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One-step preparations of tractable polycarbosilanes are achieved through silicon-carbon bond-forming reactions of vinylic or chloromethyl ($ClCH_2$-) silanes. These polymers are directly convertible to silicon carbide compositions by atmospheric pressure pyrolysis. Backbone branching is recognized as essential for practical conversion of such polycarbosilanes to silicon carbide.

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ORGANOSILANE POLYMERS, IV.

POLYCARBOSILANE PRECURSORS FOR SILICON CARBIDE,

by

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ORGANOSILANE POLYMERS, IV:

POLYCARBOSILANE PRECURSORS FOR SILICON CARBIDE

INTRODUCTION

Background

Previous work on this project dealt with the preparation and properties of polydialkylsilanes.[1-3] The objective was the characterization of high molecular weight polydimethylsilanes and improvement of their solubility properties by replacing some of the methyl substituents with ethyl, propyl, or phenyl groups. The discovery by Yajima of a two-step pyrolytic conversion of polydimethylsilanes to silicon carbide articles, including fibers,[4] prompted screening of many of the polydialkylsilanes prepared in this project as precursors for silicon carbide. These materials achieved the desired solubility properties but were not useful silicon carbide precursors in that one-step, unconfined pyrolysis did not yield significant amounts of silicon carbide.

Objectives

The current objectives of this project are:

1. Optimized preparations of tractable polycarbosilane precursors for silicon carbide.
2. Conversion of such polycarbosilanes to silicon carbide including shaped articles thereof, such as fibers.
3. Development of fundamental understanding of the preparative and pyrolytic chemistry.

Scope

The bulk of the work discussed in this report on preparations and pyrolyses of polycarbosilanes was done in the period September 1979-December 1980. Isolated screening experiments which provided direction for the current effort were performed from August 1978 to August 1979.

ORGANOSILICON APPROACHES TO SILICON CARBIDE

Silicon carbide (SiC) has been prepared from organosiloxane resins as early as 1953[5] and from chlorosilanes via vapor phase deposition[6] as disclosed in 1964. More recently, Yajima in Japan has developed an organosilicon route to SiC fibers based on polydimethylsilanes.[4] Other Japanese groups have disclosed minor variations of the Yajima process in preparing SiC precursors.[7-9] R. West, University of Wisconsin, has prepared copolymers from dimethyldichlorosilane and phenylmethyldichlorosilane which are effective SiC precursors in certain applications.[10] R. H. Baney, Dow Corning Corporation, has derived SiC precursors from the residue stream from the methyl chloride/silicon metal direct reaction.[11]

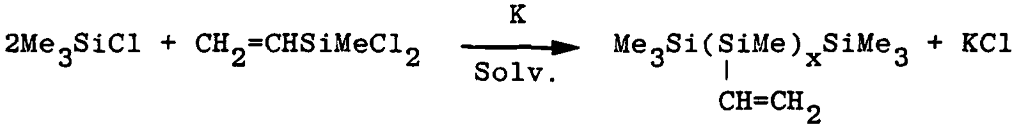
In the present project, routes to polycarbosilane precursors for SiC have been developed based on silicon-carbon bond-forming reactions of vinylic or chloromethyl ($ClCH_2$-) silanes with other chlorosilane monomers. These routes possess certain advantages over prior art approaches.

SCREENING EXPERIMENTS

Unconfined atmospheric pressure pyrolyses of the various polydialkylsilanes prepared earlier in this project[1-3] revealed that they were not effective precursors for SiC. The use of vinylmethyldichlorosilane instead of saturated alkylmethyldichlorosilanes or diphenyldichlorosilane did yield polymeric products which were convertible in good yields to SiC compositions. The materials derived from methylvinyldichlorosilane were unfortunately insoluble and intractable, but did provide a basis for continued study.

MODEL CHEMISTRY

Since the utility of vinylmethyldichlorosilane ($CH_2{=}CHSiMeCl_2$) in forming SiC precursors was established, it was decided to study its dechlorination chemistry in reactions in which molecular weight build-up would be minimized. Thus, if active metal dechlorination and $\equiv SiSi \equiv$ bond formation were the only reactions occurring, a 2/1 molar mixture of Me_3SiCl/$CH_2{=}CHSiMeCl_2$ would yield a homologous series of methylvinyl-



$$2Me_3SiCl + CH_2{=}CHSiMeCl_2 \xrightarrow[\text{Solv.}]{K} Me_3Si(\underset{\substack{|\\ CH=CH_2}}{SiMe})_xSiMe_3 + KCl$$

polysilanes where x = 0, 1, 2, 3..... but has an average value of 1. The reactions in fact give low yields of those products and substantial yields of nonvolatile heavies (42.4-71.9% depending on solvent). The heavies are low in free vinyl groups implicating some reaction of the vinyl groups.

The reaction occurring with the vinyl groups was demonstrated by dechlorination of 1/1 molar mixture of Me_3SiCl/$CH_2{=}CHSiMe_3$. The yield of $Me_3SiCH_2CH(SiMe_3)_2$[12] was 62.4% based on

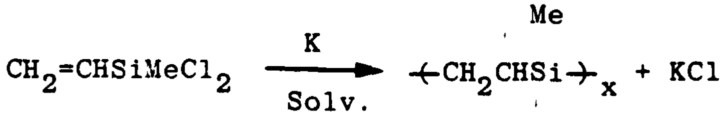
$$Me_3SiCl + CH_2{=}CHSiMe_3 \xrightarrow[\text{THF}]{K} Me_3SiCH_2CH(SiMe_3)_2 + KCl$$

Me_3SiCl, with 51.3% of $CH_2{=}CHSiMe_3$ being recovered unchanged.

