are replaced by stronger ones are predicted to be thermodynamically favorable. Indeed, just such an ordering of metathesis patterns has been observed experimentally.[8a,b]

Finally, the present data provide information, with use of $D(\mathrm{Cp_3U{-}R})/D(\mathrm{Cp'_2Sm{-}R})$ parallels,[11b] on the viability of divalent samarium-mediated oxidative-addition routes to heterobimetallic compounds (eq 44). It is evident that

$$2\mathrm{Cp'_2Sm} + \mathrm{HMPh_3/HM'(CO)_2Cp} \rightarrow \mathrm{Cp'_2Sm{-}MPh_3/M'(CO)_2Cp} + \tfrac{1}{2}(\mathrm{Cp'_2SmH})_2 \quad (44)$$

$$\Delta H_{\mathrm{calcd}}\ (\mathrm{kcal/mol}) \approx -11\ (\mathrm{Si}),\ -19\ (\mathrm{Ge}),\ -23\ (\mathrm{Sn}),\ -31\ (\mathrm{Fe}),\ -33\ (\mathrm{Ru})$$

such transformations are favorable,[40] with the predicted exothermicity increasing as $D(\mathrm{M/M'{-}H})$ falls. Experimental evidence supporting this analysis comes from the observation that $\mathrm{Cp'_2Sm}$ and $\mathrm{Cp'_2Sm(THF)_2}$ are effective precatalysts for the dehydrogenative polymerization of silanes (see Scheme I) and that trivalent samarium complexes are rapidly formed upon mixing of the reagents.[35a]

Conclusions

This study provides the first detailed information on absolute metal-metal bonding energetics for an archetypical series of heterobimetallic complexes—uranium-group 14 element and uranium-transition-metal carbonyl. The bond enthalpies are found to be rather modest and to span a relatively narrow range compared to $D(\mathrm{U{-}X})$ values for X = a first-row or more electronegative element. A major chemical consequence of these trends is that relative reaction thermodynamics are far more sensitive to bond enthalpies in other reactants and in products than in the heterobimetallic complex. Nevertheless, these linkages can access a rich diversity of known or thermodynamically plausible stoichiometric and catalytic reaction patterns.

Acknowledgment. We are grateful to the NSF for support of this research under Grant No. CHE8800813. M.P. thanks the CNR (Rome) for a postdoctoral fellowship. We also thank Prof. C. D. Hoff for disclosure of data in advance of publication and Dr. C. M. Forsyth for helpful discussions.

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(40) This analysis assumes Sm–Fe and Sm–Ru bond formation rather than isocarbonyl (e.g., Sm–OC–M′) bond formation, which could be more exothermic. For relevant examples of the latter compounds, see: Boncella, J. M.; Andersen, R. A. *Inorg. Chem.* **1984**, *23*, 432–437 and references therein.

Poly(vinylsilane): A Precursor to Silicon Carbide. 1.[1] Preparation and Characterization

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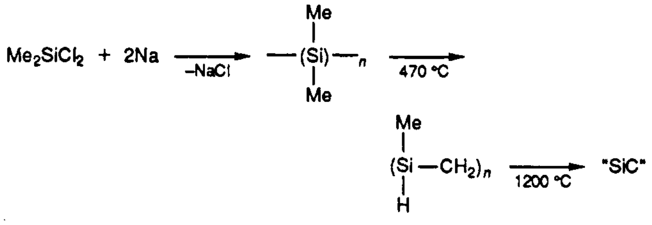
Poly(vinylsilane), $(\mathrm{H_2SiC_2H_4})_n$, has been synthesized by a hydrosilylation route. Depending on the experimental conditions, the average molecular weight varies from 640 to 5500. The structure of these polymers, which was investigated by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, is explained on the basis of the two possible modes of addition in the hydrosilylation reaction. Pyrolysis of either low or high molecular weight polymers gives similar ceramic yields (32–40%), which are higher than for non-cross-linked poly(silapropylene), $(\mathrm{CH_3SiHCH_2})_n$. This result emphasizes the role of the latent SiH functions in the pyrolysis step.

