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Poly(vinylsilane), "[CH$_2$CH(SiH$_3$)]$_n$": Preparation, Characterization, and Utilization as a Preceramic Polymer

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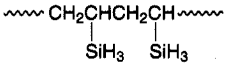
Lithium aluminum hydride reduction of poly(vinyltrichlorosilane), prepared by ^{60}Co γ-radiation-induced polymerization of CH$_2$=CHSiCl$_3$, gave poly(vinylsilane), PVSiH$_3$. The composition of this low molecular weight polymer was determined by ^{1}H and ^{29}Si NMR spectroscopy to be CH$_2$=C(SiH$_3$)(CH$_2$CH(SiH$_3$))$_x$(CH$_2$CH(SiH$_3$)CH(SiH$_3$)CH$_2$)$_y$(>CHCH$_2$-SiH$_2$)$_z$– ($x > y \gg z$). Pyrolysis of PVSiH$_3$ in argon to 1500 °C gave only a moderate (ca. 40%) ceramic residue yield. However, PVSiH$_3$ could be cross-linked by the action of various group 4 metallocene derivatives to give soluble polymers whose pyrolysis in argon gave substantially improved yields (70–80%) of ceramic residue composed of silicon carbide together with 10–13 wt % of carbon.

Introduction

The search for the optimum polymeric precursor for silicon carbide during the past 20 years has led to the preparation of many different organosilicon polymers whose properties, it was hoped, would allow their application in the preparation of ceramic and metal matrix composites, as the precursor for the SiC continuous fiber component and, in the case of the former, as precursor for the silicon carbide matrix itself. Of interest also was the application of such polymers as low loss binders in ceramic powder processing. Among the polymer types that have been prepared and investigated have been polysilylenes, polycarbosilanes, and polysiloxanes.[1] The silicon atoms of these polymers for the most part are in the main chain. Notably absent among the organosilicon polymers that have been prepared for these purposes are those in which the silicon atoms are contained in pendant groups on a carbon atom chain. A polymer of this type is poly(vinylsilane), PVSiH$_3$, which in the ideal case has SiH$_3$ substitution on every other carbon atom of a polyethylene chain, **1**.

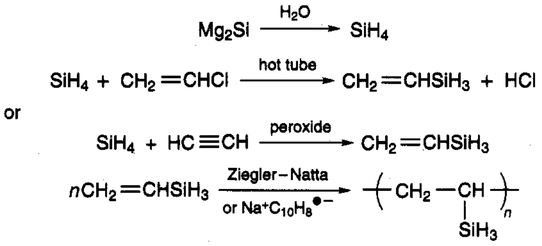


$$\sim\sim CH_2\underset{SiH_3}{CH}CH_2\underset{SiH_3}{CH}\sim\sim$$

1

Poly(vinylsilane) has been prepared by workers at Mitsui Toatsu Chemicals, Inc.[2] The synthetic route used is outlined in Scheme 1. The handling of the starting materials, SiH$_4$ and acetylene, both gases, and of the intermediate monomer, CH$_2$=CHSiH$_3$, also a gas, is not without potential dangers, and a more practical, less hazardous route to this polymer seemed desirable.

Scheme 1



Vinyltrichlorosilane, CH$_2$=CHSiCl$_3$, is a readily available, relatively inexpensive, nonhazardous organosilicon compound. Its polymerization, initiated by radicals derived from thermolysis of di-*tert*-butyl peroxide[3] or by ^{60}Co γ-irradiation,[4] was reported over 30 years ago. Reduction of poly(vinyltrichlorosilane), PVSiCl$_3$, should give PVSiH$_3$. The molecular weights of PVSiCl$_3$ prepared by the ^{60}Co γ-ray initiation route were not high (M_n = 530–880[4a]), but a high molecular weight is not a requirement for a useful preceramic polymer.[5] Accordingly, we have chosen this synthetic route for our study of PVSiH$_3$.

Results and Discussion

Preparation and Characterization. The polymerization of vinyltrichlorosilane, initiated by ^{60}Co γ-ra-

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(1) Laine, R. M.; Babonneau, F. *Chem. Mater.* **1993**, *5*, 260 (review).

(2) (a) Takeuchi, A.; Ito, M.; Iwata, K.; Kobayashi, M. Jpn. Kokai Tokkyo Koho JP 01 234 408 (89,234,408), Sept 1989; *Chem. Abstr. 112*, 119624c. (b) *Ibid.* Jpn. Kokai Tokkyo Koho JP 01 242 593 (89,242,593), Sept 1989; *Chem. Abstr. 112*, 119628g. (c) Ito, M.; Wakimura, K.; Takeuchi, A.; Iwata, K.; Kobayashi, M.; Asanuma, T.; Ohnaka, J.; Tokura, Y.; Yamamoto, K. Eur. Pat. Appl. EP 321 259, June 1989; *Chem. Abstr. 111*, 233877s. (d) Takeuchi, A.; Ito, M.; Iwata, K.; Kobayashi, M. Jpn. Kokai Tokkyo Koho JP 01 266 113 (89,266,113), Oct 1989; *Chem. Abstr. 112*, 158632y.

(3) (a) Wagner, G. H.; Bailey, D. L.; Pines, A. N.; Dunham, M. L.; Mc Intire *Ind. Eng. Chem.* **1953**, *45*, 367. (b) Andrianov, K. A.; Andronov, Yu. I. *Dokl. Akad. Nauk SSSR* **1967**, *175*, 345.

(4) (a) Hayakawa, K.; Kawase, K.; Yamakita, H.; Inagaki, S. *Polym. Lett.* **1967**, *5*, 1077. (b) Hayakawa, K.; Kawase, K.; Yamakita, H.; Yumoto, T. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 3145.

(5) Seyferth, D. In Silicon-Based Polymer Science – A Comprehensive Resource; *Adv. Chem. Ser.* No. 224; Zeigler, J. M., Fearon, F. W. G., Eds.; American Chemical Society: Washington, DC, 1990; pp 565–591.

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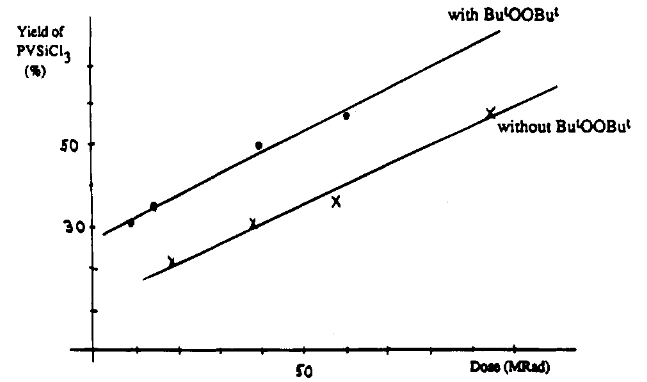


Figure 1. Poly(vinyltrichlorosilane) yield as a function of radiation dose in the absence and presence of 1 wt % of di-*tert*-butyl peroxide.