This observation implicated disilylation of vinyl groups as the major polymer-forming reaction in our systems, and demonstrated that $CH_2{=}CHSiMeCl_2$ yields tetrafunctional units on

$$2{\equiv}SiCl + CH_2{=}CHSi{\equiv} \xrightarrow[\text{Solv.}]{K} {\equiv}SiCH_2CH(Si{\equiv})_2 + 2KCl$$

dechlorination. The high functionality explains the



$$CH_2{=}CHSiMeCl_2 \xrightarrow[\text{Solv.}]{K} \left(CH_2CH\overset{Me}{\underset{|}{Si}} \right)_x + KCl$$

insolubility and intractability of polymers based solely on $CH_2{=}CHSiMeCl_2$.

Active metal silylations of vinyl groups have been reported,[12] as have reactions in which silicon-bound vinyl groups have survived active metal dechlorination.[13] The present work represents the first case of reactions at both vinyl and chlorine groups in vinylchloroalkylsilanes.

MOLAR FUNCTIONALITY CONCEPT

Recognition of vinyl group reactions enabled the assignment of molar functionality values, f, to several vinylic silanes. These are listed in Table I as are values for standard chlorosilane monomers and chloromethyl ($ClCH_2-$) silanes. The molar functionality values are useful in calculating average molar functionality values, F, for polycarbosilanes prepared from known mixtures of chloroorganosilane monomers. The chemistry of bond formation is straightforward, involving active metal dechlorination (1) or disilylation (2) of vinyl groups. Vinyl groups can also be mono- or trisilylated[12] with disilylation being the major reaction in our systems.

$$(1)\quad \begin{cases} 2{\equiv}SiCl + 2K \longrightarrow {\equiv}SiSi{\equiv} + 2KCl \\ {\equiv}SiCl + {\equiv}CCl + 2K \longrightarrow {\equiv}SiC{\equiv} + 2KCl \end{cases}$$

$$(2)\quad 2K + 2{\equiv}SiCl + CH_2{=}CHSi{\equiv} \longrightarrow {\equiv}SiCH_2CH(Si{\equiv})_2 + 2KCl$$

For example, the molar functionality, F, of a polycarbosilane prepared from a mixture of chlorosilane monomers M_1, M_2, and M_3 having respective functionality values f_1, f_2, and f_3 in the molar ratio x/y/z, can be calculated from the equation:

$$F = \frac{xf_1 + yf_2 + zf_3}{(x + y + z)}$$

Experience derived from numerous preparations shows that molar functionality values of greater than two ($F>2$) are preferred for obtaining tractable solid polycarbosilanes. This requires that at least one of the monomers has an f value of 3 or higher, and that the polycarbosilanes be branched rather than linear.

In addition to providing sufficient average molar functionality, monomers should be selected such that the number of Si-reactive sites (≡SiCl groups) equals or exceeds the number of C-reactive sites (2 for each vinyl group, 1 for $ClCH_2$- groups) in any given mixture. In other words, the formation of ≡SiC≡ bonds must be favored. The need for this proviso becomes evident when polycarbosilanes are pyrolytically converted to silicon carbide.

Thus, the molar functionality concept is useful in preparing tractable polycarbosilanes in predictable fashion, but does not predict effective conversion of those polycarbosilanes to silicon carbide. The consideration of favoring ≡SiC≡ bond formation in preparing polycarbosilanes adds predictability to the polycarbosilane/silicon carbide conversion step.

POLYCARBOSILANE PREPARATIONS

Tractable, soluble solid polycarbosilanes were prepared as copolymers or terpolymers from appropriate mixtures of chlorosilane monomers. Most reactions typically yield products spanning the molecular weight range from soluble liquids to insoluble solids, with separation of soluble liquid, soluble solid, and insoluble solid fractions occurring as a natural consequence of the work-up method. The following are typical reactions, optimized to maximize yields of soluble solid polycarbosilanes. It should be noted that all product fractions are convertible to silicon carbide, although yields of SiC are lower for soluble liquid products.

$$\begin{array}{ll} \underline{0.8} & Me_3SiCl \\ 1.0 & CH_2{=}CHSiMeCl_2 \end{array} \xrightarrow[THF]{K} \begin{array}{l} 43.7\% \text{ Soluble Liquid} \\ 25.2\% \text{ Soluble Solid} \\ 16.5\% \text{ Insoluble Solid} \end{array}$$

$$\begin{array}{ll} \underline{0.5} & Me_3SiCl \\ \underline{1.0} & Me_2SiCl_2 \\ 1.0 & CH_2{=}CHSiMeCl_2 \end{array} \xrightarrow[THF]{K} \begin{array}{l} 19.1\% \text{ Soluble Liquid} \\ 61.0\% \text{ Soluble Solid} \\ 19.5\% \text{ Insoluble Solid} \end{array}$$

Successful SiC precursors have been prepared wherein branching sites are introduced by trifunctional $MeSiCl_3$ instead of tetrafunctional $CH_2{=}CHSiMeCl_2$. These reactions have not been optimized; they are promising in view of the low cost and high theoretical SiC yield of $MeSiCl_3$.

$$\frac{0.67}{1.00}\ \begin{matrix}\mathrm{MeSiCl_3}\\ \mathrm{CH_2{=}CHSiMe_3}\end{matrix}\ \xrightarrow[\mathrm{THF}]{\mathrm{K}}$$

20% Soluble Solid plus Other products.

$$\frac{0.67}{1.00}\ \begin{matrix}\mathrm{MeSiCl_3}\\ \mathrm{ClCH_2SiMe_2Cl}\end{matrix}\ \xrightarrow[\mathrm{THF}]{\mathrm{K}}$$

39% Soluble Solid plus other products.

