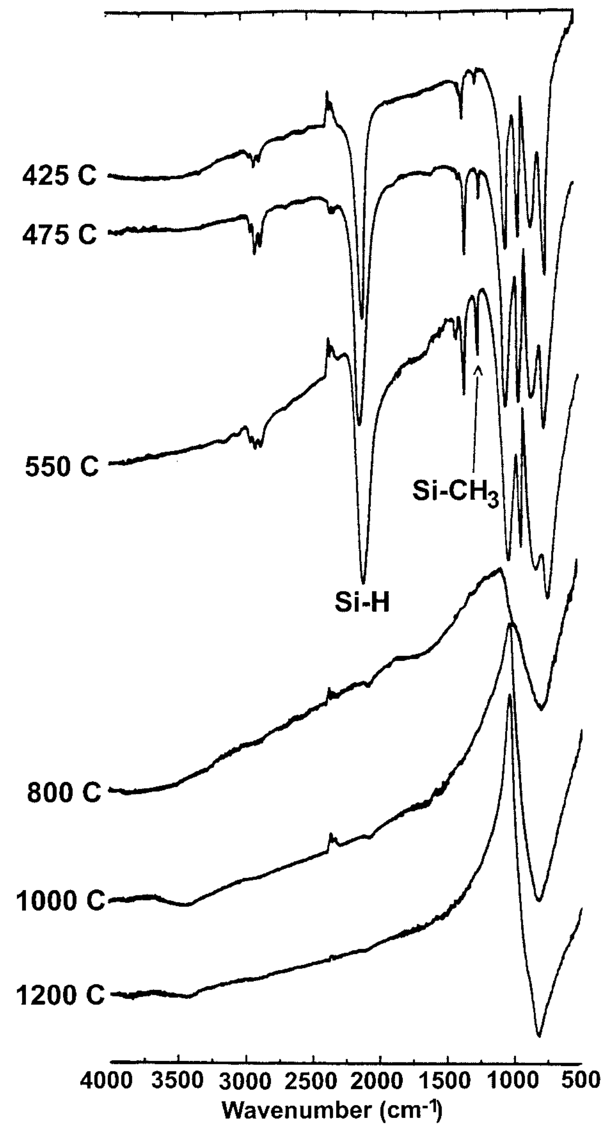


Figure 2. IR spectra for PSE after heating to various temperatures (under N_2).

samples of the partially pyrolyzed polymer at different temperatures.

The changes occurring in the IR spectra are shown in Figure 2. No appreciable changes were observed up to ca. 400 °C; thus the spectrum obtained at 425 °C is essentially the same as that of the original polymer.[17,19,21] Relative to the spectrum obtained after the 425 °C heating, the sample obtained from the 475 °C treatment shows a somewhat broader Si−H stretching band at 2127 cm^{-1}, suggesting an increasingly complex Si−H environment. The 550 °C sample showed a further broadening of the Si−H band and a decrease in its relative intensity [Si−H (2127 cm^{-1})/C−H (2923 cm^{-1})]. The progressive growth of the band at 1255 cm^{-1} (assigned to $Si-CH_3$ groups) throughout this temperature range is also apparent. The gradual broadening of the absorption bands at 2127 and 851 cm^{-1} is consistent with expectations for a polymer which is undergoing increased cross-linking and/or branching and the trend toward lower frequency for the broadened Si−H band is indicative of the formation of C_3SiH.[25] After the 800 °C heating, almost all of the absorption bands resulting from Si−H and C−H are absent, leaving a strong absorption at 780 cm^{-1} attributable to the SiC framework structure.[26] Further heating to 1000 °C leads to the sharpening of this band and a shift in its position from 780 to 800 cm^{-1}, consistent with the formation of crystalline SiC.[26]

The pyrolytic conversion of PSE to SiC was also investigated by observing the changes in the ^1H, ^{13}C, and ^{29}Si solid-state NMR spectra as a function of temperature. The ^1H solid-state NMR spectra are shown in Figure 3. For the material pyrolyzed at 425 °C, the spectrum shows three peaks at 0.2, 3.8, and 4.2 ppm. At this heat treatment temperature, the sample changed from the originally viscous liquid to a translucent rubbery solid, indicating the onset of cross-linking of the polymer chains. This is also evidenced by the fact that the two major peaks at 0.2 and 4.2 ppm are broader compared to those in the spectrum of the original PSE[16,17,21], which is presumably due, in part, to the more complicated environment induced by the cross-linking. The peak at 0.2 ppm is assigned to the $-CH_2-$ units of the polymer chain and the peak at 4.2 ppm is assigned to the $-SiH_2-$ units.[16,17,21,27] Two possible structures could be responsible for the peak at 3.8 ppm—one is the $-SiH_3$ end group,[28] the other is a $Si-SiC_2H$ structure (the chemical shift of ^1H in $HMe_2Si-SiMe_2H$ is 3.9 ppm[29]). On the basis of the ^{29}Si NMR spectrum obtained for this sample, which is described below, the existence of both structures seems likely. The peaks for these two structures may overlap with one another because of their similar chemical shift values. The ^1H SS NMR spectrum of the PSE sample heated to 550 °C indicates substantial structural changes. The main broad peak at 0.6 ppm is attributable to a range of $-Si_{4-x}CH_x$ ($x =$ 1−3) environments.[1] The intensity of the peak at 4.3 ppm has decreased, indicating the decrease of $-SiH_2-$ units in the sample. The general observation that $SiHC_3$ resonances are shifted to lower shielding than that of SiH_2C_2[28] suggests that the peak at 5.8 ppm might be due to the $SiHC_3$ unit. After the 800 °C heating, a main broad peak at 0.8 ppm, attributed to the various $Si_{4-x}CH_x$ units, dominates. Only a small peak at 5.4 ppm is observed which is attributed to a small amount of C_3-SiH species in this sample. For the sample that was heated to 1000 °C, the ^1H spectrum shows single broad peak at 0.9 ppm, suggesting that essentially all of the remaining H in this sample exists in the form of $Si_{4-x}CH_x$ type units.[8]

The ^{29}Si {H} SP/MAS NMR spectra of PSE heated to various temperatures are shown in Figures 4 and 5. For the 425 °C sample (Figure 4), in addition to the main peak at −34.6 ppm, which is attributed to the internal linear backbone structure, $-CH_2SiH_2CH_2-$, peaks at −32.3, −33.6, −36.0, and −37.2 ppm are also observed.