Table 1

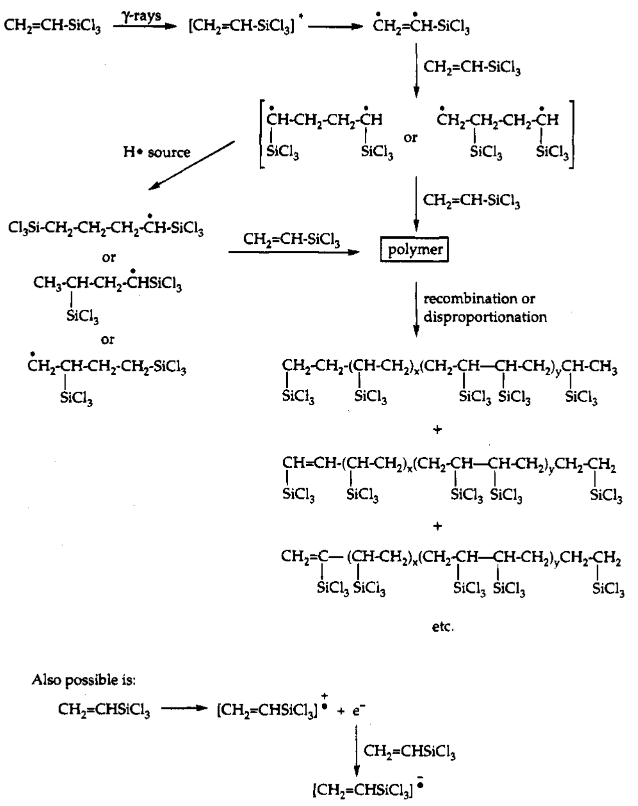
dose (MRads)	yield (%) without Bu^{t}OOBu^t	yield (%) with Bu^{t}OOBu^t
11		31
15		34
20	21	
40	29	
41		49
60	34	57
96	54	

diation as described by Hayakawa et al.,[4] was used in the present work. In the initial experiments, CH_2=C-$HSiCl_3$ was added to a thick-walled Pyrex ampule which then was sealed under vacuum and placed in a ^{60}Co γ-radiation chamber. The dose rate was 1.195 MRad/day. Relatively high doses (~100 MRad) were required in order to obtain reasonable yields of polymer, as the data in Table 1 and Figure 1 show. The radiation yield was calculated[6] to be $G = 4.53$ μmol J^{-1}. Further experiments showed that addition of 1 wt % of di-*tert*-butyl peroxide to the CH_2=$CHSiCl_3$ served to increase the polymerization rate (Table 1, Figure 1); the radiation yield was increased to 5.88 μmol J^{-1}. The polymer yield in each case increased almost linearly with radiation dose.

All further preparative experiments were carried out using a di-*tert*-butyl peroxide additive. Upon completion of the irradiation volatile components were removed at reduced pressure with heating. The residue was a pale yellow, transluscent solid that was quite sensitive toward atmospheric moisture. It reacts with bulk water to give a fluffy, white, insoluble solid with copious evolution of HCl. The $PVSiCl_3$ obtained after a radiation dose of 20 MRad gave an elemental analysis that agreed very well with the theoretical values for C and H (14.94% C, 2.06% H observed vs 14.86% C and 1.86% H calculated), but with higher radiation doses minor deviations from the calculated values were found (to 15.44% C at 96 MRad).

The structure of the $PVSiCl_3$ thus provided was of interest. The mechanism of γ-radiation-induced vinyl polymerization is complex[7] but can be simplified as shown in Scheme 2 (using vinyltrichlorosilane as an example). Absorption of energy can produce an excited monomer state which may be converted to a diradical species. The latter can add to another monomer molecule to form another diradical which in turn can add to a monomer molecule (propagation). Hydrogen atom transfer processes can give monoradicals. Additions can occur head-to-tail or head-to-head. Termination can take place either by radical recombination or by disproportionation. In any case, the simple $[CH_2CH(SiCl_3)]_n$ structure is not the expected one.

Scheme 2



Molecular weight measurements of the γ-radiation-derived $PVSiCl_3$ were not possible because of its great sensitivity toward moisture. Its IR spectrum did not provide much useful information but did indicate the presence of CH_2= end groups. On the basis of the integration of the aliphatic to vinylic proton signals in the ^1H NMR spectrum of our $PVSiCl_3$ (ca. 37.5:1), a degree of polymerization of around 10 may be calculated, if one assumes that all vinylic protons are contained in vinylic end groups. Thus, as the Japanese workers had found,[4] $PVSiCl_3$ is not a high molecular weight polymer. In line with expectation, the ^{29}Si NMR spectrum of $PVSiCl_3$ contained not one, but several, resonances in the region δ_{Si} 10−13.

$PVSiCl_3$ could be reduced cleanly to $PVSiH_3$ by reaction with $LiAlH_4$ in diethyl ether. The product, obtained in 70% yield, was a clear, thick oil. Its molecular weight, determined by vapor pressure osmometry (VPO) was 580, which, based on the simple $[CH_2CH(SiH_3)]_n$ formula, would indicate a degree of polymerization of about 10. Gel permeation chromatographic (GPC) studies of $PVSiH_3$ (in THF vs polystyrene standard) gave $M_w = 850$ g/mol, with a broad distribution of molecular weights (170−5100).

The spectroscopic data (IR, ^1H, ^{13}C, ^{29}Si NMR) obtained for $PVSiH_3$ allow us to write a compositional

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[6] (a) Comprehensive Polymer Science: Eastman, R. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon: Oxford, 1989; Vol. 4, p 318. (b) *Organic Radiation Chemistry Handbook*; Milinchuk, V. K., Tupikov, V. I., Eds.; Ellis Horwood: Chichester, UK, 1989.

[7] Allcook, H. R.; Lampe, F. H. Contemporary Polymer Chemistry; Prentice-Hall: Englewood Cliffs, NJ, 1981; p 103.

