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SYNTHESES, STRUCTURES AND PROPERTIES OF POLYCARBOSILANES FORMED DIRECTLY BY POLYMERIZATION OF ALKENYLSILANES

JOHN MASNOVI*, XIN Y. BU*, KASSAHUN BEYENE*, PAULA HEIMANN*, TERRENCE KACIK*, A. HARRY ANDRIST* AND FRANCES I. HURWITZ**

* Cleveland State University, Cleveland, OH 44115
** NASA Lewis Research Center, Cleveland, OH 44135

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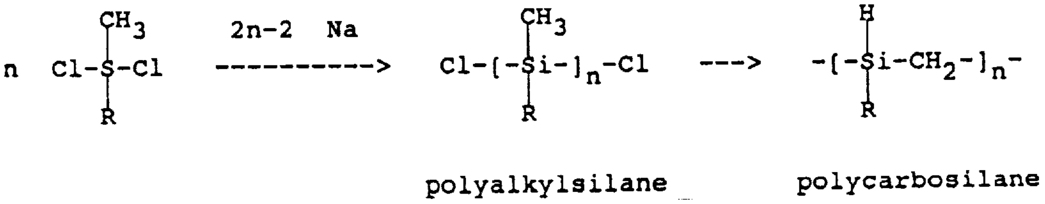
ABSTRACT

Vinylsilane polymerizes to form predominantly a carbosilane polymer using dimethyltitanocene catalyst. This is in contrast to alkylsilanes, which afford polysilanes under the same conditions. The mechanism of polymerization of alkenylsilanes has been shown to be fundamentally different from that for the polymerization of alkylsilanes. The silyl substituent apparently activates a double bond to participate in a number of polymerization processes in this system, particularly hydrosilation. Isotopic labeling indicates the involvement of silametallocyclic intermediates, accompanied by extensive nuclear rearrangement. Polymers and copolymers derived from alkenylsilanes have relatively high char yields even for conditions which afford low molecular weight distributions. Formation of crystalline ß-SiC is optimum for a copolymer of an alkylsilane and an alkenylsilane having a silane/carbosilane backbone ratio of 85/15 and a C/Si ratio of 1.3/1 .

INTRODUCTION

Preceramic polymers represent a useful strategy for formation of fibers, coatings and composite matrices. Much effort has been devoted to development of novel polymeric precursors which can be pyrolyzed to form silicon carbide in high yield and purity [1,2]. The major commercial routes to silicon carbide are based on polymerization of dichlorosilanes, such as dichlorodimethylsilane (Eq. 1, R = CH_3) [3]. Pyrolysis of the polysilane formed by coupling of the dichlorosilane is believed to involve insertion of carbon into the polymer backbone to form a polycarbosilane [4].



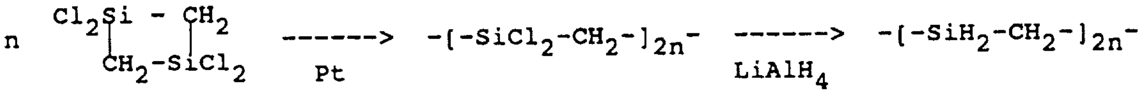
$$n\ \mathrm{Cl}-\underset{R}{\overset{CH_3}{\mathrm{S}}}-\mathrm{Cl} \xrightarrow{2n-2\ \ \mathrm{Na}} \mathrm{Cl}-[-\underset{R}{\overset{CH_3}{\mathrm{Si}}}-]_n-\mathrm{Cl} \longrightarrow -[-\underset{R}{\overset{H}{\mathrm{Si}}}-CH_2-]_n- \qquad (1)$$

Subsequent loss of small fragments (such as R-H and H_2 following Eq. 1) results in formation of silicon carbide (SiC).

Generally, linear polysilanes exhibit low ceramic yield due to cleavage of silicon-silicon bonds, leading to breakup of the polymer backbone and formation of small volatile fragments. Consequently, most such precursors require crosslinking in order to avoid this material loss [5]. The presence of hydrogen attached to silicon (Eq. 1, R = H) provides a thermosetting mechanism which minimizes mass loss due to depolymerization processes [6].

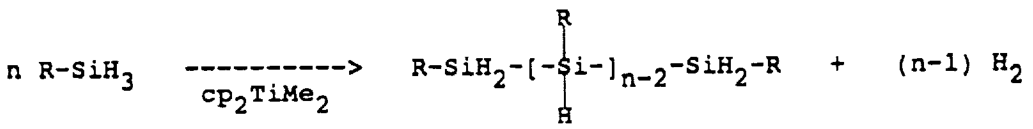
Another strategy receiving recent attention is the formation of polycarbosilanes directly. Polycarbosilanes may be formed from alkenylsilanes by hydrosilation (Eq. 2) and ring-opening polymerization (Eq. 3) [7,8]. Although low carbon/silicon ratios in the polymer can be realized using derivatives of dichlorosilane, such monomer precursors may be difficult to obtain, the yields of soluble polymer usually are low, and a subsequent reduction step is required to produce the halogen-free polymer.