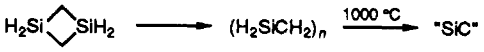
Introduction

Since the pioneering work of Yajima demonstrated that polycarbosilanes were convenient precursors to silicon carbide fibers,[2] there has been considerable interest focused on polysilanes and polycarbosilanes as polymeric precursors. The Yajima process (Scheme I) implies preparation of insoluble poly(dimethylsilane) and its thermal rearrangement to a soluble, functional poly(silapropylene). The poly(silapropylene) is melt, spun, and cured by heating in air to obtain infusible fibers, which are then pyrolyzed in argon to give silicon carbide fibers.[2] However, the polycarbosilane obtained by the thermal rearrangement[3] is not perfectly linear due to a certain degree of cross-linking.[4]

Scheme I



Scheme II



In order to correlate the structure of the preceramic polymer and its thermal behavior, it is necessay to synthesize polycarbosilanes of well-defined structure. To this end, linear poly(silapropylene), $(\mathrm{CH_3SiHCH_2})_n$, has been prepared by Dunoguès[5] and Interrante[6] using the ring-opening polymerization of substituted 1,3-disilacyclobu-

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(1) Preliminary communication: Boury, B.; Carpenter, L.; Corriu, R. *Angew. Chem.* **1990**, *7*, 785.

(2) (a) Yajima, S.; Hasegawa, Y.; Hayashi, J.; Iimura, M. T. *J. Mater. Sci.* **1978**, *13*, 2569. (b) Hasegawa, Y.; Iimura, M. T.; Yajima, S. *J. Mater. Sci.* **1980**, *15*, 720.

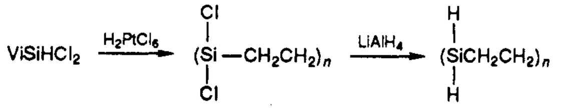
(3) Shiina, K.; Kumada, M. *J. Org. Chem.* **1958**, *23*, 139.

(4) Hasegawa, Y.; Okamura, K. *J. Mater. Sci.* **1986**, *21*, 321.

(5) Bacque, E.; Pillot, J. P.; Birot, M.; Dunoguès, B. *Macromolecules* **1988**, *21*, 34.

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

Scheme III



$$\mathrm{ViSiHCl_2} \xrightarrow{\mathrm{H_2PtCl_6}} (\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{Si}}}-\mathrm{CH_2CH_2})_n \xrightarrow{\mathrm{LiAlH_4}} (\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{Si}}}\mathrm{CH_2CH_2})_n$$

tane.[7] Thermolysis of poly(silapropylene) to 1000 °C gives poor ceramic yields, ranging from 5 to 10%, depending on the molecular weight of the starting poly(silapropylene).[5,6] In fact, linear polymers give negligible ceramic yields because of reversion reactions leading to volatile molecules during pyrolysis.[8,9] However, the ceramic yield of poly(silapropylene) can be greatly increased (60%) by thermal treatment at 400 °C, which promotes cross-linking of the polymer.[6]

Such cross-linking may be improved by latent functions such as Si–H bonds. Indeed poly(silaethylene), $(H_2SiCH_2)_n$, prepared by ring-opening polymerization of 1,3-disilacyclobutane (Scheme II) gives an 85% ceramic yield.[10] Though some doubts exist as to the linearity of this polymer,[6] the difunctionality of the silicon atoms seems to be responsible for the good ceramic yield.

Thus, our approach to this problem was to prepare a polycarbosilane containing two functional groups at silicon with the same stoichiometry as poly(silapropylene) and a well-defined structure, in order to study the different steps controlling the polymer-to-ceramic conversion.

A catalytic way to this goal is provided by the polymerization of vinylsilicon hydride via hydrosilylation according to Scheme III.

Catalytic hydrosilylation of substituted vinylhydrosilane has been reported to give cyclic dimers and linear oligomers with a degree of polymerization from 3 to 11.[11,12] The structure of the products results from α and β hydrosilylation leading to two kinds of linkage: $-Si-CH(CH_3)-Si-$ and/or $-Si-CH_2CH_2-Si-$.

However, hydrosilylation of vinyldichlorosilane was reported to lead only to the polymeric structure $(Cl_2SiCH_2CH_2)_n$ due to β hydrosilylation.[12] This polymer was easily reduced to $(H_2SiCH_2CH_2)_n$ by $LiAlH_4$ in ether.[12] Thus, by catalytic hydrosilylation, it would be possible to synthesize a highly functional linear polycarbosilane with the same stoichiometry as Yajima's, so avoiding the polysilane step.