---

(25) (a) Silverstein, R. M.; Bassler, G. C.; Morril, T. C. *Spectrometric Identification of Compounds*, 4th ed.; Wiley: New York, 1981. (b) Smith, A. L. *Analysis of Silicons*; John Wiley & Sons: New York, 1974, pp 248−280.

(26) Ramis, G.; Quintard, P.; Gauchetier, M.; Busca, G.; Lorenzelli, V. *J. Am. Ceram. Soc.* **1989**, *72* (9), 1692.

(27) This CH_2 ^1H NMR chemical shift value differs somewhat from that observed in solution (−0.1 ppm), and reported in refs 17 and 21; the differences in the line width of these resonances relative to those observed in solution could also arise, at least in part, from dipolar broadening in the solid state.

(28) Whitmarsh, C. K.; Interrante, L. V. *J. Organomet. Chem.* **1991**, *26*, 93.

(29) Herzog, U.; Roewer, G. *J. Organomet. Chem.* **1997**, *527*, 117.

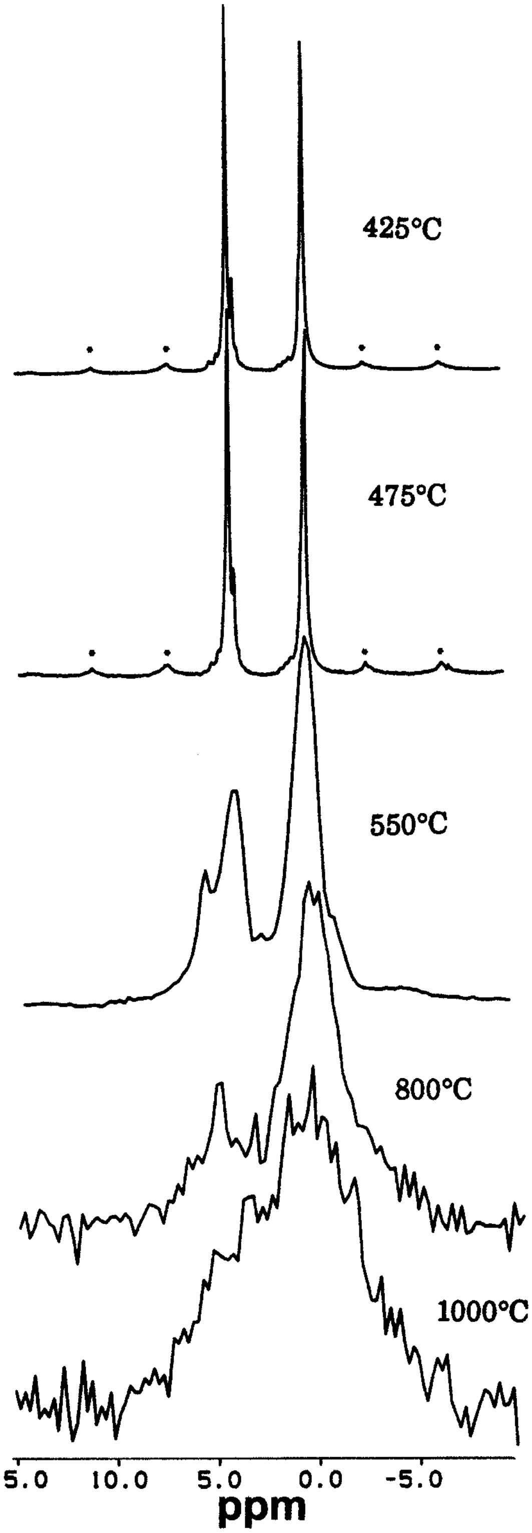


Figure 3. ^{1}H SS NMR spectra of PSE samples heated under N_2 to various temperatures; the spectra for the 425 and 475 °C samples were obtained via the SP/MAS method, whereas the spectra for samples heated at 550 °C and above employed the CRAMPS technique with the BR-24 pulse sequence.

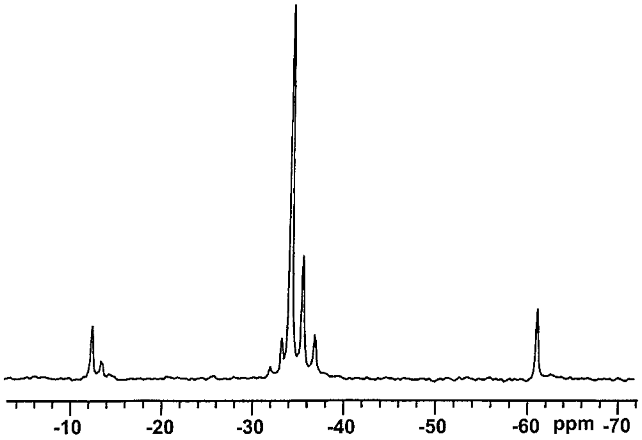
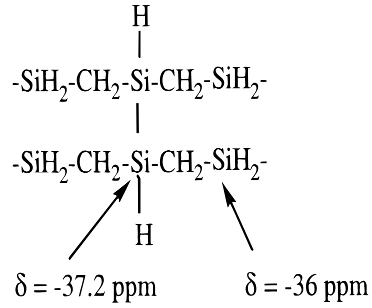


Figure 4. ^{29}Si{H} SP/MAS NMR spectra of PSE heated to 425 °C (under N_2).

The peaks at −33.6 and −36.0 ppm show up as triplets when coupled to protons ($|J| = 191$ Hz).). We attribute these triplets to *J* coupling.[30] The peak observed at −33.6 ppm could be indicative of some ring formation during the cross-linking because a low-shielding shift of the peak corresponding to the linear structure (−34.6 ppm) is typically observed in small $[SiH_2CH_2]_n$ rings (the ^{29}Si NMR shift of $[-SiH_2CH_2-]_3$ is −34.1 ppm).[31] The very weak peak at −32.3 ppm is currently unassigned.