POLYCARBOSILANE PROCESS STEPS

The general reaction procedure involves several standard steps. Initially, a weighed amount of K metal is combined with THF in an appropriate flask in a dry box (inert atmosphere). The flask is transferred to a hood, an argon atmosphere applied, and appropriate fittings added. The latter include mechanical stirrer with glass blade, thermometer, addition funnel, and Dewar condenser (wet ice). The contents of the flask are heated to reflux, melting the K, and addition of a weighed mixture of chlorosilane monomers begun, and continued at a rate which maintains reflux without external heating. After completion of addition, heating is resumed to maintain reflux for an arbitrary time, followed by cooling on a wet ice bath and termination by addition of 20% aqueous THF. The reaction mixture is filtered to remove KCl, which is dissolved in water. The aqueous mixture is filtered to remove insoluble polycarbosilane product, which is vacuum dried. The filtered THF reaction solution is dried with $MgSO_4$, filtered to remove $MgSO_4$, and concentrated by stripping. The stripped solution is added to acetone, precipitating soluble solid polycarbosilane, which is also vacuum dried. The acetone/THF mixture is stripped, leaving the soluble liquid polycarbosilane product.

The process steps are straightforward, and reactions have been run in the laboratory on a one gallon scale with no problems. As such, the process appears to be amenable to further scale-up, including in commercial equipment.

ADVANTAGES OF K/THF SYSTEM

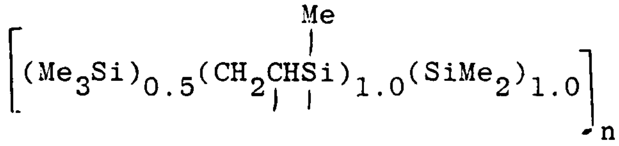
All but the earliest model reactions were run using potassium (K) as the active metal, and THF as the solvent. There are at least four advantages to this combination, including:

- Reactions are rapid, remarkably clean, and exothermic, but are controllable. The reflux temperature of THF is just above the melting point of K, keeping reactions fluid and temperatures relatively low. A slight molar excess of K ensures low residual chlorine/oxygen contents in the polycarbosilanes (oxygen arises from water used to terminate reactions) and attendant stability to long term storage.
- THF does not react in this system, while it is known to react with chlorosilanes in the presence of sodium[14] or magnesium.[15] THF is reactive toward $CH_2=CHSiMeCl_2$ in the absence of active metals.[16] Toluene yields ϕCH_2SiMe_3 in our hands and is known to react with $CH_2=CHSiMe_3$ in the presence of either Na or K.[17]
- THF is much cheaper than HMPA (hexamethylphosphoramide)[12] which is also a suspect carcinogen, and is much less toxic than dioxane.
- THF is water-miscible, allowing homogeneous termination of reactions, and is also a good solvent for the polycarbosilanes.

Disadvantages include the fact that K is more costly and hazardous than Na, Li, or Mg, and generates more by-product (KCl) by weight than the other metals.

POLYCARBOSILANE STRUCTURES

The gross structures of our polycarbosilanes have been fairly well established by the model chemistry and instrumental analyses. The molar ratios of monomer units in some cases require that $\equiv\mathrm{SiSi}\equiv$ bonds be present, probably as disilane linkages. These polymers are UV-inactive, ruling out the presence of trisilane ($\equiv\mathrm{SiSiSi}\equiv$) groups (or higher polysilane groups). Normal approaches to $\equiv\mathrm{SiSi}\equiv$ analysis, including base-catalyzed cleavage, have not been successful and newer approaches, such as bromine cleavage, are being considered. Other instrumental analyses (IR, H^1 NMR, C^{13} NMR) and elemental analyses support the proposed average structure. The solubilities and high average functionalities suggest that cyclic three-dimensional structures are present as in silicone resins.



$$\left[(\mathrm{Me_3Si})_{0.5}(\mathrm{CH_2}\underset{|}{\mathrm{CH}}\overset{\overset{\mathrm{Me}}{|}}{\underset{|}{\mathrm{Si}}})_{1.0}(\mathrm{SiMe_2})_{1.0}\right]_n$$

Typical Polycarbosilane Structure

Since our polycarbosilanes are soluble, molecular weights and distributions can be studied by gel permeation chromatography (GPC). In the absence of molecular weight GPC standards for these polymers, the scans will be more useful in relating performance to molecular weight distribution rather than in determining absolute molecular weight values.

PYROLYSIS CHEMISTRY

Pyrolyses described herein were run in two steps in different furnaces, going from ambient to about 800°C in quartz reactors, and to 1200°C in alumina reactors. The two step approach is an equipment limitation, rather than necessity, and would be run as one step with optimized equipment.

When polycarbosilane samples are pyrolyzed, most of the chemistry and weight loss occur between 350°-550°C (see Figure 3, which is a representative thermogravimetric analysis scan), leaving amorphous SiC. Volatile products evolve and collect in the cooler ends of the reactor. Weight loss above 800°C is negligible, with the chemistry involving only the change of amorphous SiC to microcrystalline β-SiC, which is detected by x-ray diffractions (see Figure 2 for representative scan). The products are referred to as SiC compositions, since they contain varying amounts of free carbon and oxygen (as SiO_2). The presence of these impurities is fortunately not detrimental to the high performance properties of these compositions, and may in fact be necessary.[18] Our x-ray diffraction scans are superimposable with those of Yajima.[18]

Pyrolysis yields for effective SiC precursors vary from 18.4% to 43.6% under our conditions, which involve shorter pyrolysis times and higher heating rates than are typical for reactions of this type. Certain of the nonlinear soluble oil polycarbosilanes have also been pyrolyzed under our conditions, yielding about 25% of SiC compositions. This shows that SiC yields increase with polycarbosilane molecular weight for each preparation, but only to a point. Yields of SiC from pyrolyses of insoluble solids and soluble solids are the same for a given preparation.