In this paper, we report a polymerization procedure leading to an improvement in the molecular weight of the poly(vinylsilane) whose structure is investigated by NMR spectroscopy. The potential of this polymer as a precursor to SiC is pointed out.

Experimental Section

General Comments. All manipulations were carried out under argon in oven-dried glassware. All solvents were distilled from appropriate drying agents prior to use.

Vinyldichlorosilane was prepared by a redistribution reaction[13] and redistilled over magnesium turnings before use.

$H_2PtCl_6{\cdot}6H_2O$ in 2-ethylhexanol was a gift from Rhône-Poulenc.

Table I. Influence of the Solvent and the Concentration of Catalyst on the Average Molecular Weight of Poly(vinylsilane)

$10^4 \times$ [H_2PtCl_6], M	solvent	vol % solvent	$\bar{M}_n$[a]	$\bar{M}_w$[a]	$\bar{D}_p$[b]	yield
2.0	hexane	50	960	1910	17	64
2.5	hexane	35	1670	2360	29	46
2.0	$F_2ClCCFCl_2$	30	640	845	11	53
4.4	$F_2ClCCFCl_2$	50	1040	1980	18	76
2.5	PhCl	50	2600	3960	45	51
5.0	PhCl	50	3960	7095	83	79
7.5	PhCl	60	5500	17200	95	78
5	neat		1330	2860	23	60

[a] Determined by GPC. [b] Average degree of polymerization.

NMR spectra were obtained by using Bruker AW 80, AC 250, and AM 300 spectrometers with $CDCl_3$ as solvent and internal standard (chemical shifts, δ, are relative to TMS). Three sequences have been used: inverse-gated decoupling (to avoid negative NOE) for the ^{29}Si nucleus, powergated broad-band decoupling (to minimize dielectric heating) for the ^{13}C nucleus, and proton-coupled or -decoupled DEPT for the two nuclei.

IR spectra were obtained by using a Perkin-Elmer 298 infrared spectrophotometer.

Mass spectra were recorded with a Jeol JMS-D 100 spectrometer (electronic impact).

Polymer molecular weights were determined by gel permeation chromatography using four μ styragel columns (porosity range 100, 500, 10^3, 10^4 Å) calibrated with polystyrene standards and with THF as eluent at a flow rate of 0.9 mL/min.

Elemental analyses were carried out by "le Service Central des Analyses" of CNRS (France).

Preparation of Poly(vinylsilane). A double-walled reactor, thermostated at 45 °C, was equipped with a mechanical stirrer, a thermometric cell, and a condenser cooled at 0 °C. Vinyldichlorosilane (88.47 g, 0.696 mol) was added to 63 mL of the relevant dried solvent as shown in Table I. H_2PtCl_6 (from 1.44×10^{-5} to 10.8×10^{-5} mol) diluted in 10 mL of solvent was introduced dropwise by means of a syringe pump. After an initial highly exothermic period, the temperature reverted to that set by the thermostat. The stirring was maintained overnight. A white, viscous suspension of solids was obtained. The whole reaction mixture was then added dropwise to a suspension of $LiAlH_4$ (29.1 g) in dry ether (766 mL) cooled to 0 °C. The mixture was warmed to room temperature, refluxed for 6 h, and finally cooled to 0 °C. Then 2 × 29 mL of water was added until H_2 evolution had stopped. Salts were removed by filtration. The filtrate was dried over $MgSO_4$ and filtered through diatomaceous silica. Ether was distilled off under vacuum, and the product was further evacuated at 40 °C under 0.1 mmHg. The product was a viscous, moisture- and temperature-sensitive liquid. On standing at room temperature, it changed to a gel in a few hours in air and in a month under nitrogen. It could be keep under nitrogen for several months at −25 °C without change.

Anal. Found: Si, 49.04; C, 39.99; H, 10.97. Calcd: Si, 48.30; C, 41.30; H, 10.40.

IR spectroscopy (neat) [wavenumber, cm^{-1} (assignment[14])]: 2940 s (CH_3), 2900 s (CH_2), 2860 s (CH), 2120 vs (Si–H), 1460 (CH_2), 1407 (CH_3), 1138 (CH), 1104, 1060 (CH_2), 1004 (CH), 937, 830 (SiH), 765, 712 (SiC).

