Organosilane Polymers, VII: Sodium-Derived Vinylic Polysilanes

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Dechlorination of mixtures of CH₂=CHSiMeCl₂ with other chlorosilanes, using sodium metal in hydrocarbon/THF solvent blends, provides vinylic polysilanes which are excellent precursors for silicon carbide ceramic compositions. These polymers are soluble, relatively inert, and are thermally curable through reactions of the vinyl groups.
ORGANOSILANE POLYMERS, VII:

SODIUM DERIVED VINYLIC POLYSILANES

by

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INTRODUCTION

Mixtures of \( \text{CH}_2=\text{CHSiMeCl}_2 \) (vinylmethyldichlorosilane) with other chlorosilanes are dechlorinated by potassium metal in tetrahydrofuran solvent to yield highly branched polycarbosilanes which are effective precursors for silicon carbide ceramic compositions.\(^1\) The costs and hazards associated with potassium metal prompted numerous attempts to prepare similar tractable ceramic precursors using the safer, less costly, and less reactive metal, sodium. These experiments achieved a low level of success, until the concept of using blended solvents was employed, and recognition made of the radically different polymeric structures which are obtained with sodium.

RESULTS AND DISCUSSION

Dechlorination of the above chlorosilane monomer mixture using sodium metal in 7/1 (w/w) toluene/THF provides a vinylic polysilane, rather than the polycarbosilane obtained with potassium. In addition to dechlorination, potassium causes disilylation of vinyl groups, incorporating them into the polymer backbone, while sodium does not. The sodium-derived vinylic polysilane also provides a higher yield of SiC ceramic composition in pyrolysis than does the potassium-derived polycarbosilane.

Replacing the \( \text{Me}_2\text{SiCl}_2 \) with \( \text{MeSiHCl}_2 \) provides polysilanes which are even more efficient precursors for SiC, demonstrating again the effectiveness of \( \text{MeSiHCl}_2 \) in providing preceramic polymers with improved ceramic yields.\(^2,3\)
It is clear that sodium is less reactive than potassium, particularly toward Me₃SiCl and CH₂=CHSiMeCl₂ groups, that CH₂=CHSiMeCl₂ possesses uniquely high reactivity toward sodium, and that the use of solvent blends moderates reactivities such that useful products can be prepared.

The low reactivity of Na toward both Me₃SiCl and CH₂=CHSiMeCl₂ groups is demonstrated by the reaction of Me₃SiCl with CH₂=CHSiMeCl₂. Sodium causes no reaction, providing neither Me₃SiSiMe₃ nor Me₃SiCH₂CH(SiMe₃)₂, while potassium provides a high yield of the latter product.

Thus, no significant reaction occurs between sodium and Me₃SiCl in refluxing 7/1 toluene/THF or xylenes/THF (or in either arene or THF separately). Addition of CH₂=CHSiMeCl₂ to a refluxing mixture, as shown, causes rapid reaction, with formation of vinylic polysilanes. The product distribution is definitely nonrandom in that a 4/3 ratio of Me₃SiCl/CH₂=CHSiMeCl₂ under the above conditions provides products at 0% yield for x = 0, 0.4% for x = 1, 20.1% for x = 2, and 11.0% for x = 3, the remainder (43.4%) being higher polysilanes. Much of the Me₃SiCl (39.2%) was recovered as Me₃SiOSiMe₃ after hydrolytic termination/neutralization, accenting the low reactivity of Me₃SiCl.

Model reactions as above wherein SiMeCl₂, EtSiMeCl₂, or Me₂SiCl₂ were substituted for CH₂=CHSiMeCl₂ were qualitatively slower and less complete than that of CH₂=CHSiMeCl₂, with reactivity decreasing in the order Ø > Et > Me.