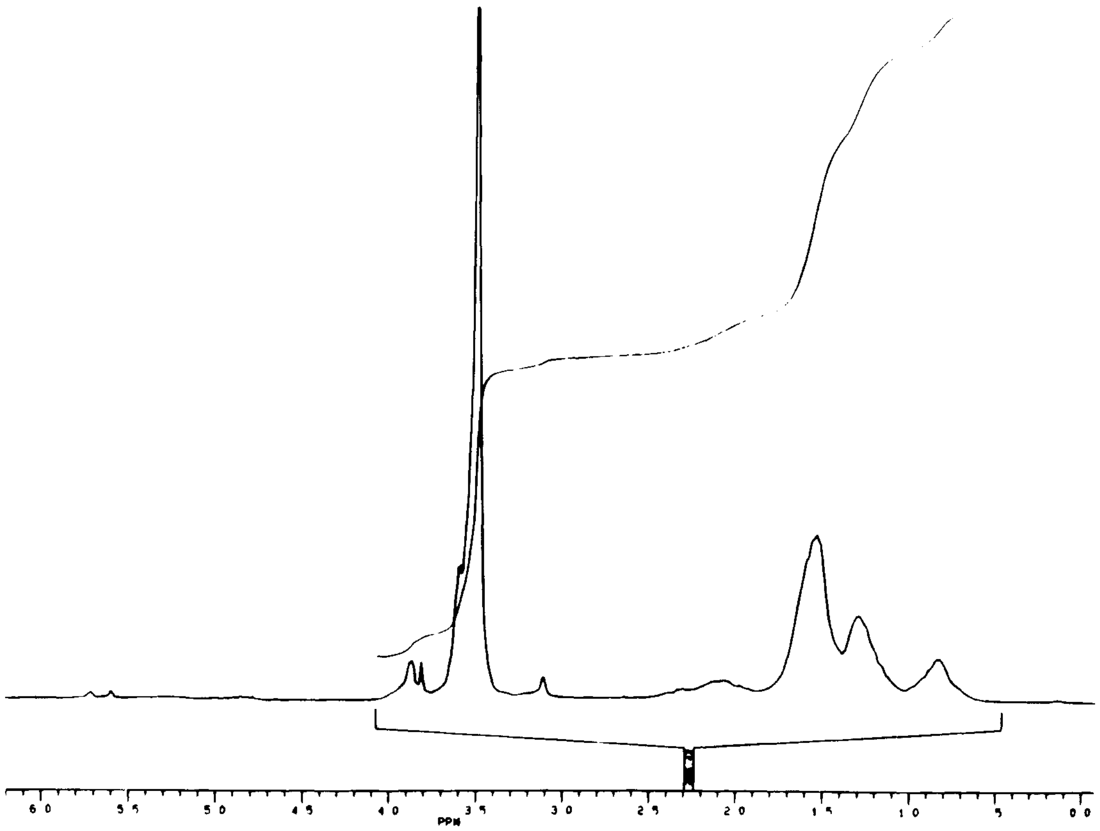
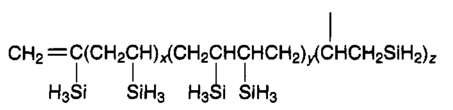


Figure 2. ^1H NMR spectrum of poly(vinylsilane).

formula **2** for the polymer, where $x > y \gg z$. The IR



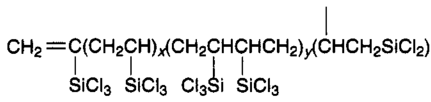
$$\mathrm{CH_2{=}\underset{H_3Si}{C}(CH_2\underset{SiH_3}{C}H)_x(CH_2\underset{H_3Si}{C}H\underset{SiH_3}{C}HCH_2)_y(\overset{|}{C}HCH_2SiH_2)_z}$$

2

spectrum showed bands at 3060 (w, ν_{CH} vinyl), 2894–2837 (m, ν_{CH} aliphatic), 2147 (vs, ν_{SiH}), 1604 (vw, $\nu_{C=C}$), 1444–1339 (w, ν_{CH}) and 912 (vs, ν_{SiH}). The ^1H NMR spectrum (Figure 2) showed broad singlets at δ 0.82, 1.29, and 1.54, assigned to head-to-head units, $(H_3Si)CHCH(SiH_3)$, and head-to-tail units, $(H_3Si)CHCH_2$ and $(H_3Si)CHCH_2$, respectively, the main components of the polymer, on the basis of a consideration of the shielding effect of the SiH_3 group. In addition, there were four broad singlet resonances in the SiH region: δ 3.50 ($(H_3Si)CHCH_2$), 3.61 ($(H_3Si)CHCH(SiH_3)$), 3.82 (SiH_2), and 3.87 ($CH_2{=}C(SiH_3)$). These assignments are based on literature data for primary alkylsilanes[8] and for carbosilanes containing the SiH_2 group in the main chain.[9] The estimated integrated intensities of the δ (1.29 + 1.54) and 3.61 signals are about equal, as required for the $CH_2CH(SiH_3)$ unit. Very weak resonances at δ 5.60 and 5.72 (d, $^2J_{HH} = 2.0$ Hz) provide confirming evidence for $CH_2{=}C(SiH_3)$ end groups. The CH/SiH integrated ratio is approximately 1:1, as required for formula **2**.

The ^{13}C NMR spectrum of $PVSiH_3$ showed resonances indicative of formula **2**: δ_C 4.09 (d, $J_{CH} = 125$ Hz) due to $(H_3Si)CHCH(SiH_3)$, 18.16 (d, $J_{CH} = 127$ Hz) due to $CH_2CH(SiH_3)$ and 36.14 (t, $J_{CH} = 127$ Hz) due to CH_2-$CH(SiH_3)$. The $^{29}Si\{^1H\}$ NMR spectrum of $PVSiH_3$ (Figure 3), like that of $PVSiCl_3$, showed five resonances at δ_{Si} −33.46, −35.92, −51.95, −57.93 and −60.50. The low-intensity resonances at −33.46 and −35.92 are in the region characteristic of SiH_2 groups.[9b,d,e] This assignment was confirmed by inversion of these resonances when a ^{29}Si NMR DEPT sequence (multiplicity 1.5) was used. The signals at −51.95 and −57.93 are values typical for SiH_3 groups.[8,9b] Tentative assignments are −51.95, $CH_2CH(SiH_3)$; −57.93, $(H_3Si)CHCH(SiH_3)$. The low-intensity resonance at −60.50 ppm is assigned to the $CH_2{=}C(SiH_3)$ end group.

Assuming that no isomerization has occurred during the $LiAlH_4$ reduction of the $PVSiCl_3$ obtained by γ-irradiation-induced polymerization of $CH_2{=}CHSiCl_3$, this polymer then would be composed of the following structural units:



$$\mathrm{CH_2{=}\underset{SiCl_3}{C}(CH_2\underset{SiCl_3}{C}H)_x(CH_2\underset{Cl_3Si}{C}H\underset{SiCl_3}{C}HCH_2)_y(\overset{|}{C}HCH_2SiCl_2)_z}$$

3, $x > y \gg z$

The presence of a small amount of $SiCl_2$ units in the polymer chain indicates that a minor amount of Cl atom abstraction from $SiCl_3$ groups also has occurred. Thus to Scheme 2 must be added the process shown in

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[8] Harris, R. K.; Kennedy, J. D.; McFarlane, W. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic: London, 1978: Chapter 10a.3. See also the papers of Schmidbaur and coworkers; e.g.: Schmidbaur, H.; Dörzbach, C. *Z. Naturforsch.* **1987**, *42b*, 1088. Schmidbaur, H.; Ebenhöch, J. *Z. Naturforsch.* **1987**, *42b*, 1543. Schmidbaur, H.; Zech, J. *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 5.

