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New Polycarbosilane Models. 2. First Synthesis of Polysilapropylene

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Received March 11, 1987; Revised Manuscript Received July 8, 1987

ABSTRACT: Linear polycarbosilanes containing (methyl- and methyldeuteriosilylene)methylene units were synthesized for the first time and characterized by ^1H, ^{13}C, and ^{29}Si NMR. These polymers provide convenient models for studying both configurational sequence effects and Yajima's thermal polydimethylsilane–polycarbosilane rearrangement. Their terminal reticulation was investigated and the main gas evolved characterized.

Introduction

Yajima's route for the production of SiC requires the pyrolysis of polycarbosilanes (PCS) which are prepared by thermal rearrangement of poly(dimethylsilane) (PDMS), the latter resulting from the polycondensation of dimethyldichlorosilane.[1,2] This strategy is represented in Scheme I.

Scheme I

$$n(CH_3)_2SiCl_2 \xrightarrow[\text{2. methanol}]{\text{1. Na, toluene}} \underset{\text{PDMS}}{-(Si(CH_3)_2)_n-} \xrightarrow{470\ ^\circ C}$$

$$PCS \xrightarrow[N_2]{1200\ ^\circ C} SiC$$

This approach suffers from many limitations. For instance, the structures of the polymers (PDMS and PCS) remain poorly defined. The insolubility of PDMS hinders any detailed characterization of this material. In particular, the quantity and the structural influence of oxygen introduced by the methanolysis work-up is not readily measurable. In addition, the polycarbosilane structure is generally represented by the alteration of methylene and methylsilylene units, on the assumption that the thermal transformation proceeds according to Kumada's rearrangement.[3] This reaction was first observed with disilanes and formally amounts to the insertion of a methylene group into a Si–Si bond according to[3,4]

$$-Si(CH_3)_2Si(CH_3)_2- \xrightarrow{\Delta} -SiH(CH_3)CH_2Si(CH_3)_2$$

Unfortunately, the actual polycarbosilane cannot be accurately represented by the ideal structure $-(MeHSiCH_2)_n^-$. Beside the presence of Si–O bonds due to the PDMS oxygenation, Yajima[2] and other authors[5] have reported that PCS possesses a certain degree of cross-linking which cannot be taken into account by Kumada's transposition. Okamura[6] has even suggested the existence of cyclic patterns resulting from unknown secondary reactions leading to a complex framework for Yajima's PCS. Except these results, little information concerning the transformations polysilane–polycarbosilane and polycarbosilane–SiC can be found in the literature. In particular, for any given PCS precursor, the misunderstanding of its backbone structure rules out establishing any correlation between its structure, its thermal behavior, and its ability to yield a high SiC conversion rate. These questions prompted us to synthesize some polycarbosilane models of unambiguous formula, in order to examine their physicochemical properties and thermal behavior.

In our previous report,[7] we described the chemical modification of poly[(dimethylsilylene)methylene], leading to a poly[(chlorosilylene)methylene], as shown in Scheme II. The reduction of this polymer, yielding the corresponding poly[(methyl- and poly[(methyldeuteriosilylene)methylenes], is described in this paper.

Scheme II

$$\underset{\mathbf{1},\ \bar{M}_n\ 250\,000}{-(Si(CH_3)_2CH_2)_n-} \xrightarrow[AlCl_3]{(CH_3)_3SiCl}$$

$$\underset{\mathbf{2},\ \bar{M}_n\ 2300}{Cl(CH_3)_2SiCH_2-(SiCl(CH_3)CH_2)_{n'}-Si(CH_3)_2Cl}$$

Results and Discussion

Synthesis of the Polycarbosilanes. Lithium aluminum hydride reduction of Si–Cl bonds is usually carried out in solvents such as diethyl or dibutyl ether, THF, etc...[8] The corresponding silanes are obtained after treatment of the reaction mixture with dilute acid, which allows dissolution of the aluminum salts formed. This workup unfortunately entails hydrolysis of a few SiH bonds to give silanols or siloxanes, thus appreciably lowering the silane yields. Obviously, any aqueous treatment must be avoided to obtain a well-defined poly[(methylsilylene)methylene]. Some authors have overcome these problems by evaporating the ethereal solvent and replacement by hydrocarbons to precipitate the salts, the final product being recovered after filtration and distillation.