The higher reactivity of vinylic chlorosilanes in certain active metal reactions has been noted. For example, Me₂SiHCl, Me₃SiCl, and CH₂=CHCH₂SiMe₂Cl are not individually dechlorinated by magnesium in THF to form the corresponding disilanes, while CH₂=CHSiMe₂Cl yields (CH₂=CHSiMe₂)₂. The high reactivity shown by CH₂=CHSiMeCl₂ in the present work is not reflected by CH₂=CHSiMeCl₂, suggesting several subtle effects on chlorosilane reactivity, including steric and electronic factors, solubility of reactive intermediates, condition of active metal surface, agitation effects, role of solvents, and so on.
MECHANISTIC CONSIDERATIONS

While sodium does not cause reactions of \( \text{CH}_2=\text{CHSi}^- \) groups, it is known to cause disilylation of hydrocarbon olefins, such as styrene\(^8\) or isoprene.\(^9\) The authors propose that such reactions begin with electron transfer from sodium

\[
2\text{Me}_3\text{SiCl} + \text{CH}_2=\text{CH} \overset{\text{Na}}{\underset{\text{THF}}{\longrightarrow}} \text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiMe}_3
\]

\[
2\text{Me}_3\text{SiCl} + \text{CH}_2=\text{CHCHMe}_2 \overset{\text{Na}}{\underset{\text{THF}}{\longrightarrow}} \text{Me}_3\text{SiCH}_2\text{CHCHMe}_2\text{SiMe}_3
\]

to the olefin, followed by attack of the resultant anion radical on an \( \text{SiCl}^- \) group, a second electron transfer to the monosilylated intermediate and attack on a second \( \text{SiCl}^- \) group. The end result is formation of two \( \text{SiCl}^- \) bonds, or disilylation.

It is also known that magnesium causes disilylation of \( \text{CH}_2=\text{CHSiMe}_3 \) in hexamethylphosphoramide (HMPA), with \( \text{FeCl}_3 \) as a catalyst.\(^4\) This reaction may occur by Michael addition of the anionic species, \( \text{Me}_3\text{SiMgCl}, \) to the \( \text{CH}_2=\text{CHSi}^- \) group, followed by attack of the resultant carbanion on \( \text{Me}_3\text{SiCl} \). The same reaction does not occur in THF.

It appears that the electron transfer mechanism may be controlled by the respective oxidation potentials of the active metals, and the reduction potentials of the olefinic reactants. Thus, \( \text{K} \) may cause disilylation of

<table>
<thead>
<tr>
<th>Oxidation Potentials</th>
<th>Reduction Potentials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium 2.925 volts</td>
<td>( \text{CH}_2=\text{CHSiMe}_3 ) Unknown (high)</td>
</tr>
<tr>
<td>Sodium 2.714 volts</td>
<td>( \text{CH}_2=\text{CHCHMe}_2 ) 2.6-2.7 volts</td>
</tr>
<tr>
<td>Magnesium 2.37 volts</td>
<td>( \text{CH}_2=\text{CH}^- ) 2.4-2.6 volts</td>
</tr>
</tbody>
</table>

\( \text{CH}_2=\text{CHSiMe}_3 \) in THF by electron transfer, while \( \text{Na} \) and \( \text{Mg} \) do not, and both \( \text{Na} \) and \( \text{K} \) cause disilylation of styrene and isoprene. Indeed, \( \text{CH}_2=\text{CHSiMe}_3 \) can be prepared in the presence of sodium.\(^3\)

Note that while \( \text{CH}_2=\text{CHSiMe}_3 \) is disilylated by \( \text{Me}_3\text{SiCl} \) with \( \text{Mg} \) in HMPA,\(^4\) vinylic disilanes can be prepared using \( \text{Mg} \) in THF\(^7\) (no reaction of \( \text{CH}_2=\text{CHSi}^- \) groups). One concludes that \( \text{CH}_2=\text{CHSi}^- \) groups may be disilylated by two

\[
\text{CH}_2=\text{CHSiMe}_2\text{SiMe}_3 \overset{\text{Mg/THF}}{\underset{\text{Me}_3\text{SiCl}}{\longrightarrow}} \text{CH}_2=\text{CHSiMe}_2\text{Cl} \overset{\text{Mg}}{\underset{\text{THF}}{\longrightarrow}} (\text{CH}_2=\text{CHSiMe}_2)_2
\]

different mechanisms, neither of which is operative with sodium in blended hydrocarbon/THF solvents.
SOLVENT CONSIDERATIONS