Filtration of the suspension of poly(dichlorovinylsilane) obtained by using $F_2ClCCFCl_2$ as solvent and 2×10^{-5} and 4×10^{-5} mol of Pt led to 60% of insoluble solid and 40% of a very viscous oil. Reduction of the solid fraction gives poly(vinylsilane) with $M_n = 1300$ and $M_w = 3200$, and that of the viscous fraction affords the polymer with $M_n = 840$ and $M_w = 2400$.

Separation of Cyclic Dimers. The solvent used in the preparation of poly(vinylsilane) was trapped at -192 °C and distilled at atmospheric pressure. The remaining product (1.21 g) was analyzed by IR and NMR spectroscopy and mass spectrometry.

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MS (relative intensity): m/z 118 (4.93), 117 (10.14), 116 (62), 88 (100), 60 (31); isotopic contribution calculated for $Si_2C_4H_{12}$ (with m/z 116 (62)), m/z 118 (4.45), 117 (9.05).

IR (cm^{-1}): 2940, 2900, 2860, 2120, 1460, 1407, 1138, 1104, 1060, 1004, 937, 830, 765, 712.

NMR: see Table IV.

Separation of Cyclic Trimers. The cyclic trimers were isolated by heating of poly(vinylsilane) at 180 °C. A small fraction distilled before the polymer turned to a solid.

MS (relative intensity): m/z 177 (2.04), 176 (12.5), 175 (22.97), 174 (100), 146 (60.0), 115 (53.4), 99 (17.6), 87 (37.2), 69 (18.3), 57 (24.2); isotopic contribution calculated for $Si_3C_6H_{18}$, m/z 177 (1.85), 176 (12.21), 175 (22.32), 174 (100).

IR (cm^{-1}): 2940, 2860, 2120, 1407, 1138, 1104, 1004, 937, 830, 765, 712.

NMR: see Table V.

The proportion of trimers formed in the reaction has been determined by GPC to be between 2 and 10% depending on dilution.

Preparation of Divinyldichlorosilane. In a 3-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel, 200 mL of a 1 M solution of vinylmagnesium bromide in THF (Aldrich) was added to a solution of 0.25 mol of vinyltrichlorosilane in 500 mL of pentane cooled at −15 °C. After the end of the addition the reaction mixture was stirred at room temperature for 2 h and then refluxed for 3 h. After filtration of the salts, distillation using a spinning-band column led to 6.8 g of divinyldichlorosilane. Bp = 118–119 °C (lit.[15] bp = 118–119 °C).

Preparation of Oligo(vinylsilane) SiH_2Vi-Terminated 1. In a 3-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel were placed 12 g (0.09 mol) of vinyldichlorosilane, 3.2 g (0.02 mol) of divinyldichlorosilane, and 13 mL of 1,2-dichloroethane. A 10^{-6}-mol amount of $H_2PtCl_6 \cdot 6H_2O$ was then added. An exothermic reaction started after few minutes. When the reflux had stopped, the solution was heated to 60 °C for 10 h. The solvent was evaporated in vacuum. The product was reduced by $LiAlH_4$ and isolated following the usual work up as described above.

Yield: 82%. GPC: M_n = 500, M_w = 740.

^1H NMR (δ, ppm): 6.1 (m), 5.9 (m, vinyl protons, 0.68 H); 3.9 (b, 0.46 H), 3.75 (b, SiH_2, 2 H); 1.25 (d, J = 7 Hz, CH_3, 0.66 H); 0.8 (b, CH_2, 3.57 H); 0.4 (m, CH, 0.22 H).

Preparation of Oligo(vinylsilane) SiH_3-Terminated 2. The same procedure was used starting from 0.07 mol of vinyldichlorosilane, 0.014 mol of trichlorosilane, and 6×10^{-6} mol of chloroplatinic acid. After the usual work up, 3.5 g of product was obtained (yield 71.6%).

GPC: M_n = 890, M_w = 1460.

