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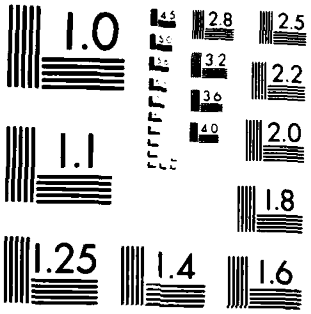

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Dechlorination of mixtures of $CH_2=CHSiMeCl_2$ with other chlorosilanes, using sodium metal in hydrocarbon/THF solvent blends, provides vinylic polysilanes which are excellent precursors for silicon carbide ceramic compositions. These polymers are soluble, relatively inert, and are thermally curable through reactions of the vinyl groups.

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ORGANOSILANE POLYMERS, VII:

SODIUM DERIVED VINYLIC POLYSILANES

by

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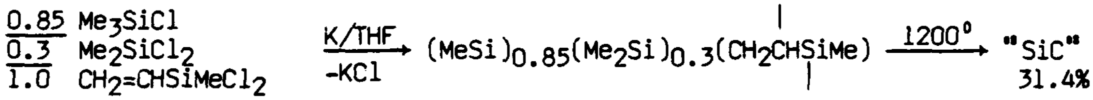
September 1983

ORGANOSILANE POLYMERS, VII:

SODIUM DERIVED VINYLIC POLYSILANES

INTRODUCTION

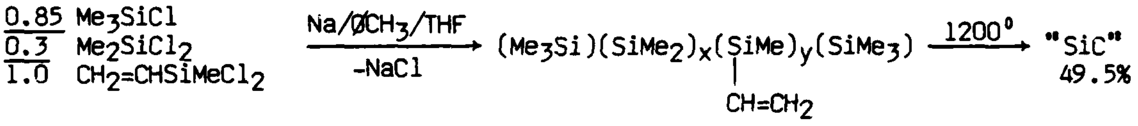
Mixtures of $CH_2{=}CHSiMeCl_2$ (vinylmethyldichlorosilane) with other chlorosilanes are dechlorinated by potassium metal in tetrahydrofuran solvent to yield highly branched polycarbosilanes which are effective precursors for silicon carbide ceramic compositions.[1] The costs and hazards associated with 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.



$$\begin{array}{ll}\underline{0.85} & Me_3SiCl \\ \underline{0.3} & Me_2SiCl_2 \\ 1.0 & CH_2{=}CHSiMeCl_2\end{array} \xrightarrow[-KCl]{K/THF} (MeSi)_{0.85}(Me_2Si)_{0.3}(CH_2CH\overset{|}{\underset{|}{Si}}Me) \xrightarrow{1200^\circ} \underset{31.4\%}{\text{"SiC"}}$$

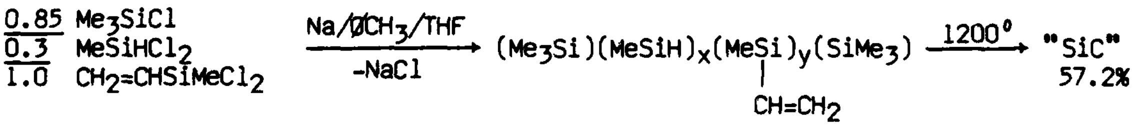
RESULTS AND DISCUSSION

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.



$$\begin{array}{ll}\underline{0.85} & Me_3SiCl \\ \underline{0.3} & Me_2SiCl_2 \\ 1.0 & CH_2{=}CHSiMeCl_2\end{array} \xrightarrow[-NaCl]{Na/\phi CH_3/THF} (Me_3Si)(SiMe_2)_x(\underset{\underset{CH=CH_2}{|}}{Si}Me)_y(SiMe_3) \xrightarrow{1200^\circ} \underset{49.5\%}{\text{"SiC"}}$$

Replacing the Me_2SiCl_2 with $MeSiHCl_2$ provides polysilanes which are even more efficient precursors for SiC, demonstrating again the effectiveness of $MeSiHCl_2$ in providing preceramic polymers with improved ceramic yields.[2,3]



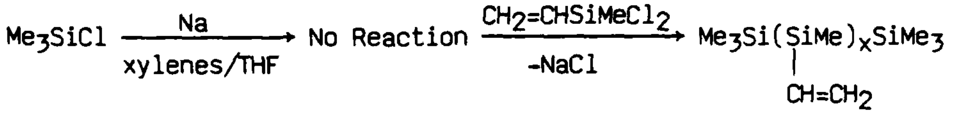
$$\begin{array}{ll}\underline{0.85} & Me_3SiCl \\ \underline{0.3} & MeSiHCl_2 \\ 1.0 & CH_2{=}CHSiMeCl_2\end{array} \xrightarrow[-NaCl]{Na/\phi CH_3/THF} (Me_3Si)(MeSiH)_x(Me\underset{\underset{CH=CH_2}{|}}{Si})_y(SiMe_3) \xrightarrow{1200^\circ} \underset{57.2\%}{\text{"SiC"}}$$