$$\begin{array}{rl} n+1\ \ CH_2{=}CH{-}SiHCl_2 \xrightarrow[Pt]{} & CH_2{=}CH{-}[{-}SiCl_2{-}CH_2{-}CH_2{-}]_n{-}SiHCl_2 \\ & \qquad\qquad \downarrow LiAlH_4 \\ & CH_2{=}CH{-}[{-}SiH_2{-}CH_2{-}CH_2{-}]_n{-}SiH_3 \end{array} \tag{2}$$



$$n\ \begin{array}{c} Cl_2Si - CH_2 \\ |\qquad\ \ | \\ CH_2 - SiCl_2 \end{array} \xrightarrow[Pt]{} -[-SiCl_2-CH_2-]_{2n}- \xrightarrow[LiAlH_4]{} -[-SiH_2-CH_2-]_{2n}- \tag{3}$$

Harrod has reported a method for polymerization of alkylsilanes to form polysilanes under mild conditions (Eq. 4). This technique involves dehydrogenative coupling of primary alkylsilanes ($R-SiH_3$) using dimethyltitanocene (cp_2TiMe_2) and related catalysts [9]. The polymers are predominantly linear, although of rather short persistence lengths (n = 10-20) [10]. Nevertheless, the polymer derived from methylsilane ($R = CH_3$, with $n > 30$) can be converted directly to silicon carbide in high yield [11]. We wish to report here some of the properties of polymers, and their pyrolysis products, derived from the polymerization of alkenylsilanes such as vinylsilane ($CH_2=CH-SiH_3$) using dimethyltitanocene catalyst.



$$n\ R{-}SiH_3 \xrightarrow[cp_2TiMe_2]{} R{-}SiH_2{-}[{-}\overset{R}{\underset{H}{Si}}{-}]_{n-2}{-}SiH_2{-}R \quad + \quad (n-1)\ H_2 \tag{4}$$

RESULTS AND DISCUSSION

Polymer characteristics and ceramic conversion

Vinylsilane polymerized at room temperature for 30 days as described previously [12] affords a soluble, low molecular weight polydisperse polymer (M_n = 540, M_w = 1800) in 82% yield following removal of the solvent. Analysis by ^1H, ^{13}C and ^{29}Si NMR indicated that the polymer contained 74% polycarbosilane and 26% polysilane. The polymer was not (<10%) cross-linked. Despite the relatively low molecular weight distribution, vinylsilane exhibited a 60% char yield. The char was slightly carbon-rich, and analyzed as 58% Si and 39% C (3% titanium originating from the catalyst would be expected to remain in the polymer). Pyrolysis to 1400°C in flowing argon indicated formation of ß-SiC crystallites together with a phase which was X-ray amorphous.

Shorter reaction times could be achieved practically without decrease in polymer yields by either increasing the concentration of catalyst or employing higher temperatures (50-80°C). Interestingly, introduction of up to 10 mole % of the potential cross-linking agent 1,2-disilylethane ($H_3Si-CH_2-CH_2-SiH_3$), BSE, during polymerization did not significantly increase polymer molecular weight of the vinylsilane polymer as determined by GPC (Table I). This is in contrast to increase in the molecular weight observed on addition of BSE to methylsilane polymerization.

An optimum composition of such monomers for conversion into silicon carbide was found to derive from the copolymer 70% methylsilane and 30% vinylsilane. This mixture corresponds to a C/Si ratio of 1.3/1 . An 86% yield of copolymer, comprised of 85% polysilane and 15% polycarbosilane linkages, was derived from this mixture of monomers. Pyrolysis of the

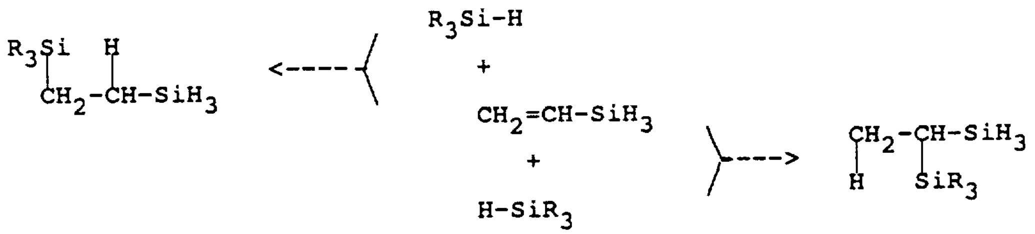
Table I. Polymer and Copolymer Properties

Monomer Composition	Yield (%)	Polymer Composition (ratio silane: carbosilane)	M_n	M_w	Char Yield (%)
100% Vinylsilane	82	26:74	540	1800	60
98% Vinylsilane:2% BSE	80	26:74	480	1200	64
95% Vinylsilane:5% BSE	90	30:70	560	1900	67
30% Vinylsilane: 70% Methylsilane	86	85:15	580	1300	73
100% Methylsilane	90	100:0	680	1960	65
95% Methylsilane:5% BSE	100	100:0	920	7400	71

copolymer to 1400 °C afforded 73% char with essentially stoichiometric analysis for SiC. The char was primarily amorphous, with some small (95 Å) crystallites of ß-SiC.