The peak at −37.2 ppm could arise from a $HC_2Si-SiC_2H$ type structure (the ^{29}Si chemical shift of 1,1,2,2-tetramethyldisilane occurs at −39.0 ppm).[29] The Si that is two bonds away from this disilane structure would have a decreased shift to higher shielding, and therefore could be responsible for the peak at −36.0 ppm. Inspection of the relative intensity of the peaks at −36.0 vs −37.2 ppm suggests about a 2:1 ratio, which is consistent with the proposed structure shown below:



The peaks at −12.4 and −13.9 ppm in this spectrum, which occur as doublets in the proton-coupled ^{29}Si NMR spectrum ($|J| = 194$ Hz), could be due to the C_3SiH groups. The peak at −61.3 ppm is attributed to the $CSiH_3$ end group, which becomes a quartet when proton coupled ($|J| = 197$ Hz).

After the 475 °C heating, the spectrum (see Supporting Information) does not show much change except the growth of the peak at −36.0 ppm and the broadening of the peaks in the −34 to −36 ppm region, which are indicative of further cross-linking. After the 550 °C treatment (Figure 5), the peak at −61.3 ppm has become much broader and decreased substantially in intensity. Also observed is the broadening of the peaks near −34.5

---

(30) Both the 425 and 475 °C samples showed splitting clearly identifiable as $^{29}Si-^{1}H$ spin−spin coupling when the proton decoupler was turned off (see Supporting Information). These samples also exhibited $^{13}C-^{1}H$ coupling in the ^{13}C SP/MAS spectra; however, neither $^{29}Si-^{1}H$ nor $^{13}C-^{1}H$ coupling was observed for the samples heated to 500 °C or higher. Note that the observation of *J* coupling in a solid is relatively rare because of dipolar broadening and line widths and suggests a high degree of segmental mobility for these Si and C atoms in the partially cross-linked 425 and 475 °C samples.

(31) Williams, E. A.; Cargioli, J. D. In *Annual Reports on NMR Spectroscopy*; Webb, G. A. Ed.; Academic Press: New York, 1979; Vol. 9, p 221.

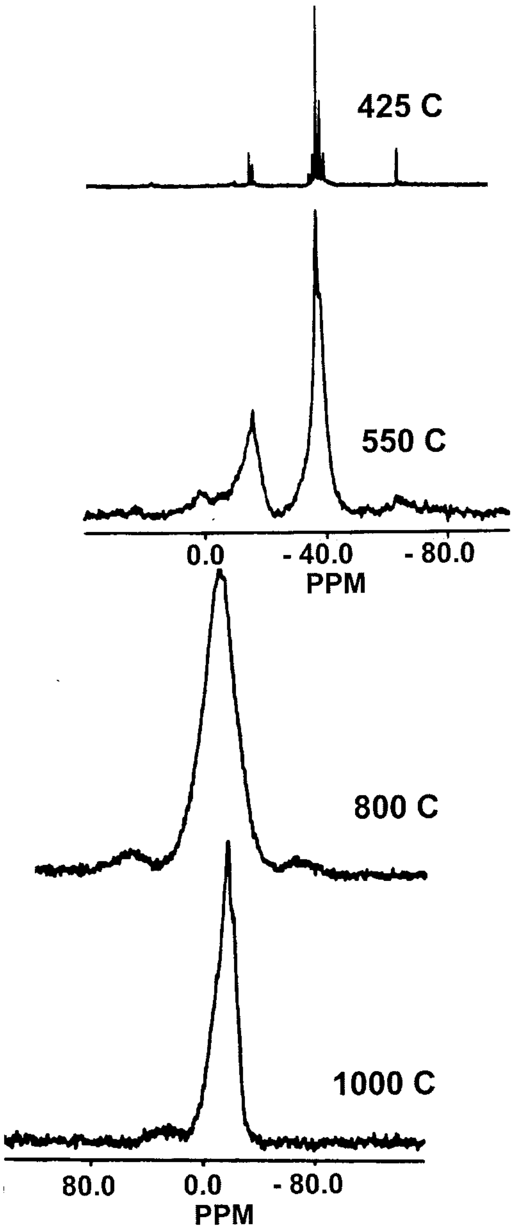


Figure 5. ^{29}Si{H} SP/MAS NMR spectra of PSE heated to various temperatures (under N_2) (note the scale change for the 800 and 1000 °C samples).

and −10.0 ppm. Deconvolution of these broad peaks indicates the following components (relative intensity[32] shown in parentheses): −32.0 ppm (16.7), −34.0 ppm (22.9), −35.5 ppm (8.7), −36.7 ppm (14), −12.9 ppm (14), and −9.6 ppm (14.8). A new broad peak appears at 1.85 ppm, indicative of the formation of the SiC_4 structure.[4] By 800 °C, a single broad peak at −5.4 ppm is observed. Further heating of this sample sharpens the peak and shifts it upfield. After the 1000 °C heating, a peak centered at −18.0 ppm is observed, which can be resolved into three peaks at −8.7 ppm (40.1), −14.2 ppm (19.2), and −20.0 ppm (38), indicating the formation of β-SiC with some residual protons.[8,33]