It is clear that sodium is less reactive than potassium, particularly toward Me_3SiCl and $\text{CH}_2\text{=CHSi}\equiv$ groups, that $\text{CH}_2\text{=CHSiMeCl}_2$ 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 Me_3SiCl and $\text{CH}_2\text{=CHSi}\equiv$ groups is demonstrated by the reaction of Me_3SiCl with $\text{CH}_2\text{=CHSiMe}_3$. Sodium causes no reaction, providing neither $\text{Me}_3\text{SiSiMe}_3$ nor $\text{Me}_3\text{SiCH}_2\text{CH(SiMe}_3)_2$,[4] while potassium provides a high yield of the latter product.[1b]

$$\text{No Reaction} \xleftarrow[\text{ØCH}_3\text{/THF}]{\text{Na}} \frac{2.0\ \text{Me}_3\text{SiCl}}{\text{CH}_2\text{=CHSiMe}_3} \xrightarrow[\text{-KCl}]{\text{K/THF}} \underset{77.4\%}{\text{Me}_3\text{SiCH}_2\text{CH(SiMe}_3)_2}$$

Thus, no significant reaction occurs between sodium and Me_3SiCl in refluxing 7/1 toluene/THF or xylenes/THF (or in either arene or THF separately[5]). Addition of $\text{CH}_2\text{=CHSiMeCl}_2$ 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 Me_3SiCl/$\text{CH}_2\text{=CHSiMeCl}_2$ 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 Me_3SiCl (39.2%) was recovered as $\text{Me}_3\text{SiOSiMe}_3$ after hydrolytic termination/neutralization, accenting the low reactivity of Me_3SiCl.



$$\text{Me}_3\text{SiCl} \xrightarrow[\text{xylenes/THF}]{\text{Na}} \text{No Reaction} \xrightarrow[\text{-NaCl}]{\text{CH}_2\text{=CHSiMeCl}_2} \text{Me}_3\text{Si}(\underset{\substack{|\\ \text{CH=CH}_2}}{\text{SiMe}})_x\text{SiMe}_3$$

Model reactions as above wherein ØSiMeCl_2, EtSiMeCl_2, or Me_2SiCl_2 were substituted for $\text{CH}_2\text{=CHSiMeCl}_2$ were qualitatively slower and less complete than that of $\text{CH}_2\text{=CHSiMeCl}_2$, with reactivity decreasing in the order Ø > Et > Me.

$$\text{Me}_3\text{SiCl} + \text{RSiMeCl}_2 \xrightarrow[\text{arene/THF}]{\text{Na}} \text{Me}_3\text{Si(RSiMe)}_x\text{SiMe}_3$$

$$\text{R} = \text{Ø, Et, Me}$$

The higher reactivity of vinylic chlorosilanes in certain active metal reactions has been noted. For example, Me_2SiHCl, Me_3SiCl, and $\text{CH}_2\text{=CHCH}_2\text{SiMe}_2\text{Cl}$ are not individually dechlorinated by magnesium in THF to form the corresponding disilanes,[6] while $\text{CH}_2\text{=CHSiMe}_2\text{Cl}$ yields $(\text{CH}_2\text{=CHSiMe}_2)_2$.[6,7] The high reactivity shown by $\text{CH}_2\text{=CHSiMeCl}_2$ in the present work is not reflected by $\text{CH}_2\text{=CHSiMe}_2\text{Cl}$, 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 $CH_2{=}CHSi\blacksquare$ 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

$$2Me_3SiCl + CH_2{=}CH\phi \xrightarrow[THF]{Na} Me_3SiCH_2CH\phi SiMe_3$$

$$2Me_3SiCl + CH_2{=}CHCMe{=}CH_2 \xrightarrow[THF]{Na} Me_3SiCH_2CH{=}CMeCH_2SiMe_3$$

to the olefin, followed by attack of the resultant anion radical on an $\blacksquare SiCl$ group, a second electron transfer to the monosilylated intermediate and attack on a second $\blacksquare SiCl$ group. The end result is formation of two $\blacksquare SiC\blacksquare$ bonds, or disilylation.