[9] (a) Corriu, R. J. P.; Leclerq, D.; Mutin, H. P.; Planeix, J.-M.; Vioux, A. *Organometallics* **1993**, *12*, 454. Boury, B.; Corriu, R. J. P.; Leclerq, D.; Mutin, H. P.; Planeix, J.-M.; Vioux, A. *Organometallics* **1991**, *10*, 1457. (c) Boury, B.; Carpenter, L.; Corriu, R. J. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 785. (d) Boury, B.; Carpenter, L.; Corriu, R. J. P.; Mutin, H. P. *New. J. Chem.* **1990**, *14*, 535. (e) Whitmarsh, C. K.; Interrante, L. V. *Organometallics* **1991**, *10*, 1336.

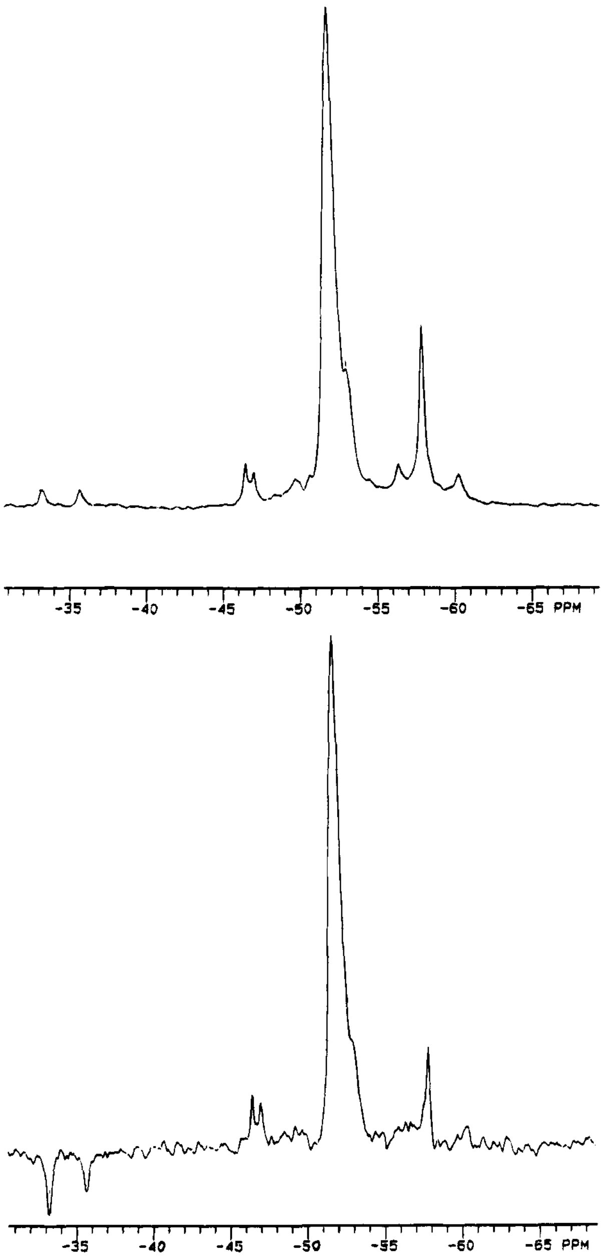


Figure 3. (a) $^{29}Si\{^1H\}$ NMR spectrum of poly(vinylsilane), DEPT, multiplicity = 0.5. (b) $^{29}Si\{^1H\}$ NMR spectrum of poly(vinylsilane), DEPT, multiplicity = 1.5.

Scheme 3. The consequence is that some chain branching may have occurred. However, since "z" in **3** is small, the extent of such branching is not great.

Pyrolysis Chemistry of Poly(vinylsilane). As noted in the Introduction, $PVSiH_3$ is a potentially useful precursor for silicon carbide. If its pyrolysis were to proceed with loss of only H_2, the residue, obtained in 89.7% yield in that case, should contain 77 wt % SiC and 23 wt % carbon. However, the ceramic residue yields, determined by thermogravimetric analysis (TGA) of samples from various preparations of polymer **2** ranged from 35% to 47%. A typical TGA trace is shown in Figure 4. A furnace pyrolysis of a larger sample of **2** (to 1500 °C in a stream of argon) gave a black ceramic residue in 39% yield. Its elemental analysis showed a nominal composition (by weight) of 94% SiC and 6% C. Powder X-ray diffraction (XRD) showed that β-SiC was the only crystalline phase present.

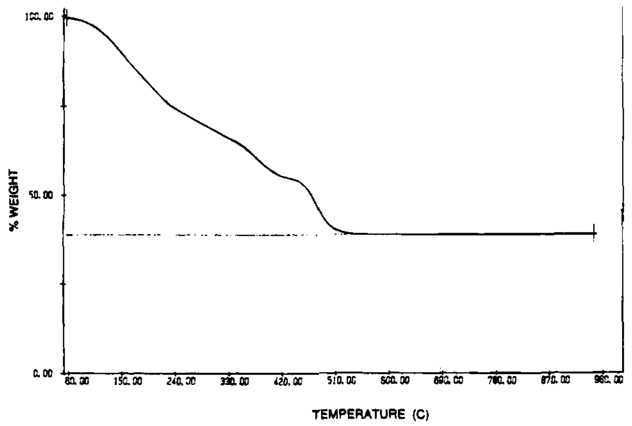
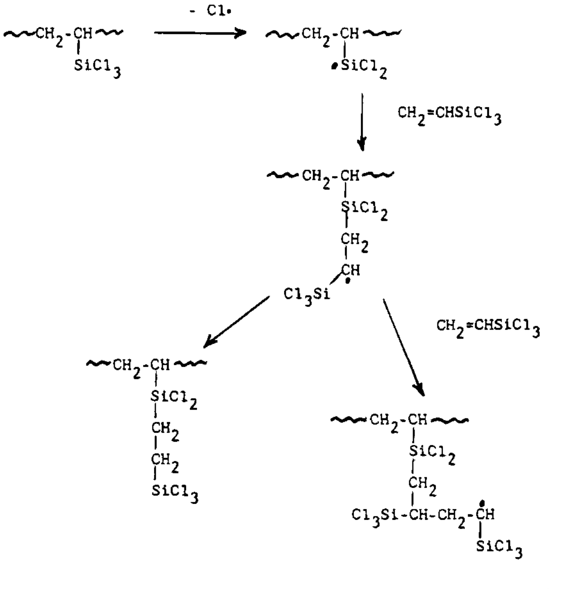


Figure 4. Thermogravimetric analysis trace of poly(vinylsilane): 25–950 °C at 10 °C/min under argon.

Scheme 3



In an experiment in which the identity of evolved volatile pyrolysis products was determined by FTIR, SiH_4 was identified in the 100–200 °C heating range and an alkylsilane in the 200–400 °C range. Methane evolution was observed in the 400–750 °C range. Dihydrogen was identified by mass spectrometry during the course of the pyrolysis. In other experiments, the evolution of nonvolatile products with temperature was examined. Heating polymer **2** at 175 °C in argon for 1 min left a very viscous oil in 89% yield whose ceramic residue yield on pyrolysis to 960 °C in argon (TGA) was 44%. When the polymer was heated in vacuum at 195 °C for 30 min, a white semisolid was obtained in 75% yield (ceramic residue yield 56%; the SiH/CH ratio after this heating period = 0.88, by ^1H NMR. Finally, heating **2** to 300 °C in vacuum left a light yellow, glassy solid in 64.5% yield (ceramic residue yield 68%) which was insoluble in most organic solvents. Its IR spectrum showed that Si–H bonds still were present.