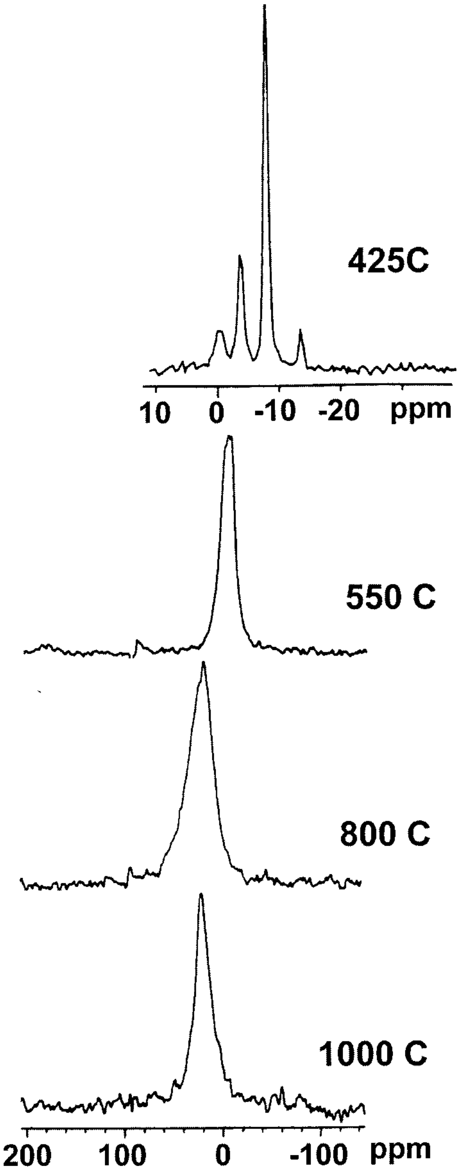


Figure 6. ^{13}C{H} SP/MAS (CP/MAS for the 800 °C sample) NMR spectra of PSE heated to various temperatures (under N_2) (note the scale change for the 550, 800, and 1000 °C samples).

The ^{13}C {H} solid-state NMR (SP/MAS) spectra are shown in Figure 6. At 425 °C, there are four peaks at −1.0, −4.3, −8.5, and −12.0 ppm. The latter three are triplets ($|J| = 113$ Hz) in the ^{13}C proton-coupled NMR spectra.[30] The main peak at −8.5 ppm is assigned to the linear $-SiH_2-CH_2-SiH_2-$ structure. On the basis of the ^{29}Si NMR spectrum of the same sample, the methylene carbon next to the disilane structure could account for the peak at −4.3 ppm. The peak at −12.0 ppm could be due to the $-CH_2-SiH_3$ end group. Possible assignments for the peak near −1 ppm include the end group $-SiH_2-CH_3$, and the branched site Si_3CH, both of which are evidenced in the IR and ^{29}Si NMR spectra of this sample. Unfortunately, the C−H coupling pattern for this resonance could not be unambiguously determined from the ^{1}H-coupled ^{13}C NMR spectrum.

By 475 °C, the ^{13}C spectrum (see Supporting Information) shows little change, only a slight growth of the peaks at −4.3 and −1.0 ppm. After the sample is heated to 550 °C, a broad peak near −5 ppm appears. Further

---

[32] Because of the possible presence of paramagnetic centers in these samples heated to 550 °C and higher, quantitation of these peaks must be considered as only approximate.

[33] Wager, G. W.; Na, B.-K.; Vannice, M. A. *J. Phys. Chem.* **1989**, *93*, 5061.

analysis (deconvolution) of this broad peak indicates that three peaks at −8.0, −4.9, and −1.0 ppm can be resolved, suggesting a mixture of the $Si_3\mathit{C}H$, $Si_2\mathit{C}H_2$, and $Si_4\mathit{C}$ units; therefore, a highly cross-linked structure is indicated. The peak at −12.0 ppm has decreased significantly, which is consistent with the observation from the ^{29}Si NMR spectrum that the $-SiH_3$ end group concentration has decreased.

The ^{13}C NMR (CP/MAS) spectrum of the 800 °C sample shows one broad peak at 16.2 ppm. Further heating of this sample to 1000 °C resulted in a sharp peak at 21.8 ppm, indicating the formation of β-SiC.[33] In neither sample is a peak seen near 120 ppm, where resonances for carbon in graphitic structures were observed in prior ^{13}C NMR studies of precursor-derived SiC_x materials;[8,34] however, note that this does not rule out the presence of graphitic carbon in these samples, because CP/MAS can detect only ^{13}C nuclei that are in the vicinity of protons.

Analysis of the Gaseous Species Evolved during the Pyrolysis. The gaseous species produced during the pyrolysis of PSE were analyzed both by MS and GC. The identified species include H_2, CH_4, C_2 hydrocarbons, CH_3SiH_3, $(CH_3)_2SiH_2$, SiH_4, and $(SiH_2CH_2)_2$. These species were identified on the basis of their MS molecular ion peaks and, in most cases, by comparison of their GC retention times to those of known gas mixtures. The conclusion that H_2 is, by far, the main gaseous product is indicated by both the MS peak intensities and by a quantitative GC analysis carried out on a mixture of the major gaseous products. Thus, the observed signal intensities were on the order of 10^{-7} for H_2, as compared to 10^{-11} for CH_4 and 10^{-12} for the other gases. The GC analysis gave the following relative amounts for the detectable gases: H_2 96.2%, CH_4 3.17%, C_2H_6 0.15%, C_2H_4 0.035%, and C_2H_2 0.034%. There was another gas with a retention time just before C_2H_4, which we presume to be SiH_4. We do not have the response factor for SiH_4, but with the assumption that it is not dramatically different from that of the other gases, we estimate it to be at the same magnitude as CH_4 (ca. 2−3%). The other gaseous products, such as CH_3SiH_3 and $(CH_3)_2SiH_2$, were not detected on this gas chromatograph; however, on the basis of their mass spectral molecular ion peak intensities, we conclude that these are minor products present in a similar concentration range as the C_2 hydrocarbons. Finally, because the overall weight loss is within ca. 6% of that expected for the quantitative conversion of the polymer to $SiC + 2H_2$, and because the solid product is essentially "SiC" with a small amount of residual H, we conclude that H_2 is >90% of the gaseous products and that all of the other gases observed are minor products.

TGA studies indicate a 7% weight loss below 300 °C. No gaseous species with $m/e < 200$ are detected by MS in this temperature range. Thus, the evaporation of oligomers is suggested.

The evolution of H_2 as a function of temperature from PSE is shown in Figure 7. The onset temperature for H_2 evolution is about 300 °C. The H_2 evolution rate increases rapidly above 425 °C and reaches a maximum at ca. 470 °C, then decreases and levels off above 800 °C. The onset temperature for CH_4 evolution is 420 °C, followed by a steady rate between 420 and 490 °C. A sudden increase in evolution rate is observed above 490 °C, which reaches a maximum at 530 °C and then decreases rapidly. No CH_4 was observed above 650 °C. The evolution of CH_3SiH_3, $(CH_3)_2SiH_2$, SiH_4, and $(SiH_2CH_2)_2$ all show a similar pattern. These silane products were only detected between 420 and 500 °C with a maximum at ca. 480 °C. The onset of evolution for the C_2 hydrocarbons is 420 °C with a maximum at 490 °C, and this peak is not observed above 600 °C.