It is also known that magnesium causes disilylation of $CH_2{=}CHSiMe_3$ in hexamethylphosphoramide (HMPA), with $FeCl_3$ as a catalyst.[4] This reaction may

$$2Me_3SiCl + CH_2{=}CHSiMe_3 \xrightarrow[FeCl_3]{Mg/HMPA} Me_3SiCH_2CH(SiMe_3)_2$$

occur by Michael addition of the anionic species, $Me_3SiMgCl$,[10] to the $CH_2{=}CHSi\blacksquare$ group, followed by attack of the resultant carbanion on Me_3SiCl. 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, K may cause disilylation of

Oxidation Potentials[11]		Reduction Potentials[12]	
Potassium	2.925 volts	$CH_2{=}CHSiMe_3$	Unknown (high)
Sodium	2.714 volts	$CH_2{=}CHCMe{=}CH_2$	2.6-2.7 volts
Magnesium	2.37 volts	$CH_2{=}CH\phi$	2.4-2.6 volts

$CH_2{=}CHSiMe_3$ in THF by electron transfer, while Na and Mg do not, and both Na and K[3] cause disilylation of styrene and isoprene. Indeed, $CH_2{=}CHSiMe_3$ can be prepared in the presence of sodium.[13]

Note that while $CH_2{=}CHSiMe_3$ is disilylated by Me_3SiCl with Mg in HMPA,[4] vinylic disilanes can be prepared using Mg in THF[7] (no reaction of $CH_2{=}CHSi\blacksquare$ groups). One concludes that $CH_2{=}CHSi\blacksquare$ groups may be disilylated by two

$$CH_2{=}CHSiMe_2SiMe_3 \xleftarrow[Me_3SiCl]{Mg/THF} CH_2{=}CHSiMe_2Cl \xrightarrow[THF]{Mg} (CH_2{=}CHSiMe_2)_2$$

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[14] 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 $Me_3SiCl/CH_2{=}CHSiMeCl_2$ 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 $Me_3SiCl/Me_2SiCl_2/CH_2{=}CHSiMeCl_2$ 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 Me_3Si- groups, with resultant higher yields of soluble products. The latter are desirable in terms of polymer procesing 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, $Me_3Si(CH_2)_4OSiMe_3$,[16] is observed and is converted to $Me_3Si(CH_2)_4OH$ by the hydrolytic workup. Silylated arenes, $ArCH_2SiMe_3$, 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 $Me_3SiCl/EtSiMeCl_2$, 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 $MeSiHCl_2$ as a comonomer) provides improved ceramic yields. The degree of retention of $\equiv$SiH groups during synthesis has not been established, but is higher than the 20% seen with potassium. The high yield (74%) preparation of $HMe_2SiSiMe_2H$[17] suggests that $\equiv$SiH retention

$$HMe_2SiSiMe_2H \xleftarrow{Na} Me_2SiHCl \xrightarrow{Li/THF} (Me_2Si)_6$$

is quite good. It should be noted that lithium causes complete loss of $\equiv$SiH groups from Me_2SiHCl.[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 $Me_3SiCl/MeSiHCl_2/CH_2{=}CHSiMeCl_2$ using either 7/1 toluene/THF or xylenes/THF. Yields of 60-65% of soluble solid

$$\begin{array}{l} \underline{0.85}\ Me_3SiCl \\ \underline{0.3}\ MeSiHCl_2 \\ 1.0\ CH_2{=}CHSiMeCl_2 \end{array} \xrightarrow[Na]{\text{arene/THF}} \begin{array}{l} \text{10-15\% Volatiles} \\ \text{60-65\% Soluble Solid} \\ \text{<5\% Insoluble Solid} \end{array} \xrightarrow{1200^\circ} \begin{array}{c} \text{"SiC"} \\ 55\text{-}60\% \end{array}$$

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.[1]

CROSSLINKING CHEMISTRY

The vinylic polysilanes crosslink, or thermoset at temperatures in the 200-240° range. The crosslinking reaction does not involve oxygen incorporation or weight loss, and appears to be a combination of ≡SiH/CH_2=CHSi≡ addition and CH_2=CHSi≡ polymerization reactions. When a mixture of roughly equivalent amounts of three liquid compounds, $Me_3Si(SiMeH)_x(SiMeCH{=}CH_2)_ySiMe_3$, 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°, 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-1,1,1,2,3,3,3-heptamethyltrisilane through the vinyl groups is believed to be responsible for its high ceramic yield.[19]