Our best yields for the two step process, i.e., polycarbosilane preparation and pyrolysis compute to 25.2%. This is higher than the corresponding figures calculated from Yajima's data[4] in going through patent examples on his three step process.

We have not yet begun an in-depth study of the volatile by-products of the pyrolysis reactions. The bulk of these products as isolated are also polymeric in nature, suggesting that highly reactive species are generated in the hot zones and are repolymerized in cooler zones. Further work will be addressed to this problem.

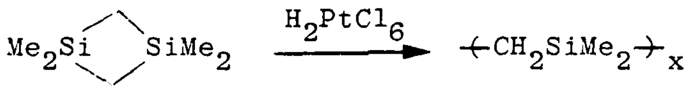
SIGNIFICANCE OF BRANCHING ON SiC YIELDS

In view of the fact that certain polycarbosilanes were convertible to SiC compositions, polycarbosilanes known in the literature were prepared and screened for conversion to SiC.

Linear polycarbosilanes (or polysilmethylenes) have been prepared by active metal dechlorination of $ClCH_2SiMe_2Cl$.[19] When such polycarbosilanes were prepared in this project, using K/THF as the dechlorinating medium, and pyrolyzed, the yield of SiC was

$$ClCH_2SiMe_2Cl \xrightarrow[THF]{K} \text{+}\!\left(CH_2SiMe_2\right)\!\text{+}_x \xrightarrow{1200^{o}} \text{Nil}$$

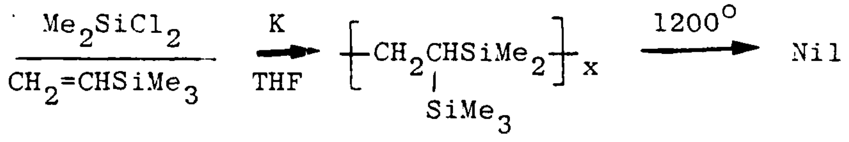
negligible. This suggests that similar linear polycarbosilanes,



prepared by polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane,[20] would also be ineffective as SiC precursors.

When $ClCH_2SiMe_2Cl$ is copolymerized with $MeSiCl_3$ (see Polycarbosilane Preparations), the resultant branched polycarbosilane is an effective SiC precursor, yielding 30.8% of SiC composition on unconfined pyrolysis.

Similarly, Me_2SiCl_2 has been reacted with $CH_2{=}CHSiMe_3$ to yield cyclic compounds and a polymer, presumably $\text{+}\!\left[CH_2CH(SiMe_3)SiMe_2\right]_x$.[21] Copolymerization of Me_2SiCl_2 and $CH_2{=}CHSiMe_3$ using K/THF yielded a polymer which produced



$$\frac{Me_2SiCl_2}{CH_2{=}CHSiMe_3} \xrightarrow[THF]{K} \text{+}\!\left[CH_2\underset{\displaystyle SiMe_3}{\underset{|}{C}}HSiMe_2\right]\!\text{+}_x \xrightarrow{1200^{o}} \text{Nil}$$

negligible SiC on pyrolysis. When trifunctional $MeSiCl_3$ was substituted for difunctional Me_2SiCl_2 (see Polycarbosilane Preparations) in the reaction with $CH_2{=}CHSiMe_3$, the resultant

$$\frac{0.67}{1.00}\quad \frac{\text{MeSiCl}_3}{\text{CH}_2\text{=CHSiMe}_3} \xrightarrow[\text{THF}]{\text{K}} \begin{matrix}\text{Soluble Solid}\\ \text{Polycarbosilane}\end{matrix} \xrightarrow{1200^{\circ}} \text{SiC}$$

polycarbosilane was an effective SiC precursor (40.9% yield).

The above examples elegantly confirm the criticality of polycarbosilane branching in obtaining good yields of SiC. A copolymer was prepared from 2/1 $\text{ClCH}_2\text{SiMe}_2\text{Cl}/\text{CH}_2\text{=CHSiMeCl}_2$ and was, quite predictably, an effective SiC precursor.

SPINNING STUDIES

Experiments will be run with the goal of melt- or solution-spinning of our polycarbosilanes to fibers. If successful, the fibers will be thermally converted to SiC fibers which will be tested for physical properties and composite applications. It should be noted that fiber preparation is only the most demanding application for polycarbosilanes. They will also be useful as high temperature-resistant binders, coatings, impregnants, and adhesives, and as additives in powder metallurgy.

CONCLUSIONS

Improved routes to tractable solid polycarbosilanes have been developed, based on potassium metal dechlorination of mixtures of vinylmethylchlorosilanes or methyltrichlorosilane with other silane monomers. The criticality of branched structures in such polycarbosilanes has been recognized in regard to their conversion to silicon carbide compositions by atmospheric pressure pyrolyses. The one step preparation of polycarbosilanes represents a significant advance in that prior art processes[4] involve an additional step wherein polysilanes are converted to polycarbosilanes.

FUTURE WORK

Further refinements in optimizing polycarbosilane Preparations will be pursued in terms of reaction, raw material, and work-up variables with the goal of maximizing yields and minimizing cost and process complexity. Relationships between polycarbosilane structure and silicon carbide yield and quality will be developed. Selected polycarbosilanes will be screened for spinnability, and samples provided as needed for outside programs. Analytical methods will be assessed for satisfactory $\equiv SiSi \equiv$ analyses and molecular weight determinations.