The 7/1 toluene/THF blend ratio was selected to provide a solvent medium which had a reflux temperature above the melting point of sodium. Equivalent blends of xylenes or octane with THF were also effective. The ethereal portion of the blend plays a significant role in providing useful products, since chlorosilane reactivities vary in its presence or absence. For example, the reaction of 1.5/1 Me₃SiCl/CH₂=CHSiMeCl₂ with sodium in toluene alone provides 27.9% of volatile/nonvolatile soluble products and 31.9% of insoluble solid product. The same reaction, run in 7/1 toluene/THF, yields 65.5% of soluble products and 4.5% of insoluble solid. Similarly a reaction of 0.5/1/1 Me₃SiCl/Me₂SiCl₂/CH₂=CHSiMeCl₂ with sodium provides 62.9% of insoluble solid in toluene alone, and 78.3% of soluble products in 7/1 toluene/THF. THF causes more efficient incorporation of molecular weight-limiting Me₃Si groups, with resultant higher yields of soluble products. The latter are desirable in terms of polymer processing properties, relative to insoluble, infusible solids.

THF is known to provide improved reactivity for other reactions involving sodium. The isoprenylation of arenes, as catalyzed by sodium naphthalene, proceeds more rapidly and under milder conditions when arene/THF blends are used.¹⁵

Both arenes and THF are incorporated into by-products to minor extents. A cleavage product of THF, Me₃Si(CH₂)₄OSiMe₃,¹⁶ is observed and is converted to Me₃Si(CH₂)₄OH by the hydrolytic workup. Silylated arenes, ArCH₂SiMe₃, have also been noted at low levels by GC/MS and NMR analyses. The degree of solvent incorporation is higher for slower reactions, such as Me₃SiCl/EtSiMeCl₂, and is higher for toluene than for xylenes.

HYDROSILYL MODIFICATION

As in earlier preceramic polymers prepared under this contract,²,³ the incorporation of hydrosilyl groups (the use of Me₂SiHCl as a comonomer) provides improved ceramic yields. The degree of retention of *SiH groups during synthesis has not been established, but is higher than the 20% seen with potassium. The high yield (74%) preparation of HMe₂SiMe₂H suggests that *SiH retention

\[
\text{HMe₂SiMe₂H} \xrightarrow{\text{Na}} \text{Me₂SiHCl} \xrightarrow{\text{Li/THF}} \text{(Me₂Si)}_6
\]

is quite good. It should be noted that lithium causes complete loss of *SiH groups from Me₂SiHCl.¹⁸

POLYMER PREPARATIONS

A variety of polymers were prepared with different monomers, different monomer ratios, and under different reaction conditions to roughly optimize (or compromise) high yields of tractable precursor polymer with high ceramic yields. Good performance was obtained at 0.85/0.3/1.0 Me₃SiCl/Me₂SiHCl₂/CH₂=CHSiMeCl₂ using either 7/1 toluene/THF or xylenes/THF. Yields of 60–65% of soluble solid
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<table>
<thead>
<tr>
<th>Reagents</th>
<th>Reaction Conditions</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85 Me₃SiCl</td>
<td>arene/THF</td>
<td>10-15% Volatiles</td>
</tr>
<tr>
<td>0.3 MeSiHCl₂</td>
<td></td>
<td>60-65% Soluble Solid</td>
</tr>
<tr>
<td>1.0 CH₂=CHSiMeCl₂</td>
<td>Na</td>
<td>&lt;5% Insoluble Solid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH 1200°</td>
</tr>
</tbody>
</table>

are routinely obtained and consistently convert to 55-60% yields of SiC ceramic composition. Both the ceramic yield and quality are improvements over those obtained with K-derived polycarbosilanes.