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°.[20] Hydrosilyl groups reappear at 350°, probably due to the rearrangement of ≡$SiCH_3$ groups to =$HSiCH_2$- groups, as noted by Yajima.[21] Weight loss due to thermal decomposition becomes fairly rapid above 400° and is essentially complete around 600°. There is little weight change from 600° - 1200°, 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[1] are virtually

$$\begin{tikzcd}
\text{Vinylic Polysilane} \arrow[dr, "1200^\circ"'] & \dfrac{Me_3SiCl}{CH_2{=}CHSiMeCl_2} \arrow[l, "Na"', "\text{arene/THF}"] \arrow[r, "K", "THF"'] & \text{Polycarbosilane} \arrow[dl, "1200^\circ"] \\
 & \text{"SiC" + Volatile Products} &
\end{tikzcd}$$

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

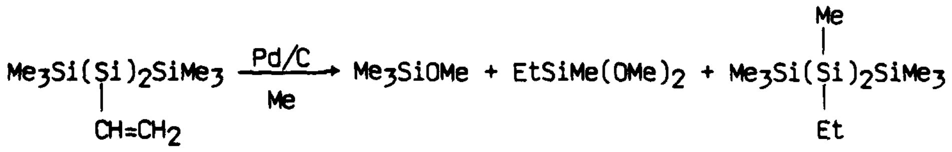
The vinylic polysilanes are not analytically pure, due to some oxygen incorporation during hydrolytic workup and some solvent incorporation during synthesis. The problem is further complicated by the facts that preceramic polymers are difficult to combust completely, that the monomers charged are incorporated 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 $Me_3SiCl/CH_2{=}CHSiMeCl_2$ has the average empirical formula or structure of $Me_3Si(SiMeCH{=}CH_2)_{1.33}SiMe_3$, 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 CO_2, and weight gain as silicon is oxidized to nonvolatile SiO_2. 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 ■SiSi■ bond cleavage as a means of converting polysilanes into easily identifiable monomeric units. A Dow Corning patent[23] disclosed the use of palladium on charcoal (Pd/C) as a means of quantitatively cleaving ■SiSi■ bonds in alcohols with formation of the corresponding alkoxysilanes and

$$\text{■SiSi■} + 2ROH \xrightarrow{Pd/C} 2\text{■SiOR} + H_2$$

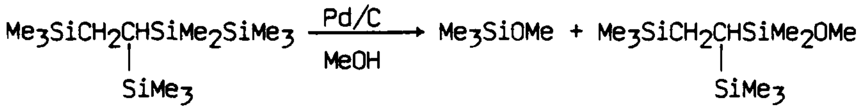
hydrogen. Volatile vinylic polysilanes underwent this reaction with two major complications. First, the vinyl groups were reduced to ethyl groups, such that $-MeSiCH{=}CH_2-$ units yielded $EtSiMe(OMe)_2$ when methanol was used. Vinyl groups were also reduced without cleavage, yielding ethylmethylpolysilanes which were



$$Me_3Si(\underset{\displaystyle CH{=}CH_2}{\underset{|}{Si}})_2SiMe_3 \xrightarrow[Me]{Pd/C} Me_3SiOMe + EtSiMe(OMe)_2 + Me_3Si(\overset{\displaystyle Me}{\overset{|}{\underset{\displaystyle Et}{\underset{|}{Si}}}})_2SiMe_3$$

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).



$$\mathrm{Me_3SiCH_2\underset{\underset{SiMe_3}{|}}{C}HSiMe_2SiMe_3 \xrightarrow[MeOH]{Pd/C} Me_3SiOMe + Me_3SiCH_2\underset{\underset{SiMe_3}{|}}{C}HSiMe_2OMe}$$

Our results with Pd/C were exactly consistent with those of Kumada[24] on cleavage of vinylic di- and trisilanes with soluble palladium metal catalysts.

CONCLUSIONS

Sodium metal in arene/THF blends effectively dechlorinates mixtures of $CH_2=CHSiMeCl_2$ 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.[1,2,3,25] 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.[26]

Reaction of 4/3 $Me_3SiCl/CH_2{=}CHSiMeCl_2$ with Na in 7/1 Xylenes/THF

In a 1l 3NRB flask were combined 338.3g xylenes and 48.5g THF. Na was added a 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 N_2 flow valves. Heat was applied to 112°, melting the Na, and 43.0g (0.4 mol) of Me_3SiCl 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 $CH_2{=}CHSiMeCl_2$ 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 H_2O in 10.9g THF. $MgSO_4$ (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	$(Me_3Si)_2O$ - 39.2% based on Me_3SiCl
1.17g	$Me_3Si(CH_2)_4OH$ - 2.0% based on Me_3SiCl
0.23g	$(Me_3Si)_2SiMeCH{=}CH_2$
0.08g	$(Me_3Si)_2SiMeCH_2CH_3$
0.16g	xylyl-$SiMe_3$ isomers
8.63g	$Me_3Si(SiMeCH{=}CH_2)_2SiMe_3$ - 20.1%
0.51g	$Me_3Si(SiMeCH_2CH_3)_2SiMe_3$
0.17g	unknowns
1.98g	$Me_3Si(SiMeCH{=}CH_2)_3SiMe_3$ - 5.6%
25.63g	

The heavies, by VPC estimate, contained 1.95g of the last compound, $Me_3Si(SiMeCH{=}CH_2)_3SiMe_3$.