^1H NMR (δ, ppm): 3.75 (b, 0.39 H), 3.5 (b, SiH_2, 2 H); 1.25 (d, J = 7 Hz, CH_3, 0.64 H); 0.8 (b, CH_2, 3.40 H), and 0.4 (m, CH, 0.21 H).

Results and Discussion

(1) Polymerization. Our preliminary efforts followed Nametkin's procedure,[12] which involves heating neat vinyldichlorosilane in the presence of $H_2PtCl_6 \cdot 6H_2O$. A very exothermic reaction occurred after an induction period. Deposition of metallic Pt and formation of only low molecular weight oligomers were observed. In order to better control the reaction, the monomer was diluted with a solvent and the reaction flask was thermostated (see Experimental Section). The poly(dichlorovinylsilane) so obtained was a very reactive product with respect to hydrolysis. It was therefore immediately reduced by $LiAlH_4$ in diethyl ether to yield poly(vinylsilane), which is more easily characterized.

As shown in Table I, the nature of the solvent dramatically changes the average molecular weight of the polymer. In a good solvent such as chlorobenzene, a molecular weight of up to 5500 could be obtained. In contrast, in hexane or 1,1,2-trichlorotrifluoroethane only oligomers were obtained. The concentration of the monomer has only a small effect on the molecular weight in the range of 35–50 mol %. However, without solvent the molecular weight is lower. The molecular weight increases with the amount of catalyst used. Thus, the average molecular weight of poly(vinylsilane) so obtained varies from 650 to 5500, which corresponds to a variation in the degree of polymerization from 11 to 95 depending on the solvent and the amount of catalyst used.

Table II. Chemical Shifts (δ, ppm) of Oligo(vinylsilane)

^1H	^{13}C	^{29}Si	
6 (vinyl)	136 (vinyl)	−17.8	triads
3.9	131	−19.9	
3.75 (Si–H)		−21.8	
3.5		−28.9	
1.25 (CH_3)	12.6 (CH_3)	−31.8	
0.80 (CH_2)	3.5 (CH_2)	−52.8	
0.4 (CH)	−4.5 (CH)	−55	

Table III. ^{29}Si Chemical Shifts (ppm) of Models 1 and 2

1	−17.8, −19.8, −21.9, −28.9, −31.8
2	−17.8, −19.8, −21.9, −52.8, −55.0

The reduction step is assumed to have no effect on the average degree of polymerization (D_p) of the polymer because $LiAlH_4$ does not cleave Si–C or C–C bonds. So the D_p measured results only from the hydrosilylation step. In fact, the molecular weight obtained does not exceed 5500. This may be due to the insolubility of poly(dichlorovinylsilane). The side reactions known in the hydrosilylation reaction, i.e., the reduction of the catalyst to Pt metal and/or the hydrogenation of the vinyl group,[16] may be involved too.

(2) Characterization. Poly(vinylsilane) as well as the low-boiling cyclic oligomers were characterized by NMR spectroscopy.

Poly(vinylsilane). The NMR spectra of high molecular weight poly(vinylsilane) (M_n = 4100, D_p = 70.5) are reported in Figures 1–3.

The ^1H NMR spectrum (300 MHz) (Figure 1) shows broad signals at 4.2, 1.3, 0.8, and 0.3 ppm. The proton-coupled ^{13}C NMR spectrum (Figure 2) is composed of three signals at 12.6 ppm (quadruplet), 3.9 ppm (triplet), and −4.5 ppm (doublet). The multiplicities observed, as well as the ^1H chemical shifts, are consistent with CH_3, CH_2, and CH groups, respectively, corresponding to α- and β-hydrosilylation modes.

The ^{29}Si NMR spectrum in Figure 3a shows three signals at −17.8, −19.9, and −21.8 ppm. The two major signals correspond to Si atoms bearing two protons, as shown by the proton-coupled spectrum (Figure 3b).