EXPERIMENTAL SECTION

All chlorosilanes were freshly distilled before use. THF was reagent grade, dried over Linde 3A molecular sieves. K metal was purchased as practical grade ingots; all K metal transfers were made under nitrogen in a dry box. All reactions (preparations and pyrolyses) were run under argon. Routine NMR spectra were recorded with a Perkin-Elmer R24A spectrometer. VPC Analyses were run on Hewlett-Packard 5830A and 5840A gas chromatographs. Pyrolyses up to 800°C were run in a quartz reactor in a Lindberg 54242 tube furance, and those up to 1200°C were run in an alumina reactor in a Lindberg 54233 tube furnace.

The following represent typical reaction conditions and methods.

Reaction of 2/1 $Me_3SiCl/CH_2{=}CHSiMeCl_2$ With K in THF

In a 500 ml three-necked round bottom flask with standard taper fittings were combined 16.8 g (0.43 mol) of K metal chunks and 131.4 g anhydrous THF. The flask was fitted with heating mantle, mechanical stirrer with glass blade, thermometer, addition funnel, and wet ice condenser plus valves for maintaining an Ar atmosphere. Flask contents were heated to reflux (66°) melting the K and addition of a mixture of 23.3 g (0.215 mol) of Me_3SiCl and 15.2 g (0.107 mol) of $CH_2{=}CHSiMeCl_2$ was begun. Addition was completed in 50 min, maintaining the reaction temperature at 66-67.5° with no external heating. Heat was applied to maintain reflux for an additional 75 min. Reaction was terminated by dropwise addition of a solution of 5 g H_2O in 15 ml THF. White solid precipitate was collected by suction filtration, rinsed with several small portions of THF, and dissolved in water. A clear solution was obtained with no insoluble polycarbosilane. The THF solution was vacuum stripped and distilled up to 25°/0.5 mm head temperature. There was obtained 16.7 g (71.9%) of non-distilled residue, a soluble polycarbosilane fluid (molar functionality F=2.0). Similar reactions using octane or toluene in place of THF gave respective yields of 46.4% or 42.4% of soluble polycarbosilane fluid. The reaction in toluene also yielded ϕCH_2SiMe_3 as a volatile product.

The major volatile products from the above reactions were identified as $CH_2=CHSiMe(SiMe_3)_2$ and $(CH_2=CHSiMeSiMe_3)_2$ by GC/MS analysis (see Figures 1 and 2 for mass spectra) and by NMR.

Reaction of 1/1 $Me_3SiCl/CH_2=CHSiMe_2Cl$ With K in THF

In the same apparatus were combined 18.6 g (0.48 mol) K metal and 136.0 g anhydrous THF. System was heated to reflux, which was maintained over 50 min by the addition of a mixture of 26.0 g (0.24 mol) of Me_3SiCl and 28.9 g (0.24 mol) of $CH_2=CHSiMe_2Cl$. Heat was applied to maintain reflux for another hr. Workup as above left 16.0 g of polycarbosilane fluid (47.2%) which did not distil below 51°/0.05 mm (molar functionality F=2.0).

GC/MS analysis of the distillate confirmed the presence of $Me_3SiSiMe_3$, $CH_2=CHSiMe_2SiMe_3$ (41.3% yield), $(CH_2=CHSiMe_2)_2$, $Me_3SiCH_2CH(SiMe_3)SiMe_2SiMe_3$, $CH_2=CHSiMe_2CH_2CH(SiMe_3)SiMe_2SiMe_3$ and isomers, plus $CH_2=CHSiMe_2CH_2CH(SiMe_3)SiMe_2SiMe_2CH=CH_2$. Assignments were supported by NMR analyses.

Reaction of 1/1 Me_3SiCl/CH_2=$CHSiMe_3$ With K in THF

Reaction procedure of above was followed with 17.3 g (0.44 mol) of K metal, 137.3 g anhydrous THF, and a mixture of 47.0 g (0.44 mol) of Me_3SiCl and 44.0 g (0.44 mol) of CH_2=$CHSiMe_3$. Workup yielded 33.8 g $Me_3SiCH_2CH(SiMe_3)_2$,[12] b.p. 38°/0.07 mm (62.4%). confirming that disilylation is the major reaction of vinyl groups in these polycarbosilane-forming reactions. Unreacted CH_2=$CHSiMe_3$ (22.6 g, 51.3%) was recovered.

Polycarbosilane Preparation

In a 5 liter, 3NRBS flask were combined 1463 g THF and 336.3 g (8.6 mol, 5% excess) of K metal. Flask was fitted with electric mantle, mechanical stirrer (glass blade), thermometer, 600 ml addition funnel, large Dewar condenser (wet ice), and valves for argon flow. Addition funnel was charged with 100.9 g (0.93 mol) of Me_3SiCl, 239.9 g (1.86 mol) of Me_2SiCl_2, and 262.3 g (1.86 mol) of CH_2=$CHSiMeCl_2$. Heat was applied to reflux with gentle stirring, melting the K (67°). Voltage to mantle was shut off, and addition of chlorosilanes begun and continued over 3 hr, maintaining reaction at 66-68.5°. Heating was resumed to maintain reflux for two more hr. Flask and contents were cooled in wet ice bath and reaction neutralized by dropwise addition of aliquots totalling 50 g H_2O in 380 ml THF. After standing overnight, solid products were collected by suction filtration and triturated with about 500 ml THF, followed by recollection by filtration. Solids were then added to 3250 ml dist. H_2O, precipitating insoluble solid polycarbosilane, which was washed with water and acetone, followed by vacuum drying. The combined THF solutions were dried over $MgSO_4$, filtered to remove $MgSO_4$, and stripped to about 300 ml volume. This concentrated solution was added dropwise to 4000 ml of 19/1 acetone/MeOH (with magnetic stirring), precipitating soluble solid polycarbosilane which was collected and vacuum dried. The solvent/non-solvent mixture was stripped leaving an oil which was vacuum distilled, yielding 52.7 g of soluble fluid polycarbosilane, b.p. greater than 55°/0.05 mm. The yields were:

58.5 g soluble fluid polycarbosilane (including 5.8 g of distillation cuts) (19.1%), 186.7 g soluble solid polycarbosilane (61.0%), and 59.7 g of insoluble solid polycarbosilane (19.5%), totalling 99.6% yield based on chlorosilanes charged.

Polycarbosilane Pyrolysis

Soluble solid polycarbosilane from above preparation (7.00 g) was placed in a 3" quartz boat in quartz reactor fitted in a Lindberg 54242 tube furnace. System was evacuated/argon purged three times and heat applied from ambient to 370^{o}C over 7 hr, at 370^{o} overnight, from 370^{o} to 746^{o} over 8 hr, followed by cooling overnight. Yield of silicon carbide composition in boat was 3.00 g (42.9%). This composition (2.80 g) was placed in alumina boat/alumina reactor in Lindberg 54233 tube furnace. System was again evacuated/argon purged three times and heat applied from ambient to 1000^{o}C over 4 hr, at 1000^{o}C for 20 hr (overnight), from 1000^{o} to 1200^{o} in 1 hr, and at 1200^{o} for 6 hr, followed by cooling overnight. Recovered 2.75 g of SiC composition, consisting of 47.8% SiC, 27.4% SiO_2 (oxygen analysis by difference), and 24.7% free carbon by weight. Microcrystalline β-SiC was detected by x-ray diffraction.

Pyrolyses were repeated as above for 12.00 g of insoluble solid polycarbosilane from above preparation (41.5% yield after 742^{o}) and for 20.35 g of soluble fluid polycarbosilane from the same preparation (21.1% yield after 726^{o}). Both samples were then pyrolyzed to 1200^{o} as above, yielding identical SiC compositions by x-ray diffraction (see Figure 3 for x-ray diffraction pattern).

Reaction of 0.8/1 $Me_3SiCl/CH_2=CHSiMeCl_2$ With K in THF

The procedure of Example I was repeated using a 1000 ml flask, 72.4 g (1.85 mol) K metal, 508.8 g anhydrous THF, and a mixture of 56.4 g (0.52 mol) of Me_3SiCl and 94.5 g (0.67 mol) of $CH_2=CHSiMeCl_2$. Similar workup yielded a yellow fluid which was added to 550 ml acetone, precipitating a white solid. The solid dissolved in an equal volume of CCl_4 and reprecipitated from 900 ml acetone, followed by filtration and vacuum drying. The organic phases were stripped and distilled to $69^{o}/0.08$ mm, leaving a polycarbosilane fluid, while addition of the reaction salt precipitate to H_2O left insoluble polycarbosilane which was collected and vacuum dried. The yields were: soluble fluid, 37.1 g (43.7%), soluble solid, 21.4 g (25.2%), and insoluble solid, 14.0 g (16.5%). The molar functionality F was 2.67. The soluble and insoluble solids were converted to SiC compositions by heating to 1200°C in an inert atmosphere at atmospheric pressure. β-SiC formation was confirmed by x-ray diffraction.

The soluble solid was analyzed by thermogravemetric analysis (see Figure 4), producing a scan which is typical for polycarbosilane precursors for SiC.

Reaction of $ClCH_2SiMe_2Cl$ With K in THF

The standard procedure was repeated using 16.7 g (0.42 mol) of K metal, 30.0 g (0.21 mol) of $ClCH_2SiMe_2Cl$, and 194.5 g anhydrous THF. Workup yielded 10.6 g (70.2%) of polysilmethylene fluid, b.p. greater than $70^{o}/0.1$ mm. Pyrolysis to only 585°C left less than 1% residue confirming that linear polycarbosilanes such as polysilmethylenes known in prior art[19,20] are not effective precursors for silicon carbide when pyrolyzed at atmospheric pressure under an inert atmosphere.

Reaction of 2/3 $MeSiCl_3/ClCH_2SiMe_2Cl$ With K in THF

The procedures above were repeated using 32.3 g (0.83 mol) of K metal, 326 g anhydrous THF, and a mixture of 19.6 g (0.13 mol) of $MeSiCl_3$ and 28.1 g (0.2 mol) of $ClCH_2SiMe_2Cl$. Workup yielded 7.8 g (39%) of soluble solid polycarbosilane. The solid was converted to an SiC composition by pyrolysis in Ar to 1200°C at atmospheric pressure. The presence of β-SiC was confirmed by x-ray diffraction. This example, with branching introduced by units derived from $MeSiCl_3$, confirms that branched structures are needed for conversion to SiC when results are compared to those of the above experiment using only $ClCH_2SiMe_2Cl$.