Mechanism of polymerization of vinylsilane

Alkenylsilanes polymerize by a different process than is seen for alkylsilanes [12]. Vinylsilane, for example, affords a polymer which is predominantly a polycarbosilane. A carbosilane type polymer would form by hydrosilation of the vinyl group of one monomer by the SiH_3 group of another. This process may lead to two types of linkages, -Si-C-Si-C- and -Si-C-C-Si-C-C- (Eq. 5). Both types are observed in roughly equal amounts.



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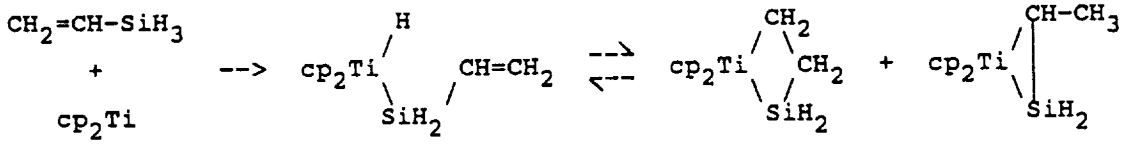
The novel results obtained with vinylsilane have a mechanistic basis. Photolytic decomposition of dimethyltitanocene in the presence of silanes ($R-SiH_3$) affords titanium complexes in reduced oxidation states, such as titanocene (cp_2Ti) and titanocene hydrides, as the apparent active catalytic species [10]. Isotopic labeling studies involving silane-SiD_3 ($R-SiD_3$) demonstrate that reaction of vinylsilane differs fundamentally from reactions of alkylsilanes. In particular, extensive nuclear rearrangements accompany polymerization of vinylsilane, unlike the alkylsilanes. This evidence is inconsistent with a mechanism for the polymerizations which is free radical in nature, although odd-electron species involving the catalyst are formed. Instead, the polymerization of alkenylsilanes likely proceeds by way of silatitanocyclic intermediates (Eq. 6), from which the rearrangements can proceed. Similar silylmetallic species are known to undergo alkene insertion and other reactions [13], and the metallocycles depicted in Eq. 6 also would be expected to be susceptible to such processes.

Other evidence demonstrates intimate participation by the catalyst in



(6)

reactions of alkenylsilanes. Several processes, including hydrosilation, hydrogenation, dehydrogenative coupling, desilylation, trans-silylation and metathesis, were observed to occur with exceptional facility. Thus, the silyl substituent is highly activating for reaction of double bonds with this catalyst. Reactions such as desilylation and trans-silylation involve translocation of the heavy atoms, and are responsible for formation of small amounts of various side-products, including silane and disilylethylene, which incorporate into the polymer more slowly. The polymer of vinylsilane appropriately should be considered a copolymer of vinylsilane, ethylsilane, and these other materials. Nevertheless, incorporation of <10% of such materials into the polymer was found to have little effect on the overall structure and molecular weight of vinylsilane polymer (again contrary to the alkylsilane polymers), as demonstrated by deliberate addition of ethylsilane and disilylethane.

This result probably is due to the high reactivity of vinylsilane (compared to alkylsilanes), and hydrosilation (as opposed to crosslinking) of vinylsilane in the presence of saturated silanes such as SiH_4 and $H_3SiCH_2CH_2SiH_3$ (BSE). Therefore, vinylsilane rapidly forms homopolymer, even in the presence of alkylsilanes, which are incorporated into the polymer more slowly. Copolymer, when formed during the early stages of polymerization, probably also is formed largely by hydrosilation; thus the disilylalkane BSE tends to afford linear polymer (with two $-SiH_3$ termini, which may be available for subsequent crosslinking) rather than altering the structure of the vinylsilane polymer. Apparently, the high char yields obtained, despite the relatively low molecular weights of the polymers, should be due at least in part to the structure of the polymer, which consists of predominantly carbosilane linkages with free H-Si-H groups [3].

CONCLUSIONS

Whereas polyalkylsilanes (except for methylsilane) produce low ceramic yields, alkenylsilanes yield polycarbosilanes which are suitable as high char yield precursors. In particular, vinylsilane polymers are suitable as precursors to carbon-rich material which may remain amorphous to higher temperature. If desired, however, stoichiometric SiC may be produced by copolymerization of vinylsilane with methylsilane.

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Polycarbosilanes from Polymerizations of Vinylsilane

Xin Ya Bu,[†] Kassahun Beyene,[†] Paula Heimann,[†] A. Harry Andrist,[†] Frances I. Hurwitz,[‡] Douglas J. Miller,[‡,#] Andrew R. Wolff,[†,‡] and John Masnovi[*,†]

Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115, and NASA Lewis Research Center, Cleveland, Ohio 44135

Abstract. Vinylsilane polymerized at room temperature with dimethyltitanocene catalyst to form a soluble polycarbosilane by hydrosilation in >80 % yield. The polycarbosilane is less air-sensitive than comparable polysilanes. Although the polycarbosilane consisted of short oligomers (M_n = 540, M_w = 1800), pyrolysis afforded 60 % of a carbon-rich char which contained small β-silicon carbide crystallites together with a phase which was X-ray amorphous. Copolymers of vinylsilane with methylsilane had lower Si/C ratios, which proved more favorable for formation of stoichiometric SiC. Addition of <10 % 1,2-disilylethane increased the yields and served to crosslink the copolymer and improve processing characteristics, making these materials attractive ceramic precursors.