CROSSLINKING CHEMISTRY

The vinyl polysilanes crosslink, or thermoset at temperatures in the 200-240°C range. The crosslinking reaction does not involve oxygen incorporation or weight loss, and appears to be a combination of =SiH/CH₂=CHSi⁻ addition and CH₂=CHSi⁻ polymerization reactions. When a mixture of roughly equivalent amounts of three liquid compounds, Me₃Si(SiMeH)ₓ(SiMeCH=CH₂)ᵧSiMe₃, where x = 0, y = 2; x = 1, y = 2; and x = 0, y = 3 (isolated by distillation from a typical polymer preparation) is heated under nitrogen to 220°C, a soluble solid is formed in which all of the =SiH groups and 60% of the vinyl groups have reacted. Since the latter were present in large molar excess, their consumption by vinyl polymerization as well as by =SiH addition is implicated and is confirmed by NMR analysis. Polymerization of 2-vinyl-1,1,2,3,3,3-heptamethyltrisilane through the vinyl groups is believed to be responsible for its high ceramic yield.

PYROLYSIS CHEMISTRY

The reactions which occur up to 240°C have been discussed above under crosslinking chemistry. Additional reactions occur as the temperature is raised, with vinyl groups being totally reacted by 350°C. Hydroxysilyl groups reappear at 350°C, probably due to the rearrangement of =SiCH₃ groups to =HSiCH₂ groups, as noted by Yajima. Weight loss due to thermal decomposition becomes fairly rapid above 400°C and is essentially complete around 600°C. There is little weight change from 600°C - 1200°C, with the major change being conversion of amorphous SiC to microcrystalline β-SiC. These changes are summarized in a typical TGA scan (see Figure 1).

The condensable volatile products from pyrolyses have been collected and analyzed by GC/MS and NMR. Quite surprisingly, volatile pyrolysis products from Na-derived polysilanes and K-derived polycarbosilanes are virtually

Vinyl Polysilane  Na  Me₃SiCl  K  Polycarbosilane
<table>
<thead>
<tr>
<th>arene/THF</th>
<th>CH₂=CHSiMeCl₂</th>
<th>THF</th>
<th>1200°C</th>
<th>&quot;SiC&quot; + Volatile Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
identical (as are the "SiC" compositions) as analyzed. This suggests that the radically different structures of vinylic polysilanes and polycarbosilanes may convert to a common intermediate at some point during pyrolyses. Further investigation is clearly needed, and is planned.

**ANALYTICAL CONSIDERATIONS**

The vinylic polysilanes are not analytically pure, due to some oxygen incorporation during hydrolytic workup and some solvent incorporation during synthesis. The problem is further complicated by the facts that preceramic polymers are difficult to combust completely, that the monomers charged are incorporated into products to extents varying with their respective reactivities, and that some of the products are removed as volatiles. For example, the product of the reaction of 1.5/1 Me3SiCl/CH2=CHSiMeCl2 has the average empirical formula or structure of Me3Si(SiMeCH=CH2)1.33SiMe3, with calculated elemental contents of 50.14% C, 10.86% H, 39.00% Si, and 0.00% of O and Cl. The values found are 46.71% C, 9.42% H, 37.95% Si, 0.12% Cl, and 5.80% O (latter by difference).22

Ceramic analyses are also difficult, with traditional modes of SiC analyses not being applicable to organosilicon-derived SiC compositions. The SiC samples as prepared are not homogeneous, for example, and while pieces as prepared are stable in air to 1000°C, crushed pieces with fresh surfaces undergo oxidation in air, showing weight loss as carbon is oxidized to volatile CO2, and weight gain as silicon is oxidized to nonvolatile SiO2. This problem was discovered by Coors Spectrochemical Laboratories, while attempting to analyze our experimental samples. The TGA curves of a typical SiC sample, uncrushed and crushed, are shown in Figure II (A and B).