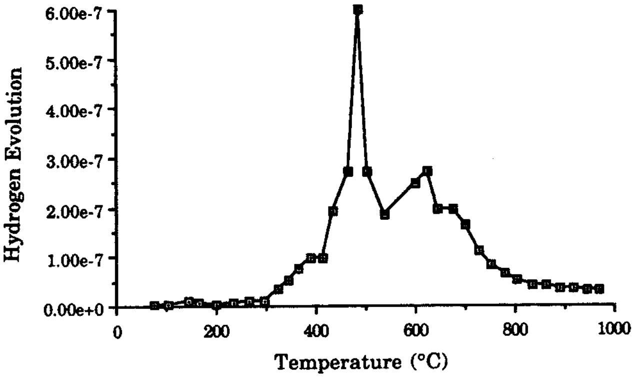


Figure 7. Evolution of H_2 during the pyrolysis of PSE (obtained from the relative intensity of the $m/e = 2$ peak in the mass spectrum).

The onset of H_2 evolution at ca. 300 °C is coincident with the observed gelation and eventual hardening of the polymer, suggesting its connection to the branching/cross-linking process. The integration of the H_2 evolution plot shows that ca. 7% of the total H_2 produced during pyrolysis evolved by 425 °C.

Pyrolysis Mechanism. Although reportedly the Si−H bond is a weaker bond than the Si−C bond,[35] the bond dissociation energies of Si−H and Si−C are actually rather close (377 kJ/mol for Me_3Si-H vs 374 for Me_3Si-CH_3;[36] 371 for Si−H vs 376 kJ/mol for Si−C, on the basis of the measured activation energies for gas-phase decomposition of $(CH_3)_3SiH$ and $(CH_3)_4Si$, respectively[37,38]). Therefore, we would expect the homolytic cleavage of Si−H to be accompanied by the homolytic cleavage of Si−C. Thus, in the pyrolysis of "Yajima's polycarbosilane", the evolution of hydrogen and methylsilanes, which are formed via the homolytic cleavage of Si−H and Si−C bonds, respectively, starts at about the same temperature.[6] For PSE, the fact that the pyrolysis between 300 and 400 °C leads only to the evolution of H_2 suggests that homolytic cleavage of Si−H to produce free radicals is unlikely.

An alternative pathway for H_2 loss in this temperature range is by 1,1-elimination from the SiH_2 groups. Prior studies of the gas-phase pyrolysis of methylsilanes of the type $(CH_3)_{4-n}SiH_n$ suggest that this is, in fact, a particularly facile pathway for decomposition when *n*

---

(34) Haworth, D. T.; Wilkie, C. A. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1689.

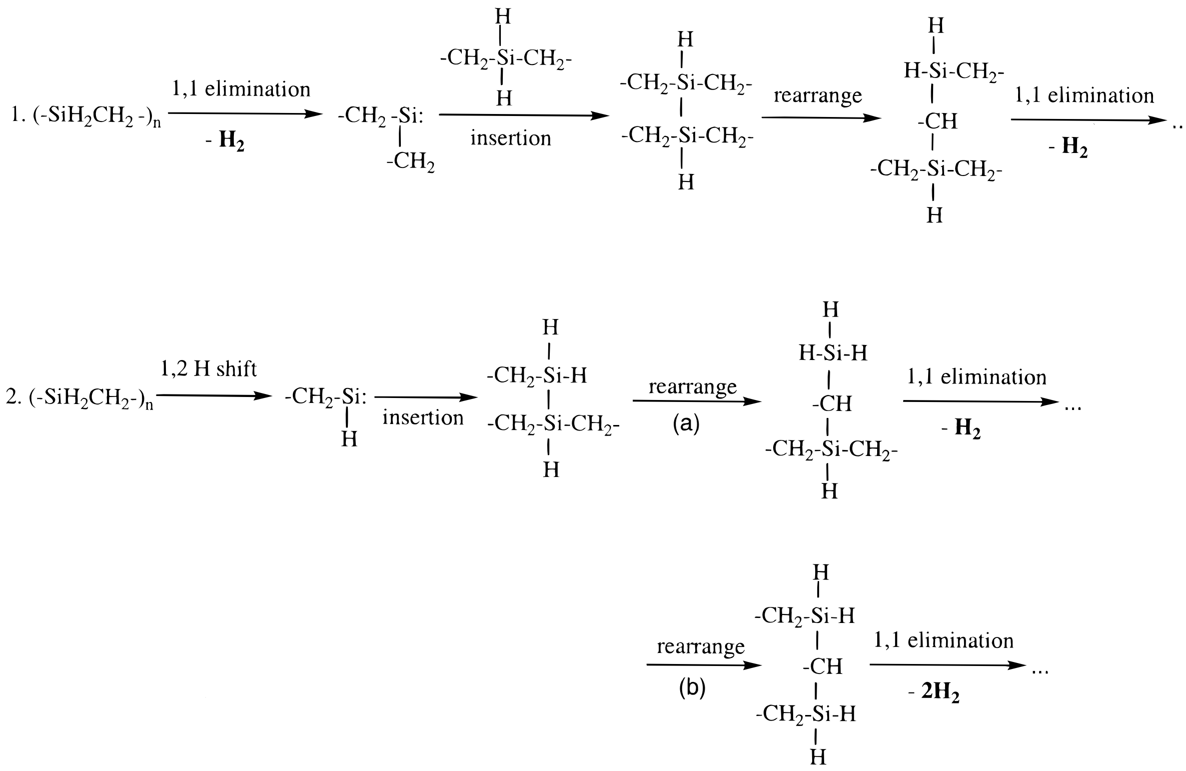
(35) Taki, T.; Inui, M.; Okamura, K.; Sato, M. *J. Mater. Sci. Lett.* **1989**, *8*, 918.