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[*] Author to whom correspondence should be addressed.

[†] Cleveland State University.

[‡] NASA Lewis Research Center.

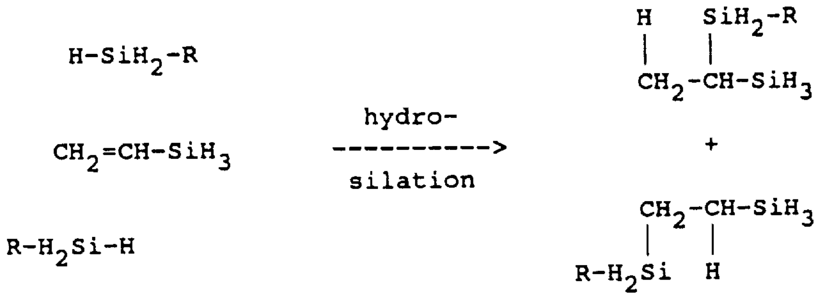
[#] Permanent address: Cedarville College, Cedarville, OH 45314

Silicon-based polymers have found use as ceramic precursors, and recent effort has been directed toward preparation of novel polymers which are more suitable for conversion into silicon carbide fibers, coatings and matrices.[1-3] Polydimethylsilane, which contains a backbone of silicon-silicon bonds [-Si-Si-Si-Si], undergoes conversion into a polycarbosilane, which contains a backbone of carbon-silicon bonds [-Si-C-Si-C-], during pyrolysis.[4-6] Polycarbosilanes are useful preceramic polymers which also can be formed directly by hydrosilation[7] or ring-opening polymerization.[8] These methods suffer serious disadvantages, such as the use of starting materials which are difficult to prepare, the requirement of a subsequent reduction step to remove halogen from the polymer, or low Si/C ratios of the polymers.

We wish to report that vinylsilane, which is readily prepared in one step by $LiAlH_4$ reduction of commercially available vinyltrichlorosilane,[9] is polymerized directly to a polycarbosilane using titanocene catalysts. The polymerizations typically were accomplished using 4 mole % dimethyltitanocene[10] and silane monomer under inert atmosphere in tetrahydrofuran, as described previously.[11] The reactions proceed under very mild conditions. An 82 % yield of mostly short oligomers with a polydisperse, monomodal distribution of molecular weights (M_n = 540, M_w = 1800 D) is obtained by evaporation of solvent following reaction for 4 weeks at room temperature. Heating at 50°C reduces the reaction time to about 1 week. Hydrogen gas, released during the dehydrogenative coupling of alkylsilanes in formation of polysilanes under these conditions,[12] is not produced. The product is soluble in hexane and incorporates oxygen slowly when exposed to air.

Spectroscopic examination of the oligomer reveals that the backbone of this material contains predominantly two types of carbosilane linkages. The ^{29}Si NMR spectrum is shown in Figure 1d. The major resonances (about 74%) are found in the region characteristic of dialkylsilanes between -10 and -23 ppm. This indicates that vinylsilane has, to a large extent, afforded a polycarbosilane, containing C-Si-C bonds. Hydrosilation of the double bonds has been observed as a minor reaction of alkylsilane polymerizations in alkene solvents,[13] and would account for polycarbosilane formation from vinylsilane.

Hydrosilation of the double bond of vinylsilane can occur in two ways, as indicated in Equation 1. Attachment of silicon to the substituted carbon produces a CH_3 group and a methine carbon, $CH(Si)_2$. Alternatively,



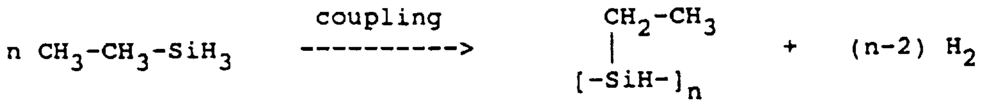
$$\begin{matrix}\mathrm{H{-}SiH_2{-}R} \\ \mathrm{CH_2{=}CH{-}SiH_3} \\ \mathrm{R{-}H_2Si{-}H}\end{matrix} \xrightarrow[\text{silation}]{\text{hydro-}} \begin{matrix}\overset{\mathrm{H}}{\mathrm{CH_2}}\mathrm{-}\overset{\mathrm{SiH_2{-}R}}{\mathrm{CH}}\mathrm{-SiH_3} \\ + \\ \underset{\mathrm{R{-}H_2Si}}{\mathrm{CH_2}}\mathrm{-}\underset{\mathrm{H}}{\mathrm{CH}}\mathrm{-SiH_3}\end{matrix} \qquad (1)$$

attachment to the terminal carbon produces two methylene groups each bonded to a single silicon, $Si{-}CH_2{-}CH_2{-}Si$.