Although the structures of the vinylic polysilanes have been clarified by model reactions and instrumental analyses of volatile products, it was decided to assess Si-Si bond cleavage as a means of converting polysilanes into easily identifiable monomeric units. A Dow Corning patent disclosed the use of palladium on charcoal (Pd/C) as a means of quantitatively cleaving Si-Si bonds in alcohols with formation of the corresponding alkoxy silanes and hydrogen. Volatile vinylic polysilanes underwent this reaction with two major complications. First, the vinyl groups were reduced to ethyl groups, such that -MeSiCH=CH2 units yielded EtSiMe(OMe)2 when methanol was used. Vinyl groups were also reduced without cleavage, yielding ethylmethyl polysilanes which were

\[
\begin{align*}
\text{Me}_3\text{Si}(\text{Si})_2\text{SiMe}_3 & \xrightarrow{\text{Pd/C}} \text{Me}_3\text{SiOMe} + \text{EtSiMe(OMe)}_2 + \text{Me}_3\text{Si(}\text{Si})_2\text{SiMe}_3 \\
\text{CH}=\text{CH}_2 & \\
\end{align*}
\]
very slowly cleaved, even under reflux conditions. Secondly, "SiH groups also react, such that -MeSiH- units yield MeSi(OMe)₃ with MeOH.

Cleavage of the single "SiSi" bond in the model compound/reaction shown was also very slow (13% conversion of starting material after 13 hr at reflux).

\[
\text{Me}_3\text{SiCH}_2\text{CHSiMe}_2\text{SiMe}_3 \xrightarrow{\text{Pd/C}} \text{Me}_3\text{SiOMe} + \text{Me}_3\text{SiCH}_2\text{CHSiMe}_2\text{OMe}
\]

Our results with Pd/C were exactly consistent with those of Kumada on cleavage of vinylic di- and trisilanes with soluble palladium metal catalysts.

CONCLUSIONS

Sodium metal in arene/THF blends effectively dechlorinates mixtures of CH₂=CHSiMeCl₂ with other chlorosilanes to yield vinylic polysilanes which are very effective precursors for SiC. This is the most economically feasible and safest approach to preceramic polymers for SiC yet developed in this program.

ACKNOWLEDGEMENTS

This is the last technical report under this contract, and I would like to acknowledge the many contributions made during this and earlier parts of the program. The laboratory assistance of D. A. Williams and J. Alfonso is gratefully acknowledged as are the prompt services provided by many staff members in both the SUI Division and the Central Scientific Laboratories of Union Carbide, regarding GC/MS, nonroutine NMR, TGA/DSC, pyrolysis studies, SEM, x-ray diffraction, and IR/UV analysis. Also acknowledged are the good works performed by Albany International Research Company on spinning tests, Galbraith Laboratories in elemental analyses, and Coors Spectrochemical Laboratories on ceramic analyses.

The continued support of Dr. Kenneth Wynne of ONR is gratefully appreciated as is ceramic screening work performed in Dr. Roy Rice's group at NRL.

EXPERIMENTAL SECTION

All chlorosilanes were freshly distilled before use. THF and arenes were reagent grade, dried over Linde 4A molecular sieves. Na metal was purchased and used as practical grade ingots. All Na transfers and reactions were run under nitrogen, as were pyrolyses to 700°. Pyrolyses to 1200° were run under argon. Routine NMR analyses were run on a Perkin-Elmer R24A spectrometer; VPC analysis were run on a Hewlett-Packard 5840A gas chromatograph. Pyrolyses to 700° were run in quartz reactors in a Lindberg 54242 tube furnace, and to 1200° in a Lindberg 54233 furnace in alumina reactors. Both furnaces have programmable controllers, allowing attendant-free operation. Heating programs are summarized in Reference 1b. Conversions of precursors to microcrystalline β-SiC compositions were confirmed by x-ray diffraction.
Reaction of 4/3 Me₃SiCl/CH₂=CHSiMeCl₂ with Na in 7/1 Xylenes/THF