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

Reaction of 2/1 $Me_3SiCl/CH_2{=}CHSiMeCl_2$ 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 Me_3SiCl, and 49.7g (0.35 mol) of $CH_2{=}CHSiMeCl_2$, 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 Me_3Si- units and $-MeSi(CH{=}CH_2)$- units; the major liquid products were $Me_3Si[SiMe(CH{=}CH_2)]_xSiMe_3$ where x is 2 or 3.

Reaction of 1.5/1 Me_3SiCl/CH_2=$CHSiMeCl_2$ 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 Me_3SiCl, and 41.9g (0.3 mol) of CH_2=$CHSiMeCl_2$. 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 115°/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 1200° yielded 47.9% of SiC composition. Equivalent results were obtained when octane was substituted for toluene in the above reaction, and when xylenes were 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, 1200°), and 7.2% of volatile products, b.p. up to 107°/0.05mm, were obtained.

Reaction of 0.85/0.3/1.0 Me_3SiCl/Me_2SiCl_2/CH[illegible]HSiMeCl_2 with Na in Xylenes/THF

The procedure of the previous reaction was u[illegible]ginning with 510.2g of xylenes, 77.2g of THF, 91.1g (3.96 mol) of Na, 100.[illegible]0.93 mol) of Me_3SiCl, 42.4g (0.33 mol) of Me_2SiCl_2, and 154.2g (1.09 mol) of CH_2=$CHSiMeCl_2$. Workup yielded 33.2g (20.3%) of volatile products, b.p. up to 128°/1.5mm and 103.7g (63.5%) of nonvolatile polymer. Pyrolysis of the latter to 1200° provided 49.5% of SiC composition.

Reaction of 1/1 Me_3SiCl/CH_2=$CHSiMeCl_2$ with Na in Xylenes/THF

The procedures of the previous reaction were followed using 510.1g of xylenes, 76.5g of THF, 96.8g (4.21 mol) of Na, 145.0g (1.34 mol) of Me_3SiCl, and 188.4g (1.34 mol) of CH_2=$CHSiMeCl_2$. Workup yielded 57.4g (30.0%) of nonvolatile soluble polymer, and 47.6g (24.9%) of liquid products, b.p. up to 132°/1.0mm. Pyrolysis of the soluble solid to 1200° yielded 41.6% of SiC composition. Pyrolysis of a liquid fraction, b.p. 106-132°/1.0mm, consisting primarily of $Me_3Si[SiMe(CH=CH_2)]_xSiMe_3$, where $x = 2$ (24.1%), and $x = 3$ (69.6%), to 1200° provided 20.1% of SiC composition.

Reaction of 1/1 Me_2SiCl_2/CH_2=$CHSiMeCl_2$ 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 Me_2SiCl_2, and 157.5g (1.12 mol) of CH_2=$CHSiMeCl_2$. 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 95°/1.0mm. Respective 1200° pyrolyses of the soluble and insoluble solids provided SiC composition yields of 49.6% and 56.6%.

Reaction of 0.5/1/1 $Me_3SiCl/Me_2SiCl_2/CH_2$=$CHSiMeCl_2$ 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 Me_3SiCl, 78.1g (0.61 mol) of Me_2SiCl_2, and 85.2g (0.60 mol) of CH_2=$CHSiMeCl_2$, yielded 4.5g (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 $CH_2=CHSiMe_2Cl/Me_2SiCl_2/CH_2=CHSiMeCl_2$ 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 $CH_2=CHSiMe_2Cl$, 60.3g (0.47 mol) of Me_2SiCl_2, and 65.9g (0.47 mol) of $CH=CHSiMeCl_2$, 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

$CH_2=CHSiMe_2(SiMe_2)_xSiMe_2CH=CH_2$ where x = 1, 2, or 3,
$CH_2=CHSiMe_2[SiMe(CH=CH_2)]_xSiMe_2\text{-}CH=CH_2$ where x = 1, 2, or 3 and
$CH_2=CHSiMe_2(SiMe_2)_x[SiMe(CH=CH_2)]SiMe_3$ where x = 1 or 2.