Models **3** and **4** were prepared in diethyl ether as the solvent (Scheme III), by modifying this latter procedure as reported later. Compound **3** can be regarded as an exact linear model of Yajima's theoretical polysilapropylene.

Scheme III

$$2 \xrightarrow[Et_2O]{LiAl\Sigma_4}$$

$$\underset{\mathbf{3},\ \Sigma\ =\ H;\ \mathbf{4},\ \Sigma\ =\ D}{CH_3Si\Sigma(CH_3)CH_2-(Si\Sigma(CH_3)CH_2)_{n'}-Si\Sigma(CH_3)}$$

The chlorinated polycarbosilane **2** was readily converted into the corresponding hydrido or deuterio polymers after refluxing the reaction mixture for 24 h in an inert atmo-

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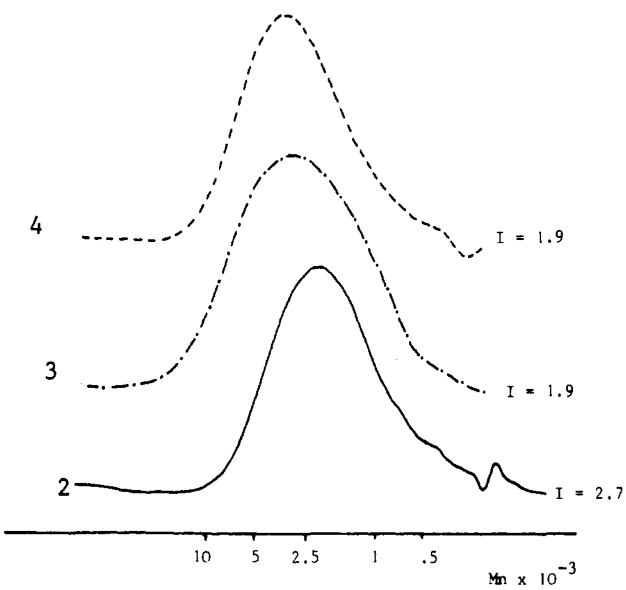


Figure 1. GPC elution curves of polycarbosilanes 2–4. Molecular weights are relative to polystyrene standards; I = polydispersity.

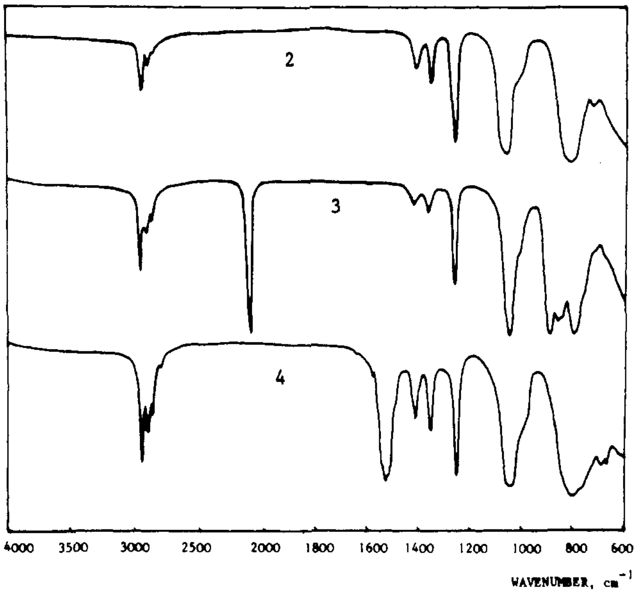


Figure 2. Infrared spectra of polycarbosilanes 2–4.

sphere. Distillation of ether under vacuum, followed by addition of pentane, and filtration, yielded a slightly cloudy, pale yellow solution. Concentration of this liquid under high vacuum at room temperature, followed by decantation, resulted in the appearance of a yellow (**3**) or orange (**4**) oil floating on the surface of a yellow liquid. This crude product was dissolved again in pentane. Centrifugation caused separation of this solution into two distinct layers. The upper layer contained the polycarbosilane in pentane solution, and the lower layer was found to be a complex of partially hydrogenated aluminium chlorides, as inferred from spectroscopic data. The IR spectrum of crude **3** exhibited a strong absorption at 1900 cm^{-1} which was assigned to the Al–H stretch in a complex of chloroaluminium hydrides and ether.[9] This was confirmed by ^1H NMR spectrum (60 MHz), which showed a triplet (CH_3) and a quartet (CH_2O) centered at 0.9 and 3.5 ppm, respectively. The precise structure of this complex was not determined. The polymer was isolated after siphoning off the pentane solution and eliminating solvent under high vacuum. The mobile oil thus obtained still contained a trace of the complex. Repeating the above operations led to polycarbosilanes **3** and **4** in over 95% yield. The aluminium complex resulting from these reductions was not soluble in CCl_4 but was soluble in C_6D_6. This facilitated the rapid verification of product's purity by ^1H NMR spectroscopy.