One of the requirements for an effective preceramic polymer is that its pyrolysis give a high ceramic residue yield (>60%, but the greater the better).[5] Organosilicon polymers that contain a multiplicity of Si–H bonds whose pyrolysis, because of the nature of the polymer, gives only low ceramic residue yields, can be converted to useful ceramic precursors by appropriate chemical cross-linking processes involving reactions of their Si–H bonds. Thus the polycarbosilane precursor for the Nicalon SiC-containing ceramic fibers, which contains the $CH_3(H)SiCH_2$ unit as a principal component, may be converted to a more highly cross-linked, but still soluble, material by photolytic or thermolytic treatment with catalytic amounts of a di- or polynuclear metal carbonyl.[10] The most effective of these were $Ru_3(CO)_{12}$ and $Co_2(CO)_8$. Such treatment of the Nicalon polycarbosilane increased the ceramic residue yield on pyrolysis in argon from 50–60% to over 90%. Although these metal carbonyls appeared to catalyze the cross-linking process, they became incorporated into the final polymer, probably via silicon–transition metal bonds.

Another organosilicon hydride polymer that could be "upgraded" in this manner was the poly(methylsilylene) of composition $[(CH_3SiH)_x(CH_3Si)_y(CH_3SiH_2)_z]_n$ ($x \gg y, z$), obtained by the action of sodium on CH_3SiHCl_2.[11] The pyrolysis of this polymer gave only low (ca. 15–20%) ceramic residue yields on pyrolysis in argon, and, furthermore, the pyrolysis involved substantial loss of CH_3 groups as CH_4, leaving a residue that contained 24% by weight of free elemental silicon, in addition to the desired SiC. It was found that heating such poly(methylsilylenes) with catalytic amounts (0.5–1 mol %, based on Si) of $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_n$ or $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$ in refluxing hexane or photolysis of a hexane solution of the polymer with a catalytic amount of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$, cross-linked the polymer with loss of Si–H functionality and incorporation of the zirconocene portion of the catalyst. Pyrolysis of the resulting solid, soluble polymer in a stream of argon gave high (80–90%) yields of a ceramic residue that was near-stoichiometric (>95%) SiC.[12] $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ also was effective, but somewhat too reactive, easily leading to formation of insoluble polymers.

This use of group 4 metallocene catalysts is based on the dehydrogenative coupling reaction of $RSiH_3$ compounds (eq 2) first reported by Aitken et al. in 1985.[13]

$$n\mathrm{RSiH_3} \xrightarrow[\text{catalyst}]{(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2} cyclo\text{-}(\mathrm{R(H)Si})_x + \mathrm{H[R(H)Si]}_y\mathrm{H} \quad (2)$$

Although no SiH_3 groups were present in the poly(methylsilylene), the $Si(CH_3)H_2$ end groups reacted completely and some of the internal CH_3SiH groups probably reacted as well, giving a material of higher molecular weight and complexity through Si–Si bond formation. The transition metal catalyst also was incorporated into the polymer.

In view of the SiH_3 groups present in the poly(vinylsilane), cross-linking by the use of group 4 metallocene derivatives via the chemistry shown in eq 2 seemed worth investigating. It was found that $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_n$, which served well in the cross-linking of poly(methylsilylene), also was effective in cross-linking $PVSiH_3$. Using 0.5 mol % (based on Si) of this compound, heating a hexane solution of $PVSiH_3$ for 3 h under argon gave a thick, yellow oil. The integrated ^1H NMR spectrum of this product showed that the SiH/CH ratio had decreased from 1 (in uncrosslinked $PVSiH_3$) to 0.72, i.e., dehydrogenative coupling had taken place. Pyrolysis, under argon to 1000 °C, of the oil in a TGA experiment gave a 70% ceramic residue yield, a substantial increase over the 35–47% ceramic residue yield of the un-cross-linked $PVSiH_3$. A longer reflux time in the presence of 0.5 mol % of the zirconocene hydride gave a soluble yellow semisolid, SiH/CH ratio = 0.64, whose pyrolysis (TGA) gave an 80% ceramic residue yield (Figure 5). A still longer reflux time (under the same conditions) of 28 h resulted in a soluble, yellow solid with a diminished SiH/CH ratio of 0.35, but the ceramic residue yield was not improved. The related monohydride, $(\eta^5\text{-}C_5H_5)_2ZrHCl$, also was found to be effective as a cross-linking agent for $PVSiH_3$, giving a soluble polymer whose ceramic residue yield was 77%.

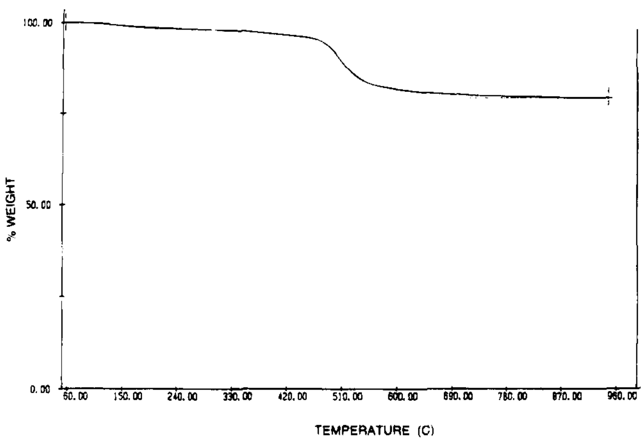


Figure 5. Thermogravimetric analysis trace of poly(vinylsilane) cross-linked by thermal treatment with $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_n$, same temperature program.

A bulk furnace pyrolysis of a zirconocene hydride-cross-linked $PVSiH_3$ sample to 1500 °C in a stream of argon gave a black ceramic residue which elemental analysis showed to contain 36.2% C and 56.6% Si. Although this accounts for only 93 wt % of the sample, it is clear that an excess of free carbon is present; ca. 87 wt % SiC and 13 wt % C. Thus the increase in ceramic yield obtained when $PVSiH_3$ is cross-linked prior to pyrolysis is due in part to a greater retention of carbon in the residue.

$(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$ also was an effective cross-linking agent, so effective, that only short reaction times (~2 h) were needed to obtain a still-soluble product when 0.5 mol % of this catalyst was photolyzed in a toluene solution of $PVSiH_3$. Longer (6 h) photolysis times resulted in an insoluble polymer. A large scale tube furnace pyrolysis of the soluble, yellow, semisolid polymer (SiH/CH ~ 0.65) obtained in such a cross-linking reaction gave a black ceramic residue in 80% yield whose nominal composition was 89 wt % SiC and 11 wt % carbon. A small amount of Zr (0.49% by elemental analysis) also was present, probably as ZrC. The Corey catalyst, in situ formed $(\eta^5\text{-}C_5H_5)_2Zr(C_4H_9\text{-}n)_2$,[14] as well

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(10) Seyferth, D.; Sobon, C. A.; Borm, J. *New J. Chem.* **1989**, *14*, 545.