Reaction of 0.5/0.5/1 $Me_3SiCl/Me_2SiCl_2/CH_2=CHSiMeCl_2$ 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 $Me_2SiHCl/CH_2=CHSiMeCl_2$ with Na in Xylenes/THF

The usual procedure was followed using 339.8g of xylenes, 51.4g of THF, 42.3g (1.84 mol) of Na, 55.3g (0.58 mol) of Me_2SiHCl, and 82.4g (0.58 mol) of $CH_2=CHSiMeCl_2$. 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 $HMe_2Si[SiMe(CH=CH_2)]_2SiMe_2H$ by GC/MS and NMR.

Reaction of 1/1 $CH_2=CHSiMe_2Cl/CH_2=CHSiMeCl_2$ 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 $CH_2=CHSiMe_2Cl$, and 82.2g (0.58 mol) of $CH_2=CHSiMeCl_2$, yielded 4.9g (5.4%) of volatiles, 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.

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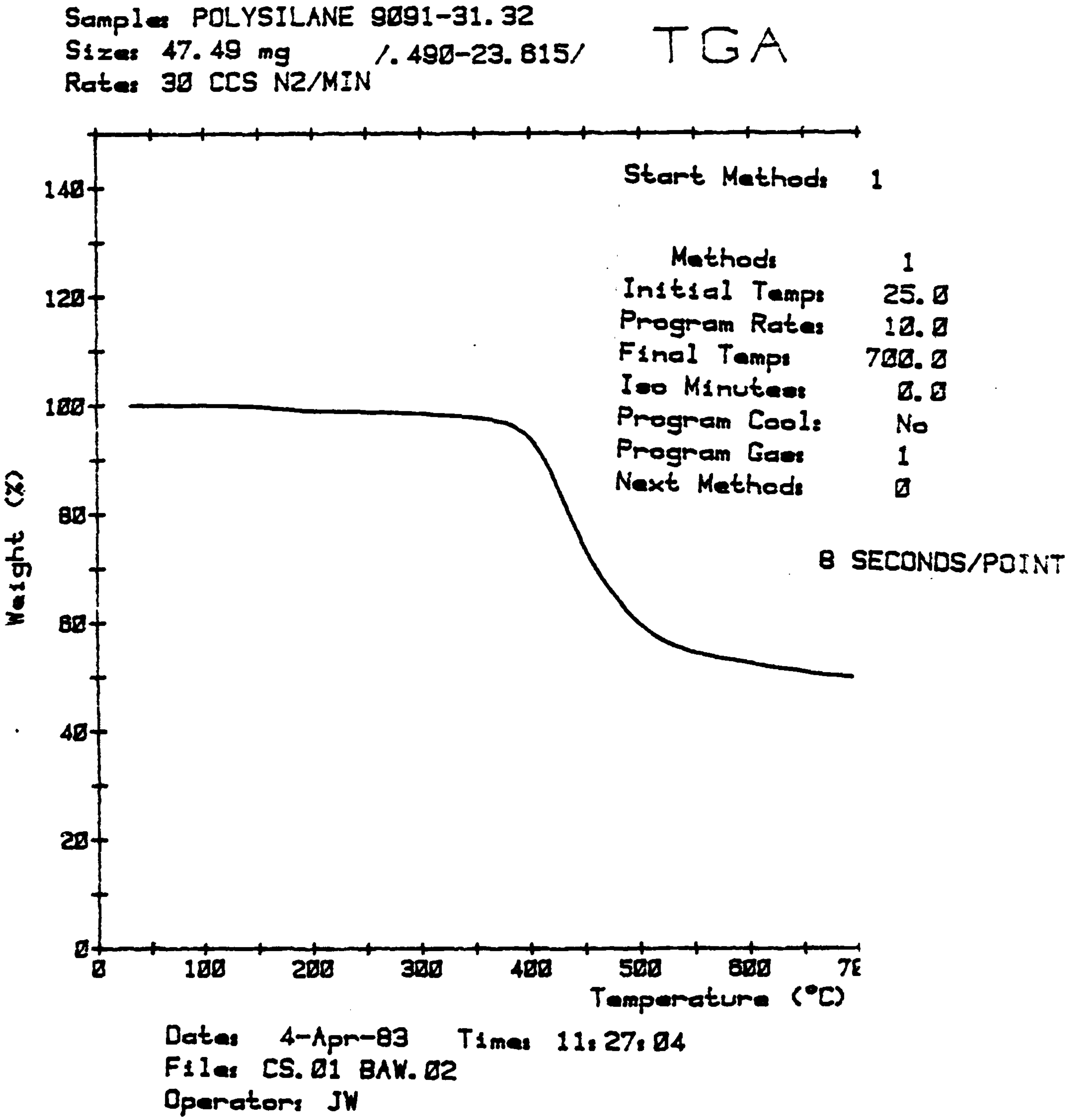
Figure I