Characteristics of Polycarbosilanes 3 and 4. The GPC curves of **3** and **4** gave reproducible $\bar{M}_n$ values in the 2000–2200 range (Figure 1). As the calculated average $\bar{n}$ is appreciably greater than the corresponding value for polymer **2**,[7] this result can be reasonably attributed to different hydrodynamic volumes for each polymer. The fluidity of these polymers was consistent with their linear backbone and contrasted with the high melting temperature interval of Yajima's PCS (220–300 °C), though the reported $\bar{M}_n$ value for this last polymer was only 1750. This difference clearly reflects the branched structure and the complexity of the Japanese polymer.[6]

IR spectra of **3** and **4** exhibited a polycarbosilane absorption at 1040 cm^{-1} (Si–CH_2–Si deformation) and a characteristic shoulder for this series at 1000 cm^{-1}. When oxygenation occurred, this shoulder disappeared under a broad band centered at 1040 cm^{-1} (ω(Si–CH_2–Si) plus ν(Si–O–Si)). The deuteriated polymer gave no absorption in the 2100-cm^{-1} range (ν(SiH)), the SiD band being located at 1530 cm^{-1} (Figure 2).

Extensive information concerning this new class of polymers was obtained from multinuclear NMR. On the one hand, 60-MHz ^1H NMR spectrum exhibited the expected multiplicities for the linear formula $-(Me(\Sigma)SiCH_2)_n-$, (Σ = H, D), since no appreciable broadening of the peaks occurred.

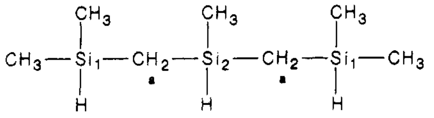
On the other hand, their 200-MHz ^1H NMR spectra revealed stereoconfigurational and chain-end effects (Figure 3a–c). In the case of **3**, the HSi(n) protons gave an octuplet centered at 4.34 ppm, owing to similar ^3J coupling constants with neighboring CH_2 and CH_3 groups (Figure 3a). Two doublets were observed for the methyl groups, and the methylene protons gave ABX_2 and A_2X_2 overlapping spectra, as can be seen by decoupling (Figure 3a,b) or by examining the spectra of polymer **4** (Figure 3c).

In addition, we succeeded in assigning the chain-end methyl groups and the internal methyl groups with the aid of the short-chain models **5** and **6**, the spectra of which are described in Chart I. The internal methyl groups gave the main doublet centered at 0.15 ppm, whereas the chain-end methyl groups gave the smaller doublet centered at 0.12 ppm. Thus it was clearly demonstrated that these latter signals did not result from stereochemical effects as one might think early in our studies; in fact, such a phenomenon could not be detected for hydrogens of the methyl groups in these series.

It can be seen from the methylene proton spectra that syndiotactic and isotactic sequences are both involved in polymers **3** and **4**, whereas only the syndiotactic configuration appeared to be present in polymer **2**[7] (Chart II).

Moreover, lithium aluminium hydride reduction of the SiCl bond does not a priori entail any loss of stereochemical information since it is known to proceed with configuration inversion at the silicon atom.[11] It can therefore be assumed that this mixture was also present in the case of polymer **2** but was not observed because H_A and H_B possess very similar magnetic environments. This unexpected observation might be attributed to the different anisotropy effects on the neighboring methylene protons caused by the differences of the Si–Cl and Si–H bond lengths: the Si–H bond being shorter than the Si–Cl one (1.48 and 2.05 Å, respectively[8]), the effect of the former on H_A and H_B might be stronger, resulting in a different magnetic environment for these protons.