Reaction of 1/1 $Me_2SiCl_2/CH_2{=}CHSiMe_3$ With K in THF

The standard procedure was repeated using 33.6 g (0.88 mol) of K metal, 187.7 g anhydrous THF and a mixture of 52.9 g (0.41 mol) of Me_2SiCl_2 and 41.0 g (0.41 mol) of $CH_2{=}CHSiMe_3$. Workup yielded 39.7 g (57.6%) of linear polycarbosilane fluid, b.p. greater than $99^o/0.04$ mm, having the average structure $\left[CH_2CH(SiMe_3)SiMe_2 \right]_x$. Pyrolysis of this fluid to only 590^o under an inert atmosphere at atmospheric pressure left less than 0.3% residue. This example confirms that the linear polycarbosilane disclosed in prior art[21] is not an effective precursor for silicon carbide when pyrolyzed at atmospheric pressure under an inert atmosphere.

Reaction of 2/3 $MeSiCl_3/CH_2{=}CHSiMe_3$ With K in THF

The procedures above were followed using 18.2 g (0.46 mol) of K metal, 180 g of anhydrous THF, and a mixture of 22.4 g (0.15 mol) of $MeSiCl_3$ and 23.0 g (0.23 mol) of $CH_2{=}CHSiMe_3$. Workup yielded 6.0 g (20%) of soluble solid polycarbosilane and 0.8 g (2.3%) of insoluble solid polycarbosilane. The molar functionality F was 2.4. The soluble solid was converted to an SiC composition by pyrolysis to 1200°C under Ar atmosphere at atmospheric pressure. X-ray diffraction confirmed conversion to β-SiC. This example confirms that the branching introduced by $MeSiCl_3$ is needed for conversion to SiC when compared to the linear polycarbosilane of the above experiment.

Reaction of 0.5/1/1 $Me_3SiCl/ClCH_2SiMe_2Cl/CH_2=CHSiMeCl_2$ With K in THF

The standard procedure was repeated using 32.6 g (0.83 mol) of K metal, 210.8 g of anhydrous THF, and a mixture of 9.6 g (0.09 mol) of Me_3SiCl, 25.2 g (0.18 mol) of $ClCH_2SiMe_2Cl$, and 24.8 g (0.18 mol) of $CH_2=CHSiMeCl_2$. Workup yielded 6.4 g soluble polycarbosilane fluid, b.p. greater than 50°/0.03 mm (20.4%), and 19.7 g (62.4%) of soluble solid polycarbosilane with no insoluble solid polycarbosilane. The soluble solid yielded an SiC composition on pyrolysis under Ar at atmospheric pressure.

Reaction of 3/1.2 $ClCH_2SiMe_2Cl/CH_2=CHSiMeCl_2$ With K in THF

The standard procedure was used with 50.0 g (1.28 mol) of K metal, 800 g of anhydrous THF, and a mixture of 57.9 g (0.405 mol) of $ClCH_2SiMe_2Cl$ and 22.8 g (0.162 mol) of $CH_2=CHSiMeCl_2$. Workup yielded 17.7 g (43.7%) of soluble polycarbosilane fluid and 20.2 g (49.9%) of soft soluble solid polycarbosilane. The molar functionality F was 2.57. The solid was pyrolyzed to an SiC composition under Ar atmosphere at atmospheric pressure. This example demonstrates that polysilmethylenes which are branched due to incorporation of $CH_2=CHSiMeCl_2$-derived units do yield SiC on pyrolysis while linear polysilmethylenes (see above) do not.

The soluble solid and fluid were analyzed by gel permeation chromatography (Trichloroethylene solvent, infrared detector set at 9.5 or 9.6 μ). The GPC scans and infrared scan of the soluble solid are shown in Figures 5 and 6. The GPC baseline numbers are elution volumes which do not translate into accurate molecular weights since there are no GPC standards for these materials. The GPC scans will be useful "fingerprint" analyses for relating performance vs molecular weight trends.

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TABLE AND FIGURES

TABLE I

FUNCTIONALITY VALUES FOR ORGANOSILANE MONOMERS IN FORMATION OF POLYCARBOSILANES[(a)]

Monomer	Formula	f
Trimethylchlorosilane	Me_3SiCl	1
Dimethyldichlorosilane	Me_2SiCl_2	2
Methyltrichlorosilane	$MeSiCl_3$	3
Tetrachlorosilane	$SiCl_4$	4
Chloromethyltrimethylsilane	Me_3SiCH_2Cl	1
Bis(chloromethyl)dimethylsilane	$Me_2Si(CH_2Cl)_2$	2
Tris(chloromethyl)methylsilane	$MeSi(CH_2Cl)_3$	3
*Tetrakis(chloromethyl)silane	$Si(CH_2Cl)_4$	4
Chloromethyldimethylchlorosilane	$ClCH_2SiMe_2Cl$	2
Bis(chloromethyl)methylchlorosilane	$(ClCH_2)_2SiMeCl$	3
Tris(chloromethyl)chlorosilane	$(ClCH_2)_3SiCl$	4
Chloromethylmethyldichlorosilane	$ClCH_2SiMeCl_2$	3
Bis(chloromethyl)dichlorosilane	$(ClCH_2)_2SiCl_2$	4
Chloromethyltrichlorosilane	$ClCH_2SiCl_3$	4
Vinyltrichlorosilane	$CH_2{=}CHSiCl_3$	5
Vinylmethyldichlorosilane	$CH_2{=}CHSiMeCl_2$	4
Vinyldimethylchlorosilane	$CH_2{=}CHSiMe_2Cl$	3
Vinyltrimethylsilane	$CH_2{=}CHSiMe_3$	2
Vinyldimethylchloromethylsilane	$CH_2{=}CHSiMe_2CH_2Cl$	3
*Bis(chloromethyl)vinylmethylsilane	$CH_2{=}CHSiMe(CH_2Cl)_2$	4
*Vinyltris(chloromethyl)silane	$CH_2{=}CHSi(CH_2Cl)_3$	5
*Bis(chloromethyl)vinylchlorosilane	$CH_2{=}CHSiCl(CH_2Cl)_2$	5
Chloromethylvinyldichlorosilane	$CH_2{=}CHSiCl_2CH_2Cl$	5
Chloromethylvinylmethylchlorosilane	$CH_2{=}CHSiMeClCH_2Cl$	4