(11) (a) Wood, T. G., Ph.D. Dissertation, Massachusetts Institute of Technology, 1984. (b) Brown-Wensley, K. A.; Sinclair, R. A. U.S. Patent 4,537,942, Aug 1985.

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as the titanium analogue, also served well in the cross-linking of $PVSiH_3$, at room temperature and 0 °C, respectively.

Another effective cross-linking catalyst for $PVSiH_3$ was $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$, the compound reported in Harrod's first paper on polysilylene synthesis. A room-temperature reaction (in the dark) of 0.5 mol % of this complex with $PVSiH_3$ in hexane solution resulted in formation of a soluble, dark green, semisolid, cross-linked polymer (SiH/CH = 0.7). (The green color no doubt was due to reduced titanium species). Pyrolysis of this product under argon (TGA) gave a black ceramic residue in 78% yield. Less effective was $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$, whose photolysis in the presence of $PVSiH_3$ gave a pale yellow, soluble, semisolid polymer. The ceramic residue yield of the latter was only 61%.

Our experiments thus have shown that all Harrod-type dehydrogenative coupling catalysts for polysilylene preparation from $RSiH_3$ compounds are useful cross-linking agents for $PVSiH_3$, provided that relatively mild reaction conditions are used. In particular, use of $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_n$ permits variation of the cross-linking such that oils, semisolids, or solids can be obtained. No doubt, the same mechanism of Si−Si coupling obtains here as in the $RSiH_3$ molecule coupling process, so this product requires no comment. However, as our experiments have shown, thermal cross-linking of $PVSiH_3$ also is possible, although this process has not been optimized.

In view of the fact that the C/Si ratio in $PVSiH_3$ = 2, it is not surprising that the ceramic material obtained in the pyrolysis of this material in argon contains a moderate amount of free carbon in addition to the desired SiC. While for some applications the presence of free carbon is desirable (e.g., when the organosilicon polymer is used as a binder for SiC powder[15]), in other applications this is not the case. In previous research we found that the amount of free carbon obtained in the pyrolysis of an organosilicon polymer can be minimized or even eliminated when the polymer in question is combined, chemically or physically, with an organosilicon polymer whose pyrolysis gives some free Si in addition to SiC.[16] At the high pyrolysis temperatures the free carbon and silicon formed in the pyrolysis of the respective polymers react to give SiC. Poly(methylsilylene) is a polymer whose pyrolysis (in the un-cross-linked state) gives free silicon in addition to SiC.[11] Thus pyrolysis of a 1:1 mixture (based on Si) of $PVSiH_3$ and poly(methylsilylene) gave less free carbon than did pyrolysis of $PVSiH_3$ alone (3.8% vs 6%). Appropriate adjustment of the reactant stoichiometry used should result in formation of near-stoichiometric SiC. Similar pyrolysis of a 1:1 mixture of these organosilicon polymers after it had been treated (6 h UV irradiation in hexane) with $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$ (0.3 mol %), gave a ceramic residue in 68% yield. This product contained 4 wt % of free carbon, in addition to SiC, as well as a very small amount of ZrC.

Because of a change in direction of our current research, we have not undertaken an investigation of the ceramics applications of $PVSiH_3$ in its un-cross-linked and cross-linked forms. However, we believe that these applications—as a binder for ceramic and metal powders and as a precursor for SiC fibers, coatings, and matrices—are well worth further investigation.

Experimental Section

General Comments. All reactions and manipulations were performed under prepurified nitrogen or argon using Schlenk techniques or an inert-atmosphere box. Solvents were purified and dried by standard procedures. Photolysis experiments were carried out using Pyrex flasks. Irradiations were effected with a Hanovia medium-pressure mercury lamp (140 W, λ = 300 nm) which was positioned ca. 10 cm from the flask. Slight warming of the reaction solution resulted.

Infrared spectra were obtained using a Perkin-Elmer 1600 FT-IR spectrophotometer. Furnace FT-IR spectra were recorded on an IBM IR-85 spectrophotometer equipped with a furnace. With the experimental design used only volatile compounds formed on pyrolysis to 1000 °C could be detected.

Proton NMR spectra were acquired using a Bruker WM-250, a Varian XL-300, or a Varian Gem-300 spectrometer using $CDCl_3/CHCl_3$ as a reference at 7.24 ppm downfield from TMS. Carbon-13 NMR spectra were obtained using a Varian XL-300 or Gem-300 (operating at 75.5 MHz) spectrometer using $CDCl_3$ (δ_C 77.0) as reference. Silicon-29 NMR spectra were obtained on a Varian XL-300 instrument (operating at 59.59 MHz) using TMS (0.00 ppm) as standard. Either standard pulse sequence or distortionless polarization transfer (DEPT) techniques were employed.

Number average molecular weights (M_n) were determined by vapor pressure osmometry in HPLC-grade chloroform using a Wescan Model 233100 osmometer and/or by cryoscopy in benzene solution. Gel permation chromatography (GPC) was performed on a Waters Millipore GPC III liquid chromatograph. The calibrant used was monodisperse polystyrene (M = 470 000−2 350). The calibrant and the samples were dissolved in THF and separately eluted from an Ultrastyragel GPC column series (sequence 10^2, 10^3, 10^4, 10^5 Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standard.

Crystalline phases of the ceramic samples were identified by powder X-ray diffraction (XRD) using a Rigaku 300 rotating anode X-ray powder diffractometer with a Cu Kα (λ = 1.5415 Å) and a Ni filter. Typically, the diffractometer was operated at 100 mA and 40 kV scanning 20−125° 2θ) at a rate of 20°/min. The crystalline phases in the powder diffraction pattern were identified by comparison of the 2θ values and the corresponding d spacings with values in available literature sources.

Thermogravimetric analysis (TGA) of polymer samples was performed on a Perkin-Elmer TGS-2 system under a 40 mL/min argon flow. All samples were heated from 50 to 950 °C at 10 °C/min. Ceramic residue yields are reported as the percentage of the sample remaining after completion of the heating cycle.

Large-scale tube furnace pyrolyses were performed in graphite boats in a Mullite tube in a Lindberg 59344 tube furnace equipped with a Lindberg Model E5 controller. Samples were placed in the boat on a 6 in. alumina dee tube. The following temperature program was used: 25 to 1000 °C at 5 °C/min; hold for 1 h; then 1000 to 1500 °C at 5 °C/min; hold for 4 h. The furnace was purged with argon for 30 min prior to sample introduction and for another 30 min when the sample was in place.