TGA of Vinylic Polysilane



Sample: POLYSILANE 9091-31.32
Size: 47.49 mg /.490-23.815/
Rate: 30 CCS N2/MIN

TGA

Start Method: 1

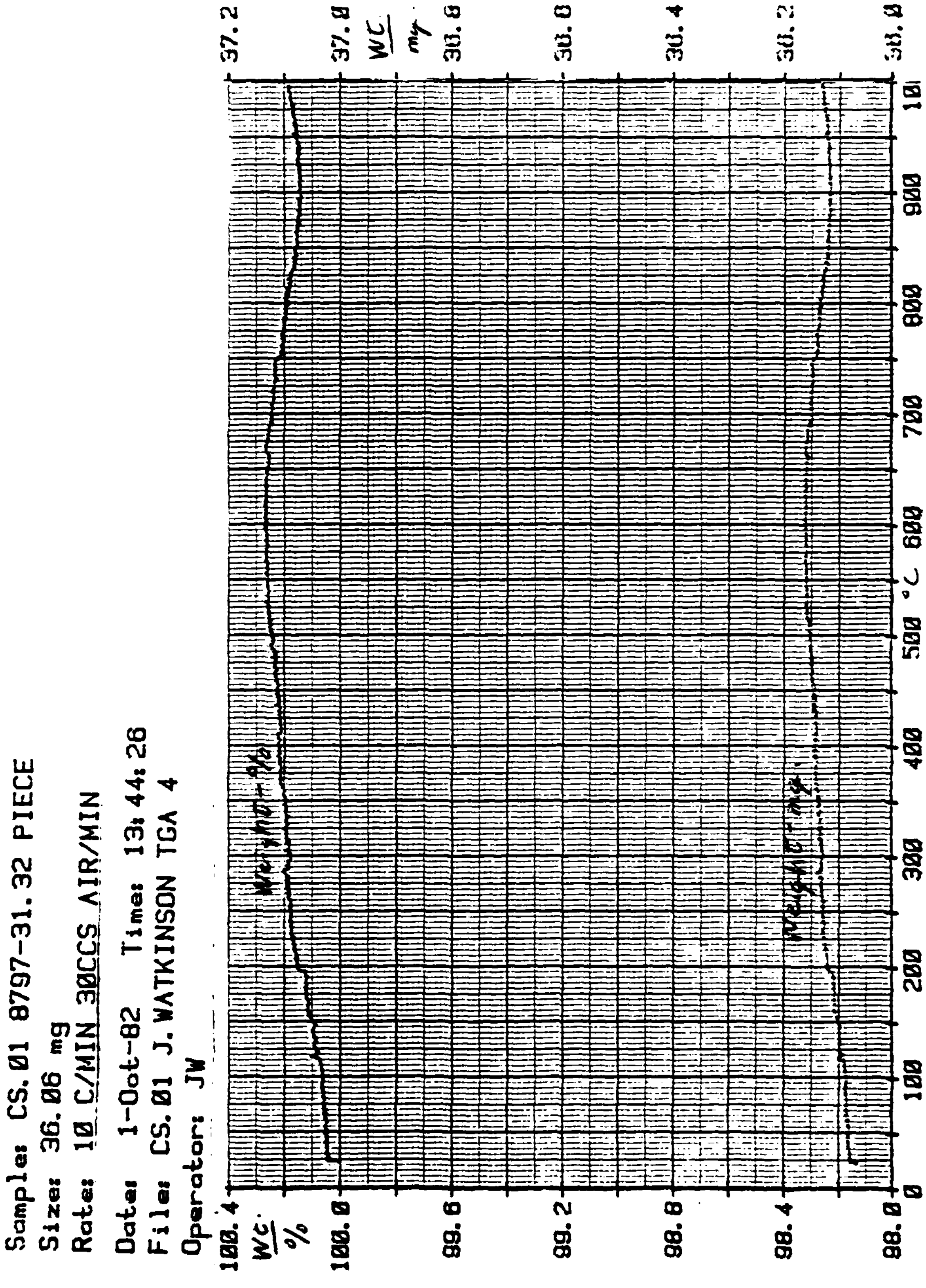
Method: 1
Initial Temp: 25.0
Program Rate: 10.0
Final Temp: 700.0
Iso Minutes: 0.0
Program Cool: No
Program Gas: 1
Next Method: 0