The ^1H NMR spectrum of vinylsilane polymer (Figure 1b) is consistent with this interpretation. Despite the presence of vinyl groups in the monomer, no unsaturation is present after polymerization, and the polymer was not (<10%) crosslinked. Two types of aliphatic linkages are present in nearly equal amounts. Double resonance experiments and comparison with related compounds as models allow the following assignments to be made. A broad resonance near 3.70 ppm is evident for $Si\underline{H}$. The carbons of the ethylene groups, $C\underline{H}_2{-}C\underline{H}_2$, each bonded to silicon, appear in the region near 0.8 ppm. A pair of coupled resonances near 0.40 and 1.18 ppm is consistent with a methine connected to two silicon groups and one methyl group, as in $(Si)_2C\underline{H}{-}C\underline{H}_3$. The increased shielding of the methine proton due to the presence of two silicon substituents is distinctive. An overall hydrogen ratio $Si\underline{H}/C\underline{H}$ of 0.43 is found, whereas a ratio of 0.5 is expected for a polycarbosilane formed solely by hydrosilation (Equation 1). Thus there is a small excess of aliphatic $C\underline{H}$ compared to that expected for a polymer formed exclusively by hydrosilation.

Indeed, two additional coupled resonances are found near 0.78 ppm and 1.07 ppm in the ^1H NMR spectrum. These peaks are found in the same region as those due to the $C\underline{H}_2$ and $C\underline{H}_3$ present in the ethyl group of polyethylsilane (Figure 1a), and are assigned to $C\underline{H}_2{-}C\underline{H}_3$ substituents in vinylsilane polymer. The presence of a minor amount of ethyl groups indicates partial hydrogenation of the double bond of vinylsilane occurs (Equation 2). The cohydrogenation of alkenes has been reported as a principal process in the

$$CH_2{=}CH{-}SiH_3 \quad + \quad H_2 \quad \xrightarrow[\text{genation}]{\text{hydro-}} \quad CH_3{-}CH_3{-}SiH_3 \qquad (2)$$



$$n\ CH_3\text{-}CH_3\text{-}SiH_3 \xrightarrow{\text{coupling}} \overset{CH_2\text{-}CH_3}{\overset{|}{[\text{-}SiH\text{-}]_n}} + (n-2)\ H_2 \qquad (3)$$

dehydrogenative coupling of alkylsilanes by titanocene catalysts.[14] Incorporation of ethylsilane into the polymer by dehydrogenative coupling[3] (Equation 3) would account for the formation of about 26% polysilane-type linkages, appearing between -52 and -64 ppm in the ^{29}Si NMR spectrum of Figure 1d.[15] Analogously, the ^{13}C NMR spectrum of the polymer exhibits resonances principally in the regions 9 to 14 ($\underline{C}H_3$), 1 to 5 ($Si\underline{C}H_2$), and -8 to -3 ppm ($Si_2\underline{C}H$).

The mechanism by which vinylsilane forms polymer differs considerably from that of polymerization of alkylsilanes.[16] Hydrogenation of the double bonds of cyclohexene and norbornene has been reported to be the major pathway accompanying polymerization of alkylsilanes, and hydrosilation, although observed, was much less prominent with titanocene catalysts.[13] Vinylsilane, on the other hand, reacts predominantly by hydrosilation, with hydrogenation occurring to a lesser extent. Apparently, a silyl group activates a double bond toward hydrosilation. Isotopic labeling experiments indicate that the polymerization of vinylsilane involves extensive nuclear rearrangements. Exchange of hydrogen between silicon and carbon, for example, probably occurs by way of metal hydrides, and involving silametallocycles[14]. (Thus, observation of $CHDCl_2$ at 5.28 ppm in the ^1H and ^2H NMR spectra is explained by reduction of the NMR solvent, $CDCl_3$, by titanium hydrides[16] formed during the polymerizations.) Other processes, including desilylation and transilylation, also occur. Studies concerning the mechanism of polymerization of vinylsilane will be reported subsequently in more detail.

Despite a relatively low molecular weight, the vinylsilane polymer exhibits a char yield of 60%. The TGA-FTIR analysis indicates weight loss occurs principally in two stages. An initial loss (~ 15 %) of volatile organosilanes occurs near 200°C. This is followed by a more substantial loss (~ 20 %) between 375-550°C. Less than 3% mass loss is observed above 600°C. Analysis reveals the char contains 39 % C and 58 % Si (3% titanium originating from the catalyst would be expected to remain in the polymer). Analysis by XRD following pyrolysis to 1400°C in flowing argon indicated formation of small β-SiC crystallites together with a phase which was X-ray amorphous.

Table 1. Properties of Vinylsilane Polymers and Copolymers.