In a 11 3NRB flask were combined 338.3g xylenes and 48.5g THF. Na was added in chunks (23.3g, 1.0 mol) in a dry box under nitrogen. Flask was transferred to a hood and fitted with mantle, mechanical stirrer (stainless steel blade), thermometer, addition funnel, Dewar condenser (filled with toluene cooled by ice water immersion coil), and N₂ flow valves. Heat was applied to 112°, melting the Na, and 43.0g (0.4 mol) of Me₃SiCl added over 1 hr with constant heating, and heating continued at 106-108° for four hours. VPC analysis showed no reaction was occurring. Heating at reflux was resumed and 42.3g (0.3 mol) of CH₂=CHSiMeCl₂ added in 15 min. Reflux temperature rose from 106° to 112° during addition, and to 114° after 5 hrs. additional heating at reflux. After cooling on wet ice bath, reaction was terminated by addition of 5.73g (0.32 mol) of H₂O in 10.9g THF. MgSO₄ (45.5g) was added and the mixture stirred briefly, followed by filtration to remove solids, washing of filtrate with 70 ml 7/1 xylenes/THF, and refiltration. The solids were treated with water in a Waring blender, leaving insoluble solid product (1.8g, 3.6% yield after washing and vacuum drying). The organic mixture was stripped and vacuum distilled, yielding volatile products (25.63g up to 96°/0.52 mm, 51.1%) and heavies (23.73g, 47.3%).

The volatile fractions analyzed as follows in terms of weights and yields:

- 12.7g (Me₃Si)_2O - 39.2% based on Me₃SiCl
- 1.17g Me₃Si(CH₂)₂OH - 2.0% based on Me₃SiCl
- 0.23g (Me₃Si)₂SiMeCH=CH₂
- 0.08g (Me₃Si)₂SiMeCH₂CH₃
- 0.16g xylyl-SiMe₃ isomers
- 8.63g Me₃Si(SiMeCH=CH₂)₂SiMe₃ - 20.1%
- 0.51g Me₃Si(SiMeCH₂CH₃)₂SiMe₃
- 0.17g unknowns
- 1.98g Me₃Si(SiMeCH=CH₂)₃SiMe₃ - 5.6%
- 25.63g

The heavies, by VPC estimate, contained 1.95g of the last compound, Me₃Si(SiMeCH=CH₂)₃SiMe₃.

Pyrolysis of the heavies to 1200° in two steps provided 47.1% of SiC composition.

Reaction of 2/1 Me₃SiCl/CH₂=CHSiMeCl₂ with Na in Toluene/THF

The above procedure was followed with 171.6g of toluene, 26.6g of THF, 34.0g (1.48 mol) of Na, 76.4 (0.7 mol) of Me₃SiCl, and 49.7g (0.35 mol) of CH₂=CHSiMeCl₂, except that the chlorosilanes were added as a mixture. Workup yielded volatile products, 15.5% yield, b.p. up to 71°/0.03mm, and 35.6% of thermoplastic solid. Pyrolysis of the latter to 1200° yielded 38.5% of SiC composition. The polymer consisted primarily of Me₃Si- units and -MeSi(CH=CH₂)- units; the major liquid products were Me₃Si[SiMe(CH=CH₂)]ₓSiMe₃ where x is 2 or 3.
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Reaction of 1.5/1 Me₃SiCl/CH₂=CHSiMeCl₂ with Na in Toluene/THF

The procedure of the last reaction was employed with 170.7g of toluene, 25.4g of THF, 25.0g (1.09 mol) of Na, 48.1g (0.44 mol) of Me₃SiCl, and 41.9g (0.3 mol) of CH₂=CHSiMeCl₂. Workup yielded 2.4g (4.5%) of insoluble solid product, 21.8g (41.2%) of soluble polymer, and 12.9g (24.3%) of volatile product, b.p. up to 115⁰/0.56mm. The products were structurally the same as those of the previous reaction. Pyrolysis of the soluble solid polymer (elemental analysis in text) to 1200⁰ yielded 47.9% of SiC composition. Equivalent results were obtained when octane was substituted for toluene in the above reaction, and when xylene was substituted for toluene. When the reaction was repeated in toluene alone (no THF), yields of 31.9% of insoluble solid, 20.8% of nonvolatile polymer (49.6% SiC yield, 1200⁰), and 7.2% of volatile products, b.p. up to 107⁰/0.05mm, were obtained.