8 SECONDS/POINT

Date: 4-Apr-83 Time: 11:27:04
File: CS.01 BAW.02
Operator: JW

Figure IIA

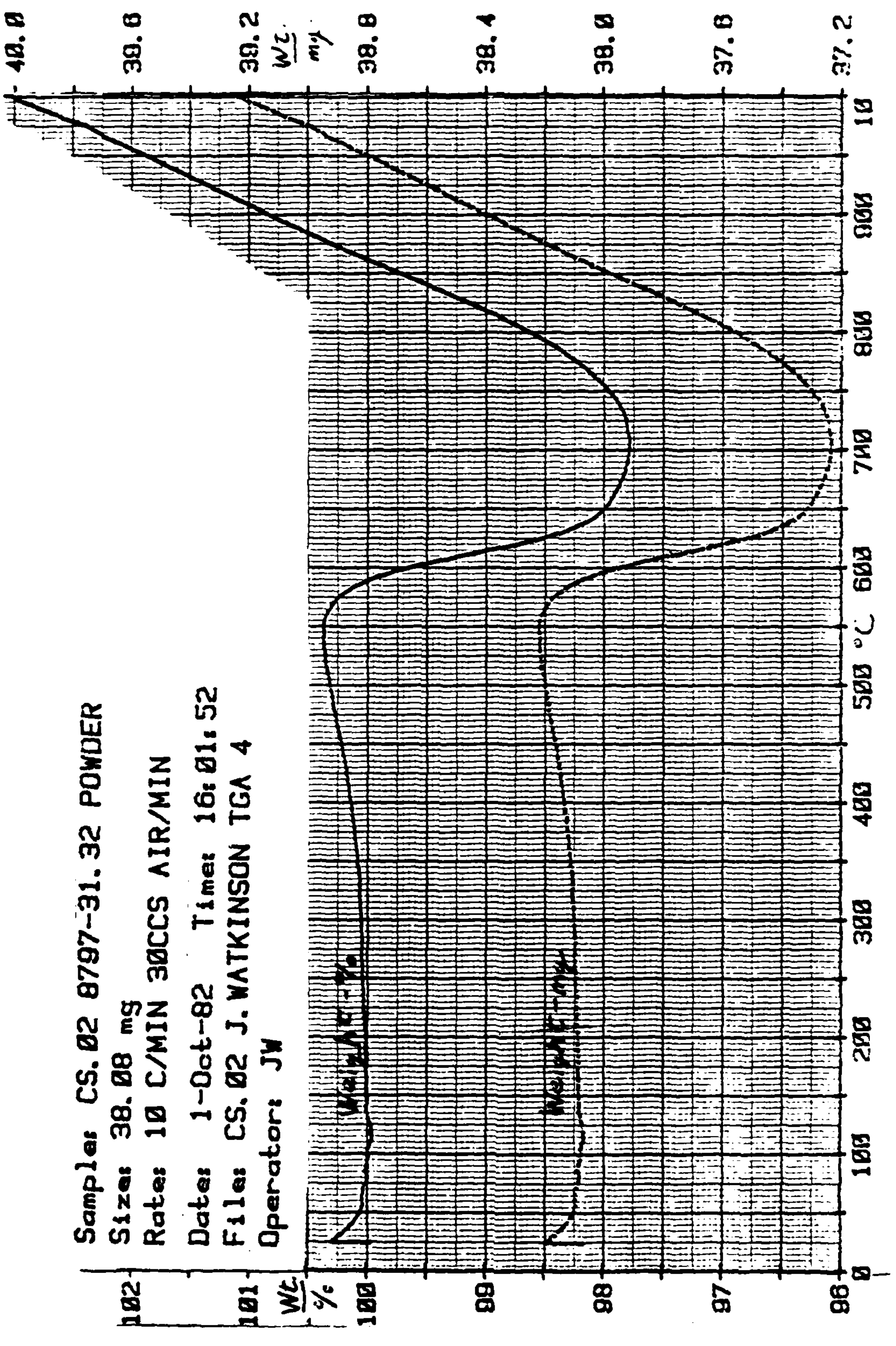
TGA of Uncrushed SiC Sample



Sample: CS.01 8797-31.32 PIECE
Size: 36.06 mg
Rate: 10 C/MIN 30CCS AIR/MIN
Date: 1-Oct-82 Time: 13:44:26
File: CS.01 J.WATKINSON TGA 4
Operator: JW

Figure IIB

TGA of Crushed SiC Sample



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