Monomer Composition	Yield (%)	Polymer Composition (ratio silane: carbosilane)	M_n	M_w	Char Yield (%)
100% Vinylsilane	82	26:74	540	1800	60
98% Vinylsilane: 2% DSE	80	26:74	480	1200	64
95% Vinylsilane: 5% DSE	90	30:70	560	1900	67
30% Vinylsilane: 70% Methylsilane	86	85:15	580	1300	73
32% Vinylsilane: 66% Methylsilane: 2% DSE	87	82:18	597	1450	71
28% Vinylsilane: 67% Methylsilane: 5% DSE	88	82:18	756	7330	77
100% Methylsilane	90	100:0	680	1960	65
95% Methylsilane: 5% DSE	100	100:0	920	7400	71

The properties of the polymer and its char (Table 1) can be modified by preparation of soluble copolymers derived from vinylsilane together with alkylsilanes. Copolymers containing methylsilane were constituted by a greater amount of polysilane linkages in their backbones (polymethylsilane is itself an air-sensitive preceramic polysilane[17]). Crystallite size is larger for the chars, probably because of the higher Si/C ratios. Stoichiometric silicon carbide could be achieved for a vinylsilane/methylsilane monomer mole ratio of about 30/70. An 86% yield of copolymer, comprised of 85% polysilane and 15% polycarbosilane linkages, was derived from this mixture of monomers (with Si/C ratio 1.3/1). Pyrolysis of the copolymer to 1400 °C afforded 73% of primarily amorphous char with some small (95 Å) crystallites of ß-SiC.

The low molecular weight of the vinylsilane and methylsilane polymers given in Table 1 could account for the higher char yields reported previously for polycarbosilane (87%, $M_n = 12{,}300$, $M_w = 33{,}000$) and polymethylsilane (>90%, $M_n \sim 1200$, $M_w \sim 11{,}000$)[17] obtained under different conditions.[8] Therefore, copolymers of vinylsilane and 1,2-disilylethane (DSE), a potential crosslinking agent, were studied in an effort to increase char yields. The backbone of the polymer derived from vinylsilane is little affected by addition of up to 8 mole % of DSE, although higher amounts (> 10%) produced partially soluble gels. The presence of lesser amounts of DSE did not significantly increase the molecular weight as determined by GPC (see Table 1). This behavior stands in contrast to the marked increase in the molecular weight evident for inclusion of even small amounts of DSE in the polymerization of methylsilane (or vinylsilane/methylsilane 30/70 copolymer). The char yields increase slightly in the presence of DSE, even for vinylsilane/DSE copolymer, and DSE may play a role in the thermosetting mechanism of the polymers during pyrolysis.

Our results establish a novel route for polymerization of vinylsilane which leads to production of carbosilane polymer using titanocene catalysts. Vinylsilane affords predominantly a polycarbosilane by hydrosilation, in contrast to alkylsilanes, which afford polysilanes by dehydrogenative coupling. The polycarbosilane forms more rapidly and is less air sensitive than comparable polysilanes, such as polyethylsilane. Furthermore, DSE serves to crosslink alkylsilane polymers, but not vinylsilane polymer, although DSE probably plays a role in the thermosetting of both types of polymers. The polycarbosilanes obtained from vinylsilane polymer, and copolymers with methylsilane or DSE, exhibit superior properties for use as preceramic polymers. Use of vinylsilane polymers and copolymers as precursors of high-temperature ceramic matrices or coatings, involving conversion to silicon carbide matrices and composites with temperatures as low as 500-600 °C, currently are being explored.

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(15) Terminal $-SiH_3$ groups also would appear in this region.

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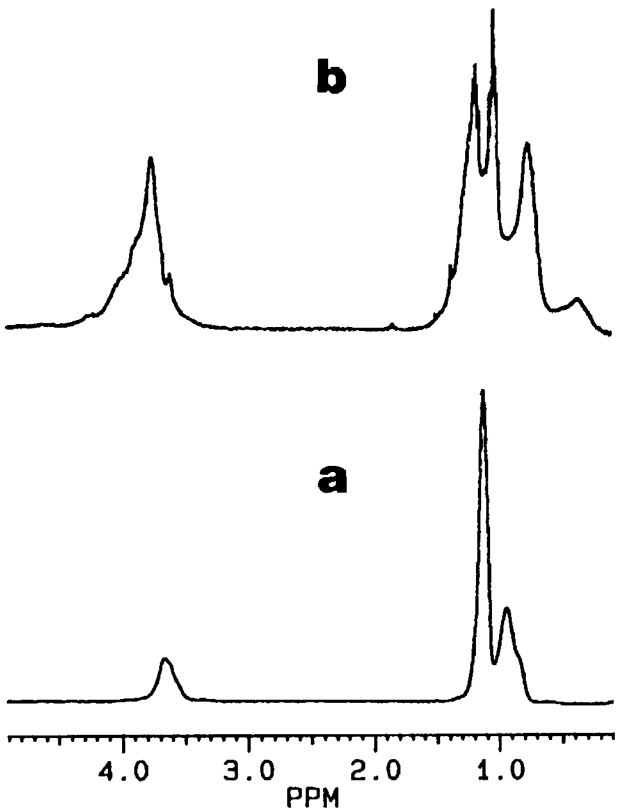
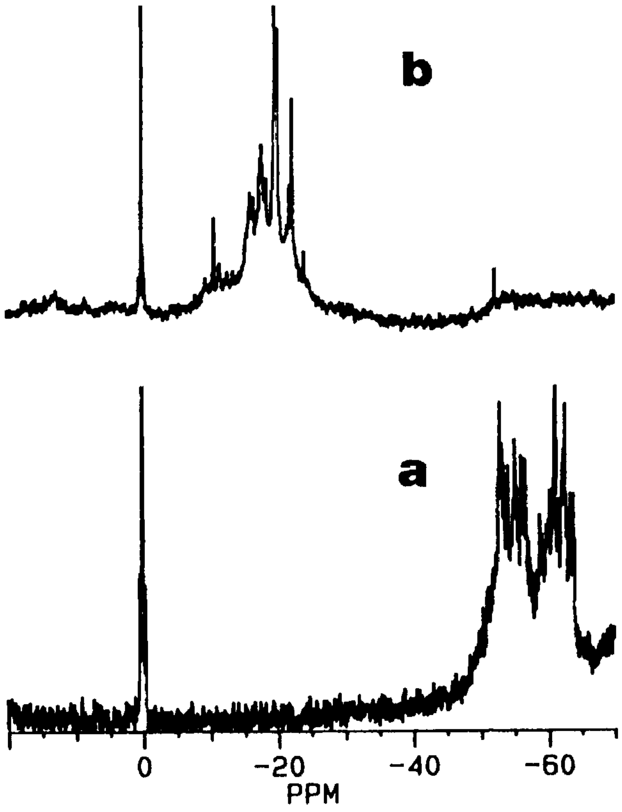
Caption to Figure