(36) Corey, J. J. In *The Chemistry of Organic Silicon Compounds, Part 1*; Patai, S., Rappoport, Z., Eds.; J. Wiley & Sons: Chichester, 1989; p 6.

(37) Ring, M. A.; O'Neal, H. E.; Richborn, S. F.; Sawyer, B. A. *Organometallics* **1983**, *2*, 1891.

(38) Walsh, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; Chapter 5.

Scheme 1. Proposed Thermolysis Reactions for PSE in the Temperature Range 300 to ca. 400 °C.



≥ 2. Thus, for $(CH_3)_2SiH_2$, the activation energy for 1,1-elimination of H_2 is 285 kJ/mol, as compared to 301 kJ/mol for the corresponding 1,2-H Si-to-C shift process.[39] The latter reaction, which results in the breaking of Si−C bonds, may also be operative in this temperature range for PSE and should become increasingly important as the temperature increases further, because it also has a relatively low activation energy compared to homolytic Si−C or Si−H bond breaking (typically ca. 370 kJ/mol[37,38]). Thus, there are two ways to form silylenes: 1,1-elimination, which releases H_2 without Si−C bond breaking, or a 1,2-H shift, which results in the breaking of a Si−C bond. The resultant silylene intermediates formed could undergo various possible sequences of reactions such as dimerization or polymerization, addition, and insertion.[40,41] Because the instantaneous local concentration of silylene intermediates would be low, dimerization or polymerization is unlikely. The addition is also excluded because of the absence of unsaturated reactants. Therefore, the insertion reactions are the predominant reactions. 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 ($E_{a(calc)} = -7.8$ kcal/mol).[41,42] On the other hand, the activation energies found for the insertion of silylenes into Si−C, C−H, or C−C bonds are much higher.[42,43] Insertions of the silylenes into Si−H bonds would lead to the formation of interchain Si−Si cross-links. The presence of such cross-linking sites in the PSE sample that was heated to 425 °C is suggested by the appearance of the peaks at −37.2 and −36.0 ppm in its ^{29}Si NMR spectrum as well as the peak at −4.3 ppm in its ^{13}C NMR spectrum. However, Si−Si bonds are not stable in this temperature range; they would undergo sequences of rearrangement reactions to form more stable Si−C−Si bridges.[44] The end units, C_3SiH/Si_3CH, formed from these rearrangements, are also evidenced by peaks in the ^{29}Si and ^{13}C NMR spectra. This thermolysis process is summarized in Scheme 1.

To verify that initial H_2 evolution during the pyrolysis of PSE occurs only at the Si site, we investigated the pyrolysis of DPSE. If the 1,1-H_2 elimination process were indeed the dominant reaction below 425 °C, we would see only D_2 and no H_2 in this temperature range. The evolution of H_2 and D_2 during the pyrolysis of DPSE as a function of temperature is shown in Figure 8.[45] The signal intensities of H_2 and D_2 are not at the same sensitivities. Because the H_2 is the main gaseous species evolved during the pyrolysis of PSE, the loss of hydrogen via the evolution of CH_4, CH_3SiH_3, and other compounds is negligible. We can assume that most of the gaseous species evolved during the pyrolysis of DPSE are H_2, HD, and D_2. Then we can normalize the data by using the assumption that the total amount of H_2 and D_2 will be the same for DPSE. This normalized result is shown in Figure 7. From this figure, it appears that the onset temperature for D_2 evolution is about 250 °C, whereas no significant evolution of H_2 can be seen before 425

---

(39) Davidson, I. M. T.; Scampton, R. J. *J. Organomet. Chem.* **1984**, *271*, 249.

(40) Gaspar, P. P. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; John Wiley & Sons: New York, 1985; Vol. 3, p 333.

(41) Tang, T. N. In *Reactive Intermediates*; Abramovitch, R. A. Eds.; Plenum Press: New York, 1982; Vol. 2, Chapter 4, p 297.

(42) Gano, D. R.; Gordon, M. S.; Boatz, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6711.

(43) Grev, R. S.; Schaefer, H. F. *J. Chem. Soc. Chem. Commun.* **1983**, 785.

(44) O'Neal, H. E.; Ring, M. A. *Organometallics* **1988**, *7* (51), 1071.

(45) HD evolution was also monitored during the decomposition; the resultant gas evolution curve closely resembles the one obtained for H_2 (see Supporting Information).

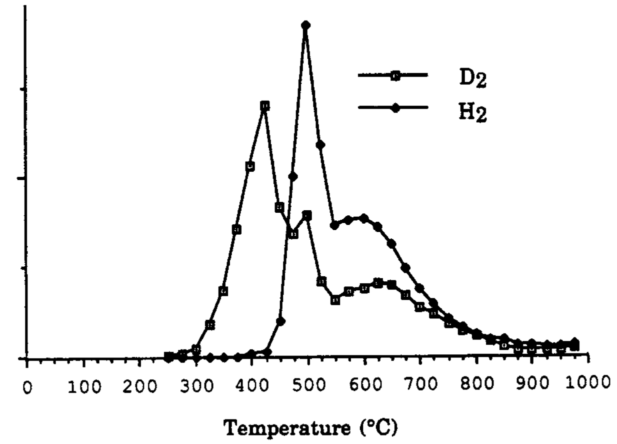
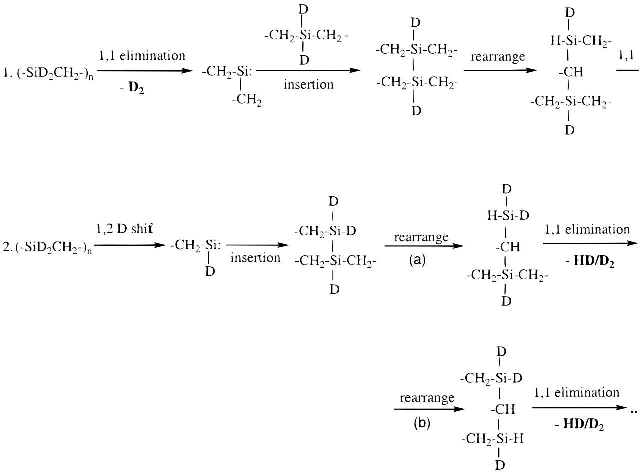


Figure 8. Evolution of H_2 and D_2 during the pyrolysis of deuterated PSE (DPSE) $[SiD_2CH_2]_n$ (obtained from the relative intensities of the $m/e = 2$ and 4, respectively, signals in the mass spectrum; the intensities of the $m/e = 2$ and 4 signals (due to H_2 and D_2, respectively) have been normalized to the same, overall, integrated intensity values, according to the assumption that the total $H_2 = D_2$).