The multiplicity agrees with the presence of three different triads resulting from α and β hydrosilylation shown in (1).

$$\begin{array}{c} SiH_2CH_2CH_2SiH_2CH_2CH_2SiH_2 \text{ (A)} \\ SiH_2CH(CH_3)SiH_2CH_2CH_2SiH_2 \text{ (B)} \\ SiH_2CH(CH_3)SiH_2CH(CH_3)SiH_2 \text{ (C)} \end{array} \tag{1}$$

Oligo(vinylsilane). The NMR spectra of oligo(vinylsilane) (M_n = 1040, D_p = 18) show additional signals due to the end groups (Table II). The chemical shifts of these end groups were assigned by using models bearing the same end group SiH_3 or SiH_2Vi. They were prepared by cohydrosilylation of vinyldichlorosilane with 0.2 equiv of

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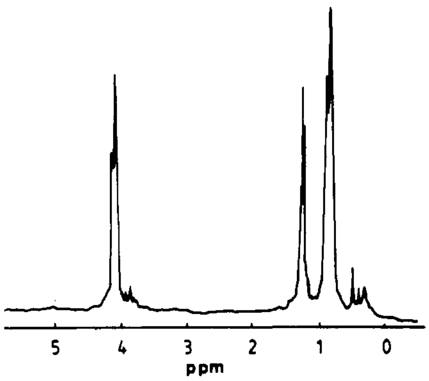


Figure 1. ^1H NMR spectrum of poly(vinylsilane).

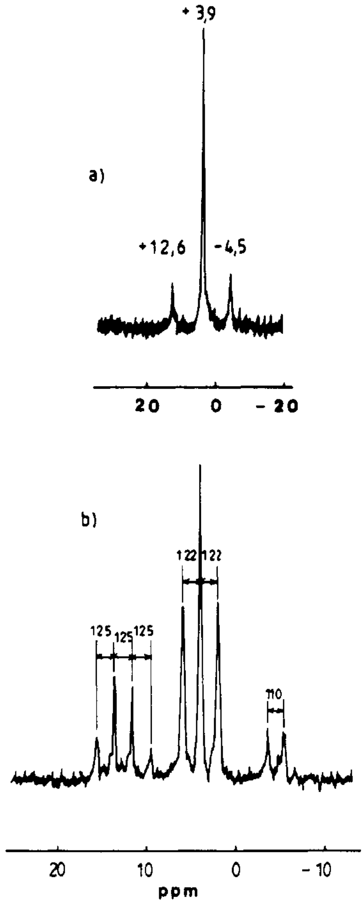


Figure 2. ^{13}C NMR spectra of poly(vinylsilane): (a) ^1H decoupled; (b) ^1H coupled (DEPT sequence).

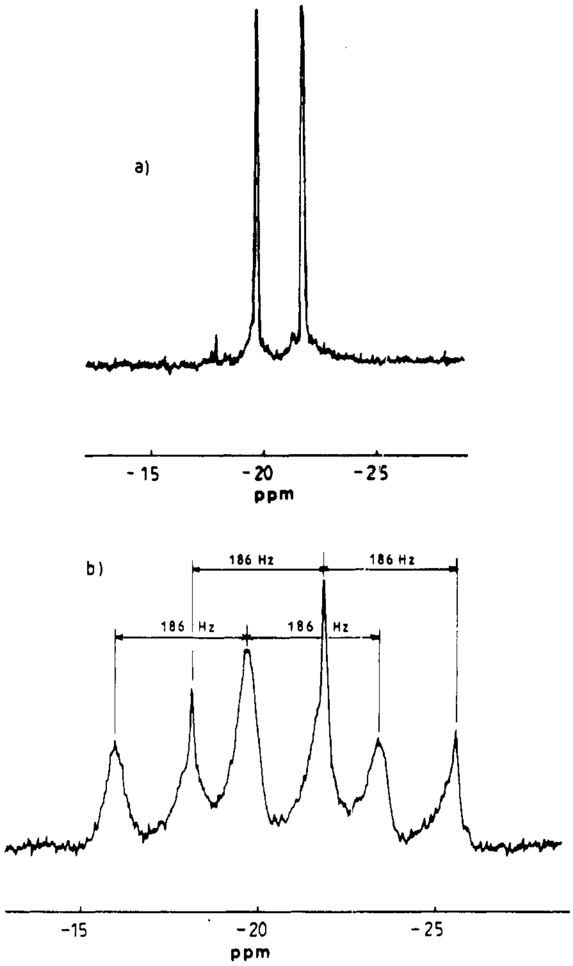
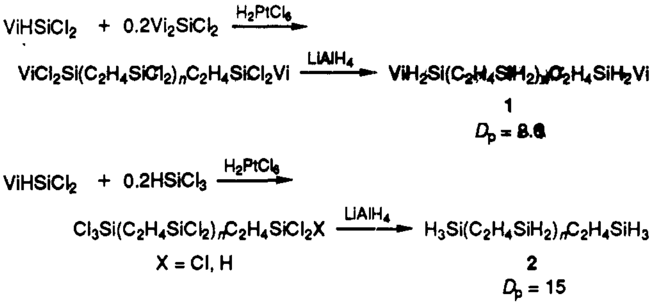