Chart I
^{1}H NMR Data, 200 MHz, of Compounds 5 and 6; Chemical Shifts (Solvent, C_6D_6) δ (ppm) and Assignments



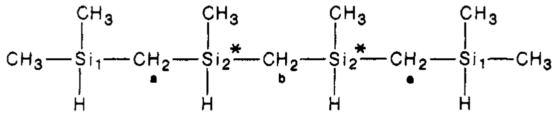
$$\mathrm{CH_3-\overset{CH_3}{\underset{H}{Si_1}}-\underset{a}{CH_2}-\overset{CH_3}{\underset{H}{Si_2}}-\underset{a}{CH_2}-\overset{CH_3}{\underset{H}{Si_1}}-CH_3}$$

5

d centered at 0.11 (12 H), Me(Si_1), $^3J = 3.6$ Hz
d centered at 0.16 (3 H), Me(Si_2), $^3J = 3.6$ Hz

ABXY spectrum { AB spectrum, δ_A −0.26, δ_B −0.21, $|J_{AB}| = 14.1$ Hz (4 H), CH_2(a)
m centered at 4.25 (9 peaks) (2 H), H(Si_1), $^3J \simeq 3.6$ Hz

m centered at 4.28 (8 peaks) (1 H), H(Si_2), $^3J \simeq 3.8$ Hz



$$\mathrm{CH_3-\overset{CH_3}{\underset{H}{Si_1}}-\underset{a}{CH_2}-\overset{CH_3}{\underset{H}{Si_2^{*}}}-\underset{b}{CH_2}-\overset{CH_3}{\underset{H}{Si_2^{*}}}-\underset{a}{CH_2}-\overset{CH_3}{\underset{H}{Si_1}}-CH_3}$$

6

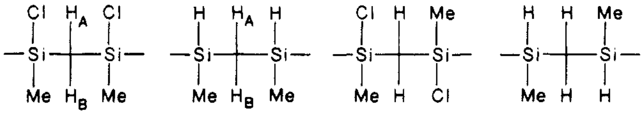
d centered at 0.11 (12 H), Me(Si_1), $^3J \simeq 3.6$ Hz
d centered at 0.18 (6 H), Me(Si_2), $^3J \simeq 3.6$ Hz

ABXY spectrum { AB spectrum, δ_A −0.24, δ_B −0.19, $|J_{AB}| = 14.1$ Hz (4 H), CH_2(a)
m centered at 4.23 (9 peaks) (2 H), H(Si_1), $^3J \simeq 4$ Hz

ABX_2 spectrum { AB spectrum, δ_A −0.205, δ_B −0.096, $|J_{AB}| = 14.2$ Hz CH_2(b)
m centered at 4.28 (8 peaks) (2 H), H(Si_2), $^3J \simeq 3.5$ Hz

s, −0.15, CH_2(b) (meso configuration)

Chart II



AB spectrum ABX$_2$ spectrum A$_2$ spectrum A$_2$X$_2$ spectrum
isotactic sequence syndiotactic sequence

These data are consistent with the 200-MHz ^{1}H NMR spectra of short-chain models such as molecule 5 and 6 and their corresponding chlorinated derivatives.[10] In the case of 6, for example, the diastereotopic methylene protons CH_2 (b) exhibit a complex pattern (ABX_2 and A_2X_2) analogous to the observed spectra of polymers 3 and 4, while these protons gave only a singlet in the chlorinated homologues. This showed that the lithium aluminium hydride reduction was not responsible for producing new stereosequences: while molecule 7 was synthesized by chlorination of 6 according to Scheme IV,[10] the same effects were also observed for this short-chain model.[7]

Scheme IV

$$\underset{\mathbf{6}}{\mathrm{CH_3\text{-}(SiH(CH_3)CH_2)_5SiH(CH_3)}} \xrightarrow{\mathrm{CCl_4/Pd\ catalyst}} \underset{\mathbf{7}}{\mathrm{CH_3\text{-}(SiCl(CH_3)CH_2)_5\text{-}SiCl(CH_3)}}$$

Such observations led us to the conclusion that the substitution of one methyl group per silicon prompted by the action of $Me_3SiCl/AlCl_3$ on the starting polydimethylsilmethylene (Scheme II) proceeded in a nonstereoselective manner. ^{1}H NMR data, 200 MHz, for polysilapropylene 3 are given in Chart III.