Figure 1. (a),(b) ^{1}H NMR spectra (300 MHz) and (c),(d) ^{29}Si (60 MHz, NOE suppressed) of polymers of ethylsilane (a),(c) and vinylsilane (b),(d).


b
a
4.0
3.0
2.0
1.0
PPM


b
a
0
-20
-40
-60
PPM

Section I. Description.

A. Title: Use of 1,2-Disilylethane as Crosslinking Agent in Processing Vinylsilane Copolymers.

B. Description: The properties of polymers of vinylsilane can be modified by addition of appropriate co-monomers, such as methylsilane and 1,2-disilylethane (DSE), to prepare materials suitable for processing into silicon carbide as matrices in ceramic matrix composites or as ceramic coatings. This invention describes the preparation of the preceramic polymers, the basic processing conditions effective for conversion, and structure-property relationships between the polymers and their chars.

1) Polymerizations: Polymerizations of vinylsilane, individually and as copolymers with comonomers such as methylsilane and/or 1,2-disilylethane (DSE), were accomplished using dialkyltitanocenes as catalysts as described previously (publication [1]). Vinylsilane alone leads predominantly to carbosilane-type polymers, containing a backbone comprised of $[Si-C]_x$ and $[Si-C-C]_y$ repeating units, and few [Si-Si] bonds. This polymer incorporates oxygen slowly when exposed to air. Pyrolysis leads to a relatively low char yield, however, and the material is not practical for composite fabrication.

Addition of DSE as a crosslinking agent has little affect on the molecular structure of the vinylsilane polymer, at least concerning the backbone of the polymer. Nevertheless, both polymer yields and char yields increase with increasing amounts of DSE, even though the polymer molecular weights are not affected (see Table). The copolymers consisting of vinylsilane containing only a few mole % DSE can be crosslinked by thermosetting reactions. The extent of crosslinking, and hence the rheological properties, can be controlled by regulation of the amounts of disilylethane employed. Such copolymers proved to be superior precursors for conversion into silicon carbide composite matrices.

Copolymers of vinylsilane and methylsilane afforded polymers and chars with greater silicon content than obtained for vinylsilane alone. Addition of methylsilane leads to formation of correspondingly greater amounts of polysilane ([Si-Si] bonds) at the expense of polycarbosilane. Copolymers consisting of predominantly methylsilane are air sensitive. For example, a composition of about 30% vinylsilane and 70% methylsilane could be pyrolyzed under inert atmosphere to form nearly stoichiometric silicon carbide (Si:C ratio close to 70:30). This copolymer contains mostly polysilane linkages, and polycarbosilane linkages comprise only 15% of the polymer backbone. Addition of DSE also lead to higher yields, with the realization of higher molecular weights, for the ternary copolymers (see Table).

2) Fabrication: Original composites are prepared by impregnating small diameter fibers with the polymer, which may also contain a particulate filler. The filler may be commercial silicon carbide or material derived from vinylsilane polymer by pyrolysis in a furnace under inert atmosphere. The ratio of filler is 0-33 % by weight to 100-67 % vinylsilane copolymer containing 0-8 % DSE. The composite is staged under vacuum or in an oven under inert atmosphere with temperature holds to remove solvent and to initiate cure. The prepreg is cut to size and then laid up in the mold. Finally, this material is hot pressed.

As an example, a copolymer of vinylsilane is prepared from 92 mole % vinylsilane, 4 % DSE, and 4 % dimethyltitanocene under argon in THF. A dispersion is obtained by mixing 20 % by weight of an amorphous silicon carbide filler into 80 % by weight of the copolymer solution under inert atmosphere. The dispersion is applied to Nicalon fiber weave, and this composite is staged under vacuum (15" Hg) with holds at 176 °F to remove solvent and 300 °F to initiate cure. The prepreg is cut to size and then laid up in the mold. This material is pressed at 200 psi under 30" vacuum with heating to 700 °F (holds at 450 °F and 700 °F).