Reaction of 0.85/0.3/1.0 Me₃SiCl/Me₂SiCl₂/CH₂=CHSiMeCl₂ with Na in Xylenes/THF

The procedure of the previous reaction was used, beginning with 510.2g of xylene, 77.2g of THF, 91.1g (3.96 mol) of Na, 100.9g (1.12 mol) of Me₃SiCl, 42.4g (0.33 mol) of Me₂SiCl₂, and 154.2g (1.09 mol) of CH₂=CHSiMeCl₂. Workup yielded 33.2g (20.3%) of volatile products, b.p. up to 128⁰/1.5mm and 103.7g (63.5%) of nonvolatile polymer. Pyrolysis of the latter to 1200⁰ provided 49.5% of SiC composition.

Reaction of 1/1 Me₃SiCl/CH₂=CHSiMeCl₂ with Na in Xylenes/THF

The procedures of the previous reaction were followed using 516.1g of xylenes, 76.5g of THF, 96.8g (4.21 mol) of Na, 145.0g (1.34 mol) of Me₃SiCl, and 188.4g (1.34 mol) of CH₂=CHSiMeCl₂. Workup yielded 57.4g (30.0%) of nonvolatile soluble polymer, and 47.6g (29.9%) of liquid products, b.p. up to 132⁰/1.0mm. Pyrolysis of the soluble solid to 1200⁰ yielded 41.6% of SiC composition. Pyrolysis of a liquid fraction, b.p. 106-132⁰/1.0mm, consisting primarily of Me₃Si[SiMe(CH=CH₂)]₅SiMe₃, where x=2 (24.1%), and x=3 (69.6%), to 1200⁰ provided 20.1% of SiC composition.

Reaction of 1/1 Me₂SiCl₂/CH₂=CHSiMeCl₂ with Na in Xylenes/THF

The same procedure was used with 516.1g of xylenes, 75.9g of THF, 107.9g (4.69 mol) of Na, 144.1g (1.12 mol) of Me₂SiCl₂, and 157.5g (1.12 mol) of CH₂=CHSiMeCl₂. Workup yielded 23.7g (16.6%) of insoluble solid, 57.4g (40.1%) of soluble solid, and 1.4g (1.0%) of volatiles, b.p. up to 95⁰/1.0mm. Respective 1200⁰ pyrolyses of the soluble and insoluble solids provided SiC composition yields of 49.6% and 56.6%.

Reaction of 0.5/1.0 Me₃SiCl/Me₂SiCl₂/CH₂=CHSiMeCl₂ with Na in Toluene/THF

The above procedure and workup, beginning with 339.6g of toluene, 50.1g of THF, 72.9g (3.17 mol) of Na, 32.8g (0.30 mol) of Me₃SiCl, 78.1g (0.61 mol) of Me₂SiCl₂, and 85.2g (0.60 mol) of CH₂=CHSiMeCl₂, yielded 4.9g (4.5%) of
insoluble solid, 66.6g (67.0%) of soluble solid, and 11.3g (11.3%) of volatile products, b.p. up to 102°/0.73 mm. Pyrolysis of the soluble solid to 1200° yielded 43.5% of SiC composition.

The same reaction, run using toluene alone (no THF) yielded 62.9% of insoluble solid.

Reaction of 1/1/1 CH₂=CHSiMe₂Cl/Me₂SiCl₂/CH₂=CHSiMeCl₂ with Na in Toluene/THF

The usual procedure and workup, starting with 347.4g of toluene, 51.5g of THF, 56.5g (2.46 mol) of Na, 56.4g (0.47 mol) of CH₂=CHSiMe₂Cl, 60.3g (0.47 mol) of Me₂SiCl₂, and 65.9g (0.47 mol) of CH=CHSiMeCl₂, provided 5.2g (5.2%) of insoluble solid, 58.8g (59.0%) of soluble solid, and 23.9g (23.9%) of volatile products. Pyrolysis of the soluble solid to 1200° yielded 40.7% of SiC composition. The volatile products, by GC/MS analysis, included