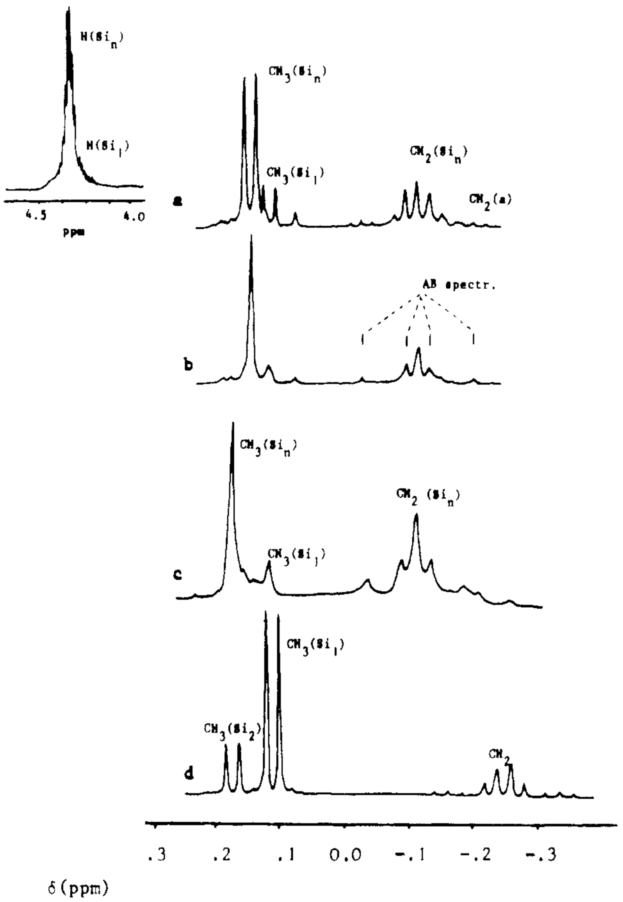
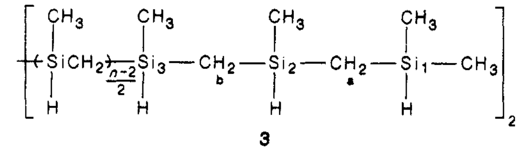


Figure 3. ^{1}H NMR spectra, 200 MHz (solvent, C_6D_6): (a) polycarbosilane 3; (b) polycarbosilane 3 with decoupling; (c) polycarbosilane 4; (d) compound 5.

Chart III
^{1}H NMR Data, 200 MHz, of Polysilapropylene 3; Chemical Shifts (Solvent, C_6D_6) δ (ppm) and Assignments



$$\left[\mathrm{+\!\!\left(\overset{CH_3}{\underset{H}{Si}}CH_2\right)_{\frac{n-2}{2}}\overset{CH_3}{\underset{H}{Si_3}}-\underset{b}{CH_2}-\overset{CH_3}{\underset{H}{Si_2}}-\underset{a}{CH_2}-\overset{CH_3}{\underset{H}{Si_1}}-CH_3}\right]_2$$

3

weak d centered at 0.13, Me(Si_1), $^3J = 3.5$ Hz
very strong d centered at 0.25, Me(Si_n), $^3J = 3.5$ Hz
shoulder (d) at 0.22, Me(Si_2)

ABX_2 spectrum { AB spectrum, $\delta_A = -0.09$, $\delta_B = +0.03$, $|J_{AB}| = 14.2$ Hz, CH_2(n) (isotactic sequences)
m centered at 4.34 (8 peaks), H(Si_n), $^3J = 3.6$ Hz

br s at −0.06, CH_2(n) (syndiotactic sequences)
very weak m centered at 0.18 (two ABXY spectra for CH_2(a,b))

octuplet centered at 4.34, H(Si_n)
weak m (partially overlapped), centered at 4.30, H($Si_{1,2}$)

In contrast with the chlorinated polymer 2, which gave somewhat complex ^{29}Si and ^{13}C spectra, the spectra of 3 and 4 were simple (Figures 4 and 5). In particular, the ^{29}Si spectra exhibited only two resonance peaks readily assigned to the internal and chain-end silicon atoms by comparison with spectra of 5.

The overall conclusion from these results is that these new silicon polymers exhibit NMR behavior different from that of well-known carbon models such as polypropylene or poly(methyl methacrylate). Further investigations of the observed configurational and conformational effects, based on NMR studies of higher homologues of compound 5 and 6, are in progress.