C. <u>Applications</u>: The polymerization method provides a mild, efficient and reliable technique for preparation of novel polymer precursors which provide characteristics suitable for fabrication of high-temperature ceramic composites or coatings involving conversion to silicon carbide with temperatures as low as 500-600 °C.

D. <u>Advantages</u>: Polymerization of vinylsilane with DSE and/or methylsilane using homogeneous titanocene catalysts affords a new kind of polymer possessing superior properties for conversion into silicon carbide. This polymer is readily prepared from commercially available starting materials.

The ease of reaction at relatively low temperature makes this technique safer and more reproducible than state of the art methods for preparation of preceramic precursors of silicon carbide, as it allows better control over the polymerization process. The polymer contains a low carbon/silicon ratio, and it is predominantly a polycarbosilane (containing a -C-Si-C-Si- and/or -Si-C-C-Si- backbone), rather than a polysilane (containing a -Si-Si-Si- backbone). This is beneficial structurally and has important consequences for processing. The polymer is formed in high yield. It is less air sensitive than polysilanes, and can tolerate at least brief handling in air with essentially no oxygen incorporation. Pyrolysis leads to a carbon-rich amorphous silicon carbide matrix containing about 3 % titanium, with a high char yield (low shrinkage). Addition of DSE increases the yield of polymer as well as the char yield, further reducing shrinkage, in a manner proportional to the amount of DSE added. The potential of DSE for forming crosslinks during curing results in a ceramic with higher structural integrity.

Other co-monomers, such as methylsilane, modify the properties of the polymer and the material obtained after processing. For example, the copolymer of vinylsilane and methylsilane (with and without DSE) affords greater amount of silane-type polymer which can serve as a high yield precursor to crystalline SiC, exhibits low shrinkage, and can be readily manipulated for processing applications.

E. <u>Limitations, continuing work</u>: The next step will involve scale-up to fabricate larger composites for pyrolysis to 1400° C or hot isostatic pressing.

Work is continuing on formulations to find blends and copolymers reactive with potential crosslinking agents (such as divinylsilanes, trivinylsilanes, polyvinylalkanes, polyvinylbenzenes, titanium alkoxides, and ammonia and amines) in order to achieve optimal polymer performance. The relationship between polymer properties and processability is being studied. The effects of formulation, treatment and processing on properties such as composition, viscosity, yields, air sensitivity, and crystallinity are currently under investigation. Techniques to aid in catalyst recovery and efficiency, including preparation of polystyrene-supported catalyst systems and use of other transition metal catalysts, also are being examined.

The use of polymer for coatings and fiber infiltration will be the subject of future investigations.

F. Products made and tested: To date, compositions of one, two, and three component systems have been made (*viz*. vinylsilane polymer, copolymer of vinylsilane and DSE, and ternary polymer and blends of methylsilane, vinylsilane, and DSE) and formed into 1.25" x 4" 4-ply preceramic composites.

Table. Properties of Vinylsilane Polymers and Copolymers.

Monomer Composition	Yield (%)	Polymer Composition (ratio silane: carbosilane)	M_n	M_w	Char Yield (%)
100% Vinylsilane	82	26:74	540	1800	60
98% Vinylsilane: 2% DSE	80	26:74	480	1200	64
95% Vinylsilane: 5% DSE	90	30:70	560	1900	67
30% Vinylsilane: 70% Methylsilane	86	85:15	580	1300	73
32% Vinylsilane: 66% Methylsilane: 2% DSE	87	82:18	597	1450	71
28% Vinylsilane: 67% Methylsilane: 5% DSE	88	82:18	756	7330	77
100% Methylsilane	90	100:0	680	1960	65
95% Methylsilane: 5% DSE	100	100:0	920	7400	71

Section II. Publications

A. Publications (copies provided):

(1) "Polymerizations of Alkenylsilanes Using Early Transition Metal Catalysts", J. Masnovi, X. Y. Bu, P. Conroy, A. H. Andrist, F. I. Hurwitz, D. Miller, (C. J. "Better Ceramics Through Chemistry IV" Brinker, D. E. Clark, D. R. Ulrich and B. J. J. Zelinsky, Eds.), Materials Research Society Symposium Proceedings, Vol. 180, 23 Nov. 1990, Pp. 779-784.

(2) "Polymeric Routes to Silicon Carbide and Silicon Oxycarbide CMC", F. I. Hurwitz, P. J. Heimann, J. Z. Gyekenyesi, J. Masnovi, X. Y. Bu, presented at the 15th Annual Conference on Composites and Advanced Ceramics, American Ceramic Society, Cocoa Beach, FL, 13-16 January 1991.

(3) "Syntheses, Structures and Properties of Polycarbosilanes Formed Directly by Polymerization of Alkenylsilanes", presented at "Better Ceramics Through Chemistry V", Materials Research Society, San Francisco, CA, 29 April 1992.

(4) "Approaches to Polymer-Derived CMC Matrices", F. I. Hurwitz, to be presented to the Society for the Advancement of Materials and Process Engineering, Toronto, Canada, 20-22 October 1992.

D. Developments by others (references to previous work):

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