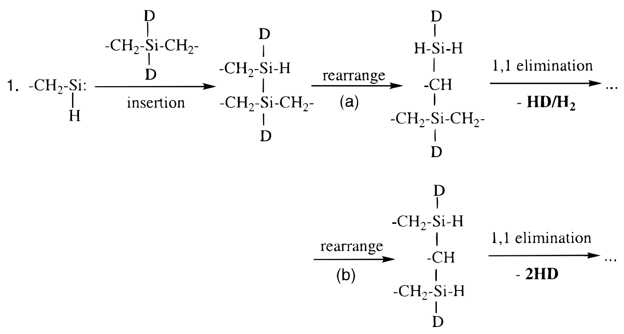
Scheme 2. Proposed Thermolysis Reactions for DPSE in the Temperature Range 300 to ca. 400 °C.



°C. The integration of these plots shows that about 22% of the total D_2 and 1% of the total H_2 (almost nothing) has evolved by 425 °C, which is consistent with our prediction. However, the integration of the corresponding HD plot[45] also shows that about 7% of the total HD evolved in this temperature range. This seems surprising at first because HD seemingly can come only from the free radical mechanism, which is operative at higher temperatures. But, if we consider the likely fate of the silylene intermediates that are initially generated from DPSE by either $1,1\text{-}D_2$ elimination or the 1,2-D shift mechanism (Scheme 2), we find that there are some alternative pathways for HD formation that are likely to occur in this temperature range. We postulate that these reactions are responsible for the 7% of the total HD evolved below 425 °C.

In an effort to obtain additional information regarding the pyrolysis process, we studied the pyrolysis of a 1:1 mixture of PSE and DPSE.[46] The onset temperature for H_2 evolution is about 300 °C, which is consistent with that of pure PSE. The onset temperature for D_2 evolution is about 250 °C, which is also consistent with that of pure DPSE. The integration of these plots shows that about 10% of the total H_2, 20% of the total HD, and 28% of the total D_2 evolved by 425 °C. The relative amount of HD evolved by 425 °C is significantly higher than that which was observed for pure DPSE. Considering the possible reactions occurring in this temperature range, we find that in addition to the reactions that occur in pure PSE and DPSE which are shown in Schemes 1 and 2, there are two new reactions that are unique to the mixtures. These are the interchain insertions, which are shown in Scheme 3. These additional pathways for H_2 and HD elimination could be at least partly responsible for the higher proportion of HD evolved by 425 °C in the mixture. Alternatively, Si−H/Si−D exchange could also be occurring at these temperatures.

Scheme 3. Possible Additional Pathways for HD Evolution in a 1:1 Mixture of PSE and DPSE on Heating to ca. 400 °C.



Above 425 °C, the $1,1\text{-}H_2$ elimination along with the 1,2-H shift continues to be operative, as evidenced by the ongoing D_2 evolution during the pyrolysis of DPSE and the continuing growth of the peak for $Si-CH_3$ stretching in the IR spectra. Also, the ^{29}Si NMR spectrum of the PSE sample that was heated to 475 °C suggests that there is still an abundance of SiH_2 units. The sudden increase in the H_2 evolution rate at ca. 425 °C for the pyrolysis of PSE and the onset of HD and H_2 evolution for DPSE suggest that free radical mechanisms have become operative in this temperature range. The observation that HD evolution starts at 400 °C and H_2 is not detected until 425 °C in DPSE, suggests that homolytic cleavage of C−H is not significant below 425 °C, which is consistent with the relative bond energies, Si−H < C−H.[36,37] Above 425 °C, where homolytic C−H cleavage is observed, it could be expected that the rate of homolytic cleavage of Si−C and Si−H would increase because of their lower bond energies, resulting in an increased rate HD and CH_4 formation. The rate of $1,1\text{-}H_2$ elimination starts to decrease at 425 °C, as is indicated by the decrease in D_2 evolution. This is presumably due to the decrease in the amount of SiH_2/SiD_2 structure and homolytic cleavage becoming more competitive.

The CH_3SiH_3, $(CH_3)_2SiH_2$, and SiH_4 detected between 400 and 520 °C could be produced via either silylene or free radical-initiated reactions. Above 475 °C, the free radical paths dominate as indicated by the higher H_2 evolution rate than that of D_2 during the pyrolysis of DPSE.

The TGA study indicates that the weight loss levels off above 520 °C. No volatile organosilane products, e.g.,

---

(46) See Supporting Information.

CH_3SiH_3, $(CH_3)_2SiH_2$, SiH_4, or $(SiH_2CH_2)_2$, were observed above this temperature, indicating that a highly cross-linked structure was formed. The loss of fragments from the polymer backbone was suppressed during the remainder of the pyrolysis. The ^{29}Si NMR spectrum of the PSE sample that was heated to 550 °C shows that the peak at −61.3 ppm becomes broadened and decreases substantially in intensity relative to the $C_3\mathit{Si}H$ peak at around 13 ppm. This could be due to a more rapid 1,1-elimination of H_2 from $-SiH_3$ groups, relative to the $-SiH_2-$ species, as would be suggested by the relative activation energies for 1,1-H_2 elimination observed for the corresponding methylsilanes,[36,37] but could also signal a higher proportion of interchain $HSi(CH_x-)_3$ cross-link sites relative to chain ends at this point in the pyrolysis process.