Elemental analyses of polymers were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Ceramic elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Note that standard analytical procedures often give poor results because of the refractory nature of the pyrolysis products, particularly in the case of SiC-containing ceramics. Low silicon values often are ob-

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tained, so that the sum of the silicon and carbon percentages can be less than 100%.

Polymerization of Vinyltrichlorosilane. Thick-walled Pyrex tubes (2.5 cm o.d., 14 cm length with a 10 cm, 8 mm o.d. neck) were charged with 20–30 g of $CH_2{=}CHSiCl_3$ under argon, cooled in liquid nitrogen, evacuated to 0.25 Torr and sealed. Polymerization was carried out in the liquid state at 25 °C with γ-rays from a 1.195 MRad/day ^{60}Co source. The samples were irradiated with different doses of γ-rays (Table 1). Subsequently, the tubes were opened and the viscous liquid contents were transferred to a distillation apparatus. Unconverted starting material was distilled under argon at 90 °C. Another minor fraction distilled at 70–75 °C at 0.3 Torr. The residue was maintained in a dynamic vacuum at 130 °C for 3–4 h, leaving a light yellow solid polymeric material, $PVSiCl_3$. This material is sensitive to moisture and reacts immediately with water to give a fluffy, white solid.

The γ-ray-induced polymerization of $CH_2{=}CHSiCl_3$ in the presence of 1 wt % of di-*tert*-butyl peroxide was carried out in the same manner. This represents the method of choice (Table 1) and was used in all subsequent preparative polymerizations.

IR (thin film, NaCl, cm^{-1}) 2920m, 2865m (ν_{CH}), 1601w ($\nu_{C=C}$), 1448m, 1395m, 1343w (δ_{CH}), 1125m, 1045s, 775s, 680s, 585vs (ν_{SiCl}). ^1H NMR ($CDCl_3$, 25 °C, 250 MHz) δ 0.80–3.0 (broad, unresolved signal, 75 H, CH_2CH backbone), 6.09, 6.20 (d, $^2J_{HH}$ = 2.0 Hz, 2H, $CH_2{=}$). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ_C 20.0–40.0 (broad, unresolved signal, CH_2CH backbone), 135.88 ($CH_2{=}C{=}$), 140.91 ($CH_2{=}C$). ^{29}Si NMR ($CDCl_3$, 59.6 MHz) δ_{Si} 10.11, 10.74, 11.73, 12.18, 12.68. Anal. Calcd for $(C_2H_3Cl_3Si)_n$: C, 14.86; H, 1.86. Found: 20 Mrad sample: C, 14.94; H, 2.06; 40 MRad sample: C, 15.21; H, 2.17; 60 MRad sample: C, 15.26; H, 1.96; 96 MRad sample: C, 15.44; H, 2.04.

Reduction of $PVSiCl_3$ with $LiAlH_4$. A 1.5 L three-necked, round-bottomed flask equipped with a reflux condenser topped with an inlet/outlet tube, a mechanical stirrer, and a pressure equalizing addition funnel was charged with 10.7 g (0.2 mol of Cl) of $PVSiCl_3$ and 200 mL of dry diethyl ether. With vigorous stirring, 3.0 g (0.4 mol H) of $LiAlH_4$ in 300 mL of diethyl ether was added at room temperature via the addition funnel. During the addition the reaction mixture became slightly warm but did not reflux. It was stirred at room temperature for 12 h. The reaction mixture was filtered and then was added slowly and cautiously to 500 mL of ice-cooled 2 N HCl (vigorous reaction). The resulting slurry was extracted with two portions of diethyl ether. The combined ether phases were washed twice with water and then dried over anhydrous Na_2SO_4. Filtration was followed by removal of the ether at reduced pressure. The residue was maintained at 100 °C in vacuo for 3 h. A pale yellow oil with the consistency of honey was isolated (2.61 g, 68%).

IR (thin film, NaCl, cm^{-1}) 3060w (ν_{CH} vinyl), 2894s, 2837m (ν_{CH} aliphatic), 2147vs (ν_{SiH}), 1880w, 1604vw ($\nu_{C=C}$), 1444w, 1408w, 1339w, 1072m, 912vs (δ_{SiH}), 855m, 649s, 578m, 526m. ^1H, ^{13}C, and ^{29}Si NMR spectra are described in the Results and Discussion. Anal. Calcd for $(C_2H_6Si)_n$: C, 41.38; H, 10.34. Found: 41.35; H, 10.17.

Furnace/FT-IR: At the temperature range 100–200 °C SiH_4 (ν_{SiH} = 2155 cm^{-1}, δ_{SiH} = 920 cm^{-1}) was the only volatile species observed. At 200–400 °C, SiH_4 and an alkylsilane (ν_{CH} = 2924, 2855 cm^{-1}, ν_{SiH} = 2182 cm^{-1}, δ_{SiH} = 906 cm^{-1}) were observed. At 400–750 °C, CH_4 (ν_{CH} = 2990 cm^{-1}, δ_{CH} = 1300 cm^{-1}) was observed. H_2 was detected by furnace/MS.

A tube furnace pyrolysis (see General Comments) of 0.486 g of $PVSiH_3$ produced 0.190 g (39%) of a black ceramic. Anal. Found: C, 32.74, Si, 62.73. XRD (*d*, Å): 2.79, 2.37, 1.58, 1.35, 1.00 (β-SiC).

Cross-Linking of $PVSiH_3$ by Group 4 Metallocene Derivatives. All experiments were carried out in three-necked, round-bottomed flasks equipped, if necessary, with a reflux condenser topped with an inert gas inlet/outlet tube, a magnetic stirbar, and rubber septa as needed. Liquids were added by syringe. Workup in general involved filtration, if necessary. Volatile materials, in the main solvent, were removed by trap-to-trap distillation in vacuo into a cold receiver. The residue was further heated in vacuo at 80–100 °C for several hours. ^1H NMR spectra of the resulting soluble polymers usually showed the presence of minor amounts of metallocene units.

(1) By $[(\eta^5\text{-}C_5H_5)_2ZrH_2]_n$. A given amount (usually 0.5–2 g) of $PVSiH_3$ was dissolved in 60–80 mL of hexane. The zirconocene hydride[17] (0.5 mol %, based on the $CH_2CH(SiH_3)$ unit) was added and the mixture was stirred and heated at reflux under argon for a given length of time. The initially insoluble zirconocene hydride dissolved and the solution became yellow in color. Subsequently, the solution was allowed to cool, causing precipitation of unreacted Zr complex. The latter was filtered and the filtrate was evaporated in vacuo to leave the cross-linked polymer. Results are described in the Results and Discussion.

(2) By $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$. (a) An orange solution of 0.5 g (8.60 mmol) of $PVSiH_3$ and 0.065 g (0.26 mmol) of the zirconocene dimethyl[18] in 50 mL of hexane was irradiated with a UV source (see General Comments) for 20 h. Removal of hexane at reduced pressure left an insoluble orange solid in quantitative yield. Ceramic residue yield (TGA): 80% (black solid). A similar result was obtained on UV irradiation of such a solution in toluene for 6 h.