Figure 3. ^{29}Si NMR spectra of poly(vinylsilane): (a) ^1H decoupled; (b) ^1H coupled (DEPT sequence).

Scheme IV



$$ViHSiCl_2 + 0.2Vi_2SiCl_2 \xrightarrow{H_2PtCl_6}$$

$$ViCl_2Si(C_2H_4SiCl_2)_nC_2H_4SiCl_2Vi \xrightarrow{LiAlH_4} ViH_2Si(C_2H_4SiH_2)_nC_2H_4SiH_2Vi$$

1

$D_p = 8.6$

$$ViHSiCl_2 + 0.2HSiCl_3 \xrightarrow{H_2PtCl_6}$$

$$Cl_3Si(C_2H_4SiCl_2)_nC_2H_4SiCl_2X \xrightarrow{LiAlH_4} H_3Si(C_2H_4SiH_2)_nC_2H_4SiH_3$$

X = Cl, H

2

$D_p = 15$

end chain reagents $HSiCl_3$ or Vi_2SiCl_2, as shown in Scheme IV.

The reduction of the chlorinated oligomers led to the oligomers 1 and 2 possessing the corresponding end groups: $SiViH_2$ for 1, and SiH_3 for 2. The ^{29}Si chemical shifts of oligo(vinylsilane) $SiViH_2$-terminated 1 and SiH_3-terminated 2 are reported in Table III. The ^{29}Si signals at −52.8 and −55 ppm are due to SiH_3 end groups. The ones at −28.9 and −31.8 ppm are assigned to SiH_2Vi end groups.

The two possible addition modes of the SiH bonds on the vinyl groups induce a triad effect for the middle groups and two signals for the end groups ($CH(CH_3)$-SiH_2R and CH_2-CH_2-SiH_2R; R = H, Vi).

Here the hydrosilylation occurs mainly at the β carbon, as suggested by the integration of the ^1H NMR peaks of the CH_3, CH_2, and CH groups. Moreover, the ^{29}Si NMR signal at $\delta = -19.8$ ppm is smaller than the one at $\delta = -21.9$ ppm. Accordingly, we can assume that the signal at −21.9 ppm corresponds to the triad A ($SiH_2CH_2CH_2SiH_2CH_2CH_2SiH_2$), the one at −19.8 ppm to the triad B, and the last one at −17.8 ppm to the triad C ($SiH_2CH(CH_3)SiH_2CH(CH_3)SiH_2$).

A similar assignment may be postulated for the end groups from the lower intensity of the downfield signals:

$-CH(CH_3)SiH_3$, $\delta = -52.8$ ppm

$-CH_2CH_2SiH_3$, $\delta = -55$ ppm

$-CH(CH_3)SiH_2Vi$, $\delta = -28.9$ ppm

$-CH_2CH_2SiH_3$, $\delta = -31.8$ ppm

Conversely, only one mode of hydrosilylation occurs in the case of allylhydrosilanes, leading to the formation of ($CH_2CH_2CH_2SiR_2$) units.[17-19]

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Table IV. Chemical Shifts of Cyclic Dimers

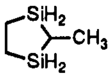
δ, ppm		
^{1}H	^{13}C	^{29}Si
3.75 (SiH_2, b, 4 H)	13.6 (CH_3)	−16 (t, J_{SiH} = 192 Hz)
1.25 (CH_3, d, J = 7.5 Hz, 2 H)	4.7 (CH_2)	
1.05 (CH_2, b, 5.33 H)		−32.9 (t, J_{SiH} = 187 Hz)
0.52 (CH, m, 0.66 H)	−5.65 (CH)	