Although the free radical reactions are the main mechanisms that are operative at these temperatures, the silylene intermediates would continue to be formed because the SiH_2 unit is still relatively abundant at ca. 550 °C, as is suggested by the substantial intensity of the −34.6 ppm peak in the ^{29}Si NMR spectrum (Figure 5). The highly cross-linked structure should lower the rate of the insertion reactions involving the silylene species because of the reduced mobility of the polymer chain. Moreover, the insertion of the silylenes into Si−H versus C−H bonds would be expected to be less selective and the C_3SiH unit could also be formed via the latter insertion.

At higher temperatures, the supply of SiH_2 units would be depleted, resulting in a negligible amount of 1,1-H_2 elimination, causing the free radical pathway to become the primary pyrolysis mechanism. The fact that no CH_4 is detected above 650 °C suggests that a network structure has formed by this temperature. About 75% of the H_2 was lost by 650 °C, as indicated by the integration of the H_2 evolution plot, suggesting the approximate formula of (SiCH) where both the silicon and carbon atoms are incorporated into a 3-D network structure and most of the remaining H is located on carbon. By 800 °C, only an inorganic network structure is observed, as indicated by the ^{13}C and ^{29}Si SS NMR and IR spectra as well as the low signal intensity observed in the ^{1}H (CRAMPS) spectrum.

If we compare the results obtained here for the pyrolysis of PSE with that of its mono- and dimethyl analogues, PSP and PSB,[11] we find a substantial similarity to those obtained by Corriu and co-workers for the $[SiH_2C_2H_4]_n$ and $[Si(Me)_2C_2H_4]_n$ polymers[12] as well as to the results of earlier studies of the thermal decomposition of the methylsilanes, $(CH_3)_{4-n}SiH_n$.[37−39,47] PSB is stable to ca. 450 °C before undergoing rapid decomposition when pyrolyzed under nitrogen. PSP begins to decompose rapidly at 420 °C, whereas PSE undergoes significant decomposition even earlier. The decomposition of PSB can only proceed via a free radical pathway at high temperatures and gives essentially no ceramic residue because of the “chain-unzipping” process. PSP, on the other hand, could potentially undergo cross-linking at relatively low temperatures via the 1,2-H shift reaction. However, as was noted above, this path is not as efficient at these temperatures (ca. 250−425 °C) as the 1,1-H_2 elimination reaction which is operative in the PSE system. Moreover, the 1,2-H shift results in chain cleavage; thus, the ceramic yield for PSP is relatively low (ca. 20%).

Because the polymerization reaction, which was used to synthesize PSE, employs a Pt complex catalyst, it is possible that trace amounts of Pt left in the polymer after workup might affect the course of the pyrolysis. Comparing the evolution of H_2 during the pyrolysis of PSE as a function of temperature in the presence of added Pt(IV) and Pt(0) complexes, we can see that these samples have a H_2 evolution pattern similar to that of pure PSE (Figure 6). The onset temperature is still ca. 300 °C and the maximum is still at around 470 °C. The integration of the plots shows that 8 and 11% of the total hydrogen evolved by 425 °C after addition of these Pt(IV) and Pt(0) complexes, respectively, as compared to 7% for PSE alone. Thus, overall, the addition of these Pt complexes appears to have little or no effect on the pyrolysis of PSE; this suggests that the effect of any residual Pt left in the polymer should also be inconsequential.

Conclusions

The combination of the structural characterization of the solid samples with the analysis of the gaseous products as a function of temperature during the pyrolysis of PSE provided useful information regarding the pyrolysis mechanism for polycarbosilanes having two or more H atoms on Si. As these polymers are heated, the formation of silylene intermediates, mainly by 1,1-H_2 elimination, followed by interchain insertion and rearrangement reactions, provide an efficient mechanism for cross-linking at relatively low temperatures; this effectively inhibits the fragmentation and subsequent volatilization of the polymer backbone. Above 425 °C, free radical reactions become operative, resulting in further cross-linking as well as cleavage of the polymer backbone; however, because of partial network formation prior to this point, volatilization of the main-chain elements is suppressed. At higher temperatures, free radical reactions become the dominant mechanism, resulting in extensive structural rearrangement and the formation of an inorganic network without appreciable mass loss by 800 °C.

The unusually high ceramic yield of linear PSE (ca. 85%) is remarkable in the context of prior experience with polymeric precursors to SiC. The general “rule-of-thumb” in the search for high-yield SiC precursors has been that linear polymers exhibit a low ceramic yield because of thermally induced chain-unzipping processes that produce volatile, low molecular weight fragments and, consequently, that cross-linked structures are a virtual requirement for suitable precursors. The results of this work, along with those of earlier investigations,[12] show clearly that high molecular weight linear polycarbosilanes, when substituted with two or more H atoms on Si, have a built-in mechanism for effective thermosetting that can overcome the tendency toward fragmentation via Si−C bond breaking during pyrolysis, leading to the effective retention of the main chain elements in the ceramic product. When these elements are present in the correct stoichiometric ratio for the desired end product, as in the case of the conversion of

---

(47) Fritz, G.; Matern, E. *Carbosilanes, Synthesis and Reactions*; Springer-Verlag: Berlin, Heidelberg, 1986; pp 26−31.

PSE to SiC, the resultant ceramic material can thus be obtained in high yield and purity.

Acknowledgment. We are grateful to the National Science Foundation for continued support of this research under Grant Number CHE-9812191. The work carried out at Colorado State University was supported by Grant No. CHE-9021003. We also thank Donna Narsavage for running the SP/MAS ^{13}C spectra on the 425 °C sample with and without ^{1}H decoupling (see Supporting Information).

Supporting Information Available: SP/MAS ^{29}Si (without ^{1}H decoupling) (3 pages) and SP/MAS ^{13}C spectra (with and without ^{1}H decoupling) (2 pages) for a PSE sample heated to 425 °C, SP/MAS ^{29}Si{H} and ^{13}C{H} spectra (2 pages) for a PSE sample heated to 475 °C, and gas evolution curves determined for PSE (CH_4), DPSE (HD), and for the PSE/DPSE mixture (H_2, HD and D_2) by mass spectrometry (4 pages). Ordering information is given on any current masthead page. This material is available free of charge via the Internet at http://pubs.acs.org.

CM981067C