\[
\text{CH}_2\text{CHSiMe}_2\text{(SiMe)}_x\text{SiMe}_2\text{CH}==\text{CH}_2 \quad \text{where } x = 1, \text{2, or 3,}
\]
\[
\text{CH}_2\text{CHSiMe}_2\text{(SiMe(CH=CH}_2\text{)}_y\text{SiMe}_2\text{CH}==\text{CH}_2 \quad \text{where } x = 1, 2, \text{or 3 and}
\]
\[
\text{CH}_2\text{CHSiMe}_2\text{(SiMe(CH=CH}_2\text{)}_x\text{SiMe}_2\text{CH}==\text{CH}_2 \quad \text{where } x = 1 \text{ or 2.}
\]

Reaction of 0.5/0.5/1 Me₃SiCl/Me₂SiCl₂/CH₂=CHSiMeCl₂ with Na in Xylenes/THF

The usual procedure and workup, beginning with the title monomer ratio, provided 15.2% of volatiles, b.p. up to 130°/1.3mm, 54.3% of soluble solid, and 5.6% of insoluble solid. Pyrolysis of the soluble solid to 1200° provided 51.0% of SiC composition.

Reaction of 1/1 Me₂SiHCl/CH₂=CHSiMeCl₂ with Na in Xylenes/THF

The usual procedure was followed using 339.8g of xylene, 51.4g of THF, 42.3g (1.84 mol) of Na, 55.3g (0.58 mol) of Me₂SiHCl, and 82.4g (0.58 mol) of CH₂=CHSiMeCl₂. Workup provided 12.1g (16.1%) of liquid products, 45.9g (60.9%) of soluble solid, and several g of insoluble solid. Pyrolysis of the soluble solid to 1200° yielded 42.2% of SiC composition. The major volatile product, b.p. 58°/0.69mm, was identified as HMe₂Si[SiMe(CH=CH₂)]₂SiMe₂H by GC/MS and NMR.

Reaction of 1/1 CH₂=CHSiMe₂Cl/CH₂=CHSiMeCl₂ with Na in Toluene/THF

The usual procedure and workup, starting with 346.0g of toluene, 52.7g of THF, 42.2g (1.84 mol) of Na, 70.4g (0.58 mol) of CH₂=CHSiMeCl₂, and 82.2g (0.58 mol) of CH₂=CHSiMeCl₂, yielded 4.9g (5.4%) of volatile, b.p. up to 100°/0.78mm, 18.3g (20.3%) of nonvolatile polymer, and 19.1g (21.1%) of insoluble solid. Pyrolysis of the soluble solid to 1200° provided 44.4% of SiC composition.
ORGANOSILANE POLYMERS, VII

REFERENCES


12. Reduction potentials as polargraphic half-wave potentials from Handbood of Organic Electrochemistry.


20. Thermal chemistry at 350° and above was assessed by IR study of thin films by the Central Scientific Laboratory.
22. Elemental analyses by Galbraith Laboratories, Knoxville, Tennessee.
Sample: POLYSILANE 9091-31.32
Size: 47.49 mg / 0.490-23.815/
Rate: 30 CCS N2/MIN

Start Method: 1

Methods: 1
Initial Temp: 25.0
Program Rate: 10.0
Final Temp: 700.0
Iso Minutes: 0.0
Program Cool: No
Program Gas: 1
Next Method: 0

8 SECONDS/POINT

Date: 4-Apr-83 Time: 11:27:04
File: CS.01 BAW.02
Operator: JW
Sample: CS.01 8797-31.32 PIECE
Size: 36.06 mg
Rate: 10 C/MIN 30CCS AIR/MIN
Date: 1-Oct-82 Time: 13:44:28
File: CS.01 J.WATKINSON TGA 4
Operator: JW

Figure II A
TGA of Uncrushed SiC Sample
Figure IIB

TGA of Crushed SiC Sample
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