Table V. Chemical Shifts of Cyclic Trimers

δ, ppm		
^{1}H	^{13}C	^{29}Si
3.75 (SiH_2, b, 2 H)	12.25 (CH_3, q, J_{CH} = 128 Hz)	−15.7
1.25 (CH_3, d, J = 8.4 Hz, 3 H)	−4.43 (CH, d, J_{CH} = 117 Hz)	−17.4
0.37 (CH, m, 1 H)		

Cyclic Oligomers. It was reported[11,12] that polymerization of vinylhydrosilane yields two cyclic dimers (1–20% yield). We isolated these low-boiling cyclic dimers by solvent distillation under reduced pressure after the reduction of the polymeric mixture. Distillation of the solvent at atmospheric pressure gave a small amount of product (3% yield based on the monomer).

The IR spectrum does not show any bands corresponding to end groups (SiH_3 or vinyl). The molecular weight determined by mass spectroscopy is 116, which corresponds to cyclic dimers. The NMR chemical shifts are reported in Table IV. The NMR spectra agree with the formation of six-membered- and five-membered-ring dimers:

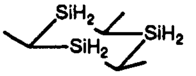


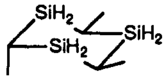
The integration of the ^{1}H NMR spectrum shows that the proportion of five-membered-ring dimer is 66% of the mixture. Since the signal at −16 ppm is the more intense one, we can attribute it to the five-membered ring, and the one at −32.9 ppm can be attributed to the six-membered-ring dimer.

We were able to isolate another cyclic oligomer by distillation of poly(vinylsilane) under reduced pressure. Its IR spectrum does not show any end groups. The molecular weight of this product determined by mass spectrometry is 174. Its ^{13}C NMR spectrum (Table V) indicates only CH and CH_3 groups. Moreover, two signals are shown in the ^{29}Si NMR spectrum. These results are consistent with the presence of isomeric cis and trans six-membered rings whose structures are shown as follows:

Table VI. Elemental Analyses of the Pyrolysis Products

	% C	% Si	% H	% O
calcd for SiC	30	70		
found				
1000 °C	30.4	65.5	0.1	3.8
1400 °C	33.4	66.2	0.1	0.6





In conclusion, the polymerization of vinyldichlorosilane catalyzed by H_2PtCl_6 leads to poly(dichlorovinylsilane) in good yield. Its structure results from both α and β hydrosilylation, which induces a triad effect as observed by ^{29}Si NMR spectroscopy. Besides the polymer, two cyclic dimers are formed in low yield, as previously described,[11,12] as well as two cyclic diastereoisomeric trimers. It is noteworthy that only α hydrosilylation occurs in the formation of the cyclic trimer. Its formation accounts for the small amount of triad C, $H_2SiCH(CH_3)SiH_2CH(CH_3)SiH_2$, observed in the polymer. Indeed, since 25% of α hydrosilylation was estimated from the integration of CH_3, CH_2, and CH in the ^{1}H NMR spectrum, we would expect 56% of triad A, 38% of triad B, and 6% of triad C from the statistical assessment. However, the ^{29}Si NMR signal corresponding to triad C is much smaller (Figure 3). The difference can be attributed to formation of the cyclic trimer. The stability of the six-membered ring seems to be the driving force of the cyclization.

(3) Thermolysis of Poly(vinylsilane). Oligo- and poly(vinylsilane) were heated to 1200 °C at a rate of 5° C/min under nitrogen. The ceramic yields are similar: 32% for the oligo(vinylsilane) (M_n = 1300) and 40% for poly(vinylsilane) (M_n = 5500). These values should be compared with the theoretical one (70%) from the equation

$$(H_2SiC_2H_4)_n \rightarrow \text{“SiC”} + \text{gases}$$

After being heated at 1200 °C for 10 h, the black residue gave an X-ray diffraction pattern corresponding to β-SiC. The elemental analyses of the pyrolysis products shown in Table VI indicate a slight excess of carbon with respect to pure SiC.

It has been shown that poly(silapropylene), $(CH_3SiHCH_2)_n$, gives lower ceramic yields, ranging from 5[5] to 10%[6] depending on its average molecular weight (from 2300 to 35 000, respectively).

The better thermal behavior of poly(vinylsilane) correlates with its greater ability to cross-link through two functional SiH bonds per unit. A detailed description of the pyrolytic conversion to ceramic will appear in a subsequent paper.

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