Thermal Behavior of the Polycarbosilane Models. Heating polycarbosilanes 3 and 4 at 350–450 °C in a carefully purged (dry argon) quartz vessel fitted with a

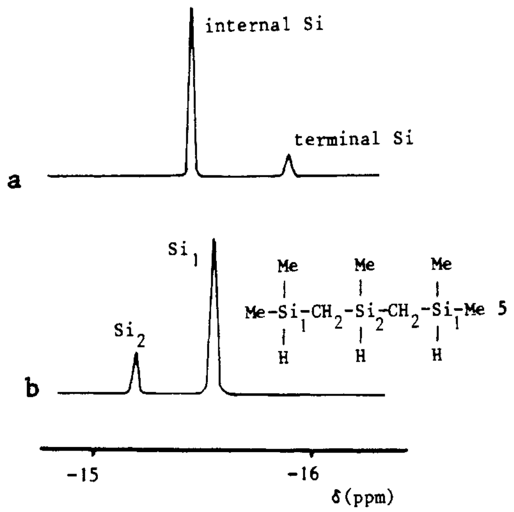


Figure 4. Decoupled ^{29}Si NMR spectra (INEPT technique): (a) polycarbosilane **3**; (b) carbosilane **5**.

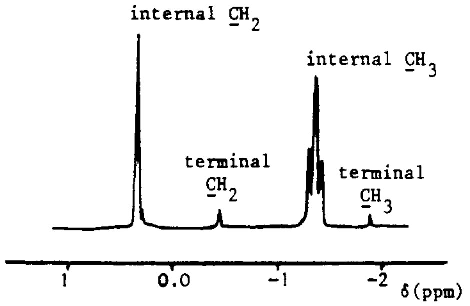


Figure 5. Broad-band decoupled ^{13}C NMR spectrum of polycarbosilane **3**.

reflux condenser resulted in evolution of gas. At the same time, refluxing volatile products were generated, and the resulting mixture slowly solidified. Whenever this thermolysis was prolonged, solid which would not melt and only a small amount of viscous liquid were mainly obtained. These phenomena resemble those observed in Yajima's thermolysis. Also, the evolved gases are the same[13] and the volatile products are mainly carbosilanes or short-chain polycarbosilanes.

GC–MS[14] allowed the identification of the main components of this gas: H_2, CH_4, CH_3CH_3, $MeSiH_3$, Me_2SiH_2, Me_3SiH, and Me_4Si. Small amounts of $CH_2{=}CH_2$ and SiH_4 also were detected. The chromatogram, obtained at the end of the thermolysis, shows these different components (Figure 6).

Pyrolysis of **3** at 1000 °C under an argon flow resulted only in poor ceramic yield (5%). This was due to the linear structure of **3**. The cleavage of Si–CH_2 bonds gave volatile products which were eliminated since they could not be trapped by a condenser, as during the thermolysis at atmospheric pressure in an open vessel. On the other hand, the Japanese PCS, which possesses a strongly branched structure, is an effective Si–C precursor.

Further results concerning mechanistic considerations on Yajima's thermolysis, derived from identification and kinetic studies of the gases evolved during the thermal transformations of **3** and **4**, will be reported in a forthcoming paper.

Conclusion

New linear functional polycarbosilanes, $-(MeHSiCH_2)_n-$ and $-(MeDSiCH_2)_n-$ have been synthesized by using a poly[(methylchlorosilylene)methylene] as the starting material. These polymers can be considered as adequate models for Yajima's theoretical linear polysilapropylene. Their viscous state clearly demonstrates the branched structure of the Japanese polymers, and their normal behavior should allow a decisive mechanistic approach of the transformation PS → PCS. Finally, multinuclear NMR investigations of their structure and conformation lead to problems thus far unknown in carbon polymer chemistry.

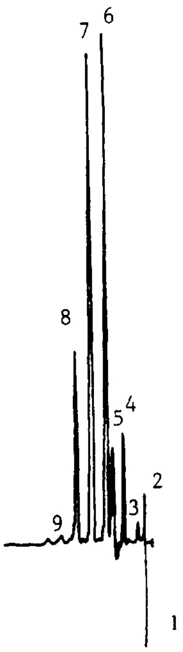


Figure 6. Chromatogram of the gas from the thermolysis of **3** (on Porapak QS column): H_2 (1); Ar (2); CH_4 (3); C_2H_6 (4); H_2O (5); $MeSiH_3$ (6); Me_2SiH_2 (7); Me_3SiH (8); TMS (9).