(b) UV irradiation of a solution of 14.0 g (0.241 mol) of $PVSiH_3$ and 0.303 g (1.20 mmol) of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$ in 300 mL of hexane for 2 h gave, after removal of solvent, 14.02 g of a soluble yellow semisolid in 98% yield. Tube furnace pyrolysis to 1500 °C of 1.510 g of this product left 1.206 g (80% ceramic residue yield) of a black solid. Anal. Found: C, 35.71; Si, 59.58, Zr, 0.49, which translates to a nominal composition of 88.5 wt % SiC, 10.5 wt % C and 0.6 wt % ZrC. XRD: β-SiC.

(3) By $(\eta^5\text{-}C_5H_5)_2Ti(CH)_3)_2$. A solution of 1.0 g (17.2 mmol) of $PVSiH_3$ and 0.018 g (0.086 mmol) of the freshly prepared titanocene dimethyl[19] in 10 mL of hexane was stirred for 15 h under argon at room temperature in the dark. During this time the color of the solution changed from orange to green (indicative of reduction of the titanium complex). Removal of volatiles at reduced pressure left 0.98 g (98%) of a soluble, dark-green semisolid, SiH/CH ratio = 0.7 by ^1H NMR; ceramic residue yield (TGA): 78% (black solid). A similar result was obtained when such a $PVSiH_3$/Ti catalyst solution was UV irradiated for 16 h.

(4) By $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$. A solution of 0.3 g (5.16 mmol) of $PVSiH_3$ and 0.018 g (0.052 mmol) of the hafnocene dimethyl[18] in 50 mL of hexane was UV irradiated for 20 h. Evaporation of volatiles at reduced pressure from the resulting pale yellow solution left 0.305 g (96%) of a soluble, pale yellow solid, SiH/CH ratio = 0.74 by ^1H NMR; ceramic residue yield (TGA) = 61% (black solid).

(5) By $(\eta^5\text{-}C_5H_5)_2ZrCl_2/2n\text{-}BuLi$. A preformed catalyst solution, prepared by reaction of 0.10 g (0.342 mmol) of zirconocene dichloride slurried in 4 mL of toluene and 0.35 mL of 2.0 M *n*-BuLi in hexane at 0 °C,[14] was cannulated into a solution of 2.0 g (34.4 mmol) of $PVSiH_3$ in 4 mL of toluene. The resulting mixture was stirred at room temperature under argon for 3 h. The resulting dark brown solution was added to 40 mL of hexane. This produced a bright yellow solution and a yellow precipitate. After filtration, removal of volatiles in vacuo left 1.95 g of soluble, yellow semisolid, SiH/CH ratio = 0.69 by ^1H NMR; ceramic residue yield (TGA): 80% (black solid).

(6) By $(\eta^5\text{-}C_5H_5)_2TiCl_2/2n\text{-}BuLi$. Using the procedure described in (5), the catalyst solution was prepared by reaction of 0.086 g (0.34 mmol) of titanocene dichloride in 4 mL of toluene with 0.7 mmol of *n*-BuLi in hexane at 0 °C. This solution was added to 2.0 g (34.4 mmol) of $PVSiH_3$ in 4 mL of toluene, cooled to 0 °C, in the dark, under argon. The reaction mixture was stirred at 0 °C for 3 h. During this time it turned dark green. Addition of 20 mL of hexane gave a light green solution and some precipitate. Workup as in (5) led to isolation

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of 1.99 g (95%) of a soluble, dark green semisolid, SiH/CH ratio = 0.69 by ^{1}H NMR; ceramic residue yield: 83% (black solid).

(7) By $(\eta^5\text{-}C_5H_5)_2ZrHCl$. A solution of 0.5 g (8.60 mmol) of $PVSiH_3$ and 0.022 g (0.086 mmol) of zirconocene chlorohydride (Aldrich) in 10 mL of toluene was heated at reflux with stirring under argon for 12 h. The resulting orange solution was evaporated in vacuo, leaving 0.495 g (99%) of a soluble, orange semisolid, SiH/CH ratio = 0.71 by ^{1}H NMR; ceramic residue yield: 77% (black solid).

(8) By $Co_2(CO)_8$. A solution of 1.0 g (17.2 mmol) of $PVSiH_3$ and 0.02 g (0.058 mmol) of $Co_2(CO)_8$ (Strem Chemicals) in 10 mL of hexane was stirred and heated at reflux under argon for 6 h. The reaction mixture was evaporated in vacuo, leaving 0.98 g (96%) of a viscous brown oil, SiH/CH ratio = 0.74 by ^{1}H NMR; ceramic residue yield: 65% (black solid).

(9) Control Reactions. (a) A solution of 0.3 g (5.2 mmol) of $PVSiH_3$ in 7 mL of hexane was heated at reflux under argon for 6 h. Evaporation of the solution at reduced pressure left 0.29 g of a light yellow residue with a honeylike consistency, SiH/CH = 0.96 by ^{1}H NMR; ceramic residue yield: 42%. (b) A solution of 0.3 g of $PVSiH_3$ in 8 mL of hexane was UV irradiated for 6 h. Evaporation of the solution at reduced pressure left a light yellow residue with a honeylike consistency (0.29 g), SiH/CH ratio = 0.96 by ^{1}H NMR; ceramic residue yield: 44%.

Pyrolysis of Poly(vinylsilane)/Poly(methylsilylene) Combinations. (1) A one-necked, round-bottomed flask equipped with a magnetic stirbar and a rubber septum was charged with 1.51 g (26 mmol) of $PVSiH_3$, 1.14 g (26 mmol) of poly(methylsilylene),[11] and 50 mL of hexane. The solution was stirred at room temperature for 2 h and subsequently the solvent was evaporated in vacuo. A colorless, viscous oil remained. The ceramic residue yield (TGA) was 45% (black solid). A furnace pyrolysis of 1.355 g of this oil (in argon to 1500 °C) produced 0.620 g (46%) of a black ceramic residue. Anal. Found: C, 30.76; Si, 63.61, which allowed calculation of a nominal composition of 96 wt % SiC and 4 wt % C.

(2) A mixture of 1.07 g (18.4 mmol) of $PVSiH_3$, 0.81 g (18.5 mmol) of poly(methylsilylene), and 0.028 g (0.11 mmol) of $(\eta^5\text{-}C_5H_5)_2Zr(CH_3)_2$ in 60 mL of hexane was UV irradiated under argon for 6 h. Subsequent evaporation of solvent at reduced pressure from the light orange solution left 1.906 g of a soluble, pale orange semisolid. Ceramic residue yield (TGA): 74% (black solid).

Tube furnace pyrolysis of 1.332 g of this product (in argon to 1500 °C) gave 0.907 g (68%) of a black ceramic residue. Anal. Found: C, 30.60; Si, 62.87; Zr, 0.25, which allowed calculation of a nominal composition of 95.7 wt % SiC, 3.96 wt % C and 0.32% by Wt ZrC. XRD: β-SiC.

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