Experimental Section

Solvents. Pentane was distilled before use (bp 35–37 °C). Ether was dried over $LiAlH_4$ and distilled under nitrogen.

Apparatus. All the reaction vessels were thoroughly dried and purged with inert dried gas before use.

Hydrides. Recently purchased $LiAlH_4$ and $LiAlD_4$ were utilized to effect the reductions of poly[(methylchlorosilylene)methylene].

Characterization. Polymer molecular weights were determined by gel permeation chromatography (GPC) using four μ-styragel columns (porosity ranges of 500, 10^3, 10^4, and 10^5 Å) and THF as the eluent at a flow rate of 1 mL/min. The detection system used was a Waters Associates Differential Refractometer R401.

Proton NMR spectra, 60 MHz, were determined with a Hitachi Perkin-Elmer R24B spectrometer, on polymer solutions in CCl_4 or $DCCl_3$. Proton (200 MHz) ^{29}Si (39.76 MHz), and ^{13}C NMR spectra (50 MHz) were determined with a Bruker AC 200 model, on polymer solutions in deuteriochloroform or benzene-d_6, using TMS as the external reference.

Infrared spectra were examined in the region 4000–600 cm^{-1} (product films between NaCl plates), on a Perkin-Elmer 1420 spectrometer.

Pyrolysis of **3** was performed on a thermogravimetric analyzer Perkin-Elmer TGS 2: heat rate, 5 deg/min; argon flow rate, 60 mL/min.

Synthesis. The following descriptions are typical.

$-(SiH(CH_3)CH_2)_n-$ (3). Into a 500-mL three-necked flask equipped with a magnetic bar, fitted with a dropping funnel, a thermometric well, and a condenser cooled by decalin at −10 °C, and connected to a $CaCl_2$ column, $LiAlH_4$ (3.19 g, 0.081 mol) and dried ether (100 mL) were successively introduced. Then a solution of polymer **2** (20 g, 0.216 mol based on the formula $-(SiCl(CH_3)CH_2)_n-$)[7] in dried ether (75 mL) was added dropwise over 2 h, the mixture being stirred under argon. At this stage, the mixture was grey-green while its temperature had risen to 30 °C. The mixture was then refluxed for 20 h before cooling, under argon.

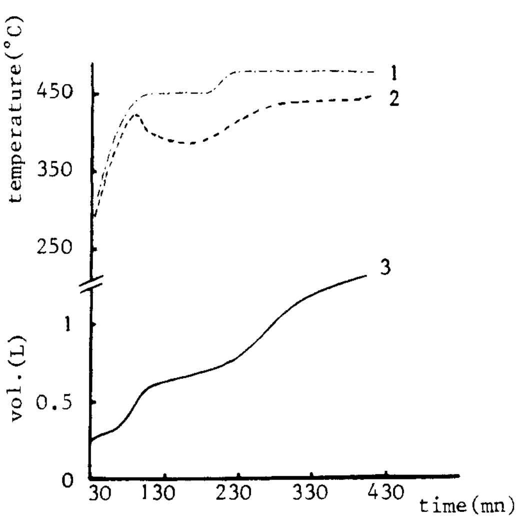


Figure 7. Thermolysis of polycarbosilane 3: (1) temperature of the bath; (2) temperature of the reaction mixture; (3) gas evolution.

Ether was eliminated under reduced pressure and the remaining grey solid was washed with pentane. The resulting mixture was filtered off under argon atmosphere, to yield a cloudy, pale yellow solution. Addition of pentane onto the insoluble solid and subsequent filtration were repeated twice more and then the whole filtrate was concentrated at room temperature, under reduced pressure (1 mmHg). From this, a yellow liquid and, on its surface, a pale yellow mobile oil were obtained. Dissolving this mixture in a few milliliters of pentane resulted once again in a cloudy solution. Centrifugation (10^4 rpm) for 30 min yielded a liquid with two phases, the upper layer (polysilapropylene in pentane) being recovered by careful siphoning. The complete procedure was repeated twice again with the remaining liquid, and the total of the pentane solutions was concentrated under reduced pressure (1 mmHg) at 20 °C. A small amount of the lower phase, however, still remained in the yellow oil, so it was redissolved in pentane, centrifuged, separated, and concentrated in order to purify the oily polymer. IR and NMR spectroscopy identified this last compound as the expected polymer and the liquid, insoluble in pentane, as a complex of Et_2O and chloroaluminium hydrides.

The above workup yielded polycarbosilane 3 in 96.5% yield (expected weight 12.55 g, based on the formula $-(SiH(CH_3)CH_2)_n-$; obtained 12.1 g).

Elemental anal. Calcd for $-(SiH(CH_3)CH_2)_n-$: C, 41.34; H, 10.33; Cl, 0; Si,[13] 48.33. Calcd for $(CH_3)_2HSiCH_2-(SiH(CH_3)-CH_2)_{23}-SiH(CH_3)_2$: C, 41.67; H, 10.56; Cl, 0. Found: C, 41.6; H, 10.35; Cl, 0.14; Si,[13] not given.

$-(SiD(CH_3)CH_2)_n-$ (4). $LiAlD_4$ (3.49 g, 0.081 mol) and dried ether (75 mL) were introduced into the apparatus previously described. A solution of polymer 2 (20 g, 0.216 mol) in ether (75 mL) was then slowly added to the mixture over 1.5 h while maintaining a constant stirring under argon. The temperature rose to 30 °C and the mixture turned grey. Once the addition was complete, the mixture was refluxed for 20 h. The preceding procedure allowed the separation of the orange liquid complex from its accompanying orange oil: this latter compound, identified as the expected deuteriated polymer, was obtained in 98% yield (expected weight 12.78 g, based on the formula $-(SiD(CH_3)CH_2)_n-$; obtained 12.5 g).

Thermolysis of 3 and 4. Into a 250-mL three-necked quartz vessel fitted with a thermometric well, an inert gas inlet connected to an argon-vacuum line, a reflux condenser joined to a gas counter, and to a filled 2-L flask in order to collect the gas for GC–MS analysis, polymer 3 (9 g) was introduced under an argon atmosphere. Then the flask was heated in a fluidized bath to 500 °C for 3 h, according to curve 1 (Figure 7). When the internal temperature reached 350 °C, a large quantity of gas was at first evolved, accompanied by white smoke, before refluxing liquid. The quantity of evolved gas and the internal temperature gradually increased (see curves 2 and 3, Figure 7) as the thermolysis proceeded, thus decreasing the amount of low boiling point products and converting the mixture into species which would not melt. After heating for 7 h, the mixture resulted in an unmeltable polymer, accompanied by a few drops of a viscous liquid. Deduction of dead volumes allowed the actual amount of gas to be estimated as 118 mL/g, whereas the weight loss was calculated as 4.6 g (remaining products in the flask, 4.4 g). After dissolution in pentane, the resulting solution was centrifuged, thus separating the mixture into a yellow gelatinous layer and a pale yellow solution. Eliminating the solvent from each of the two phases under reduced pressure yielded an orange yellow solid (2.6 g) and a viscous oil (1.7 g). Another run by the same procedure using 8.7 g gave the following results: weight loss, 1.2 g; gas, 76 mL/g; insoluble polymer, 1.2 g; viscous oil, 2.4 g; liquid, 3.9 g (removed by distillation at 300 °C (1 mmHg)).

GC–MS coupling technique led to the unambiguous identification of the main components of the gaseous mixture: H_2, CH_4, CH_3CH_3, $MeSiH_3$, Me_2SiH_2, and Me_3SiH (listed with respect to their retention times on a Porapak QS column) (Figure 6).

Similarly, 7.15 g of polymer 4 decreased by 2.4 g after thermolysis at 500 °C (evolved volume, 68 mL/g). The usual workup resulted in a white liquid (3.7 g) and a yellow solid (1.0 g).

Acknowledgment. We are indebted to Rhône-Poulenc Industries for their generous gift of 1,1,3,3-tetramethyl-1,3-disilacyclobutane. We are also grateful to Société Européenne de Propulsion (SEP) and Centre National de la Recherche Scientifique for their financial assistance.

Registry No. 2, 111113-80-5; 3, 62306-27-8; 4, 111113-81-6.

References and Notes

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(13) Silicon classical titration is usually aberrant in the polycarbosilane series.
(14) Chromatograph Intersmat IGC 121M equipped with a Poparak QS column, coupled with a mass spectrometer VG micromass AG-F (70 eV; 200 μA; 4 kV; source at 170–220 °C).