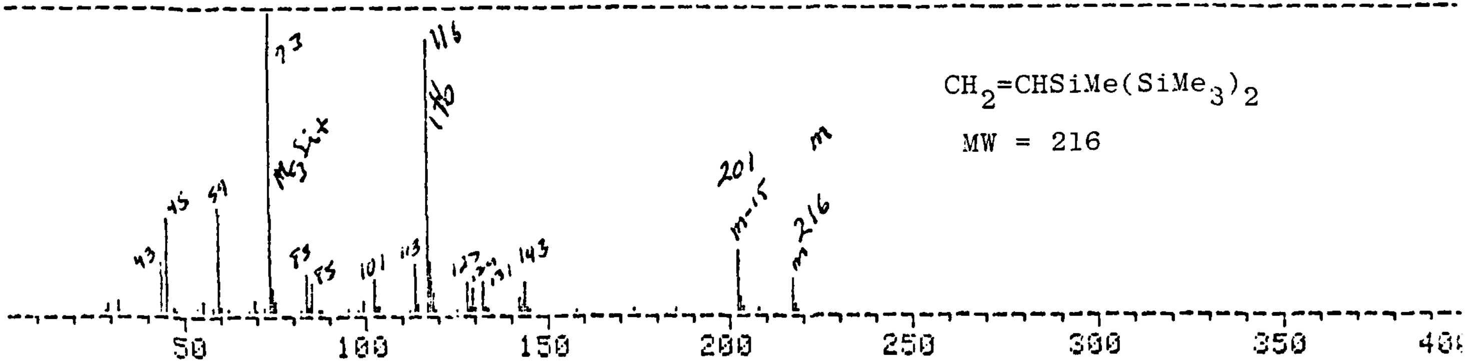
*"Paper" examples - unknown in open literature.

(a) Note that vinylic silanes can add an additional unit of functionality in higher temperature reactions (see Ref. 12).

FIGURE 1

MASS SPECTRUM OF $CH_2{=}CHSiMe(SiMe_3)_2$

```
** Spectrum #  51.011 **  Sample #   9387   Retention Time =  5.6 minutes
Scanned from  20 to 600 amu  Number of Peaks Detected =  109
File type = linear
Base Peak =  72.90  Base Peak Abundance =    1166  Total Abundance =   12152
```

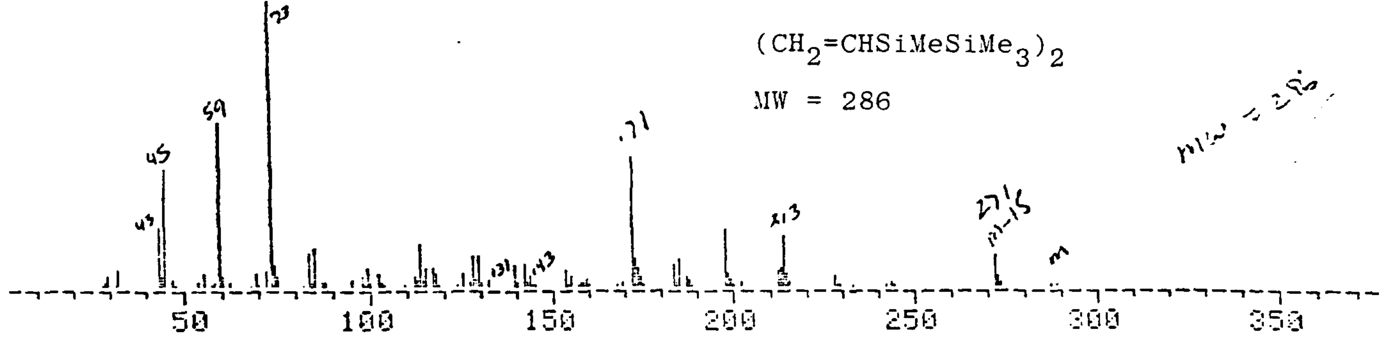


```
Lower Abundance Cutoff Level =    1.0%
  MASS     ABUNDANCE (%)             MASS     ABUNDANCE (%)           MASS     ABUNDANCE (%)
 27.90          1.4                  80.90         1.0               127.90         2.6
 28.90          3.4                  82.90        13.1               128.90         8.1
 30.90          4.2                  84.00         2.0               130.00         1.5
 42.90         16.8                  84.90        10.0               131.00        10.2
 45.00         31.1                  85.90         1.3               132.00         1.6
 45.90          7.1                  86.90         1.0               141.00         5.2
 46.90          1.0                  96.90         1.3               142.00         3.1
 52.80          1.7                  98.90         3.8               142.90        10.4
 54.90          3.5                 100.90        11.3               144.00         1.7
 56.90          1.8                 101.90         2.5               145.00         1.3
 58.90         34.7                 102.90         1.5               156.90         1.2
 59.90          2.5                 110.90         1.1               172.90         1.3
 60.90          1.0                 112.90        15.6               184.90         1.4
 68.80          3.5                 113.90         2.9               201.00        19.6
 69.90          1.0                 115.90        89.5               202.00         4.7
 70.90          2.4                 116.90        16.9               203.00         2.5
 72.90        100.0                 117.90         7.1               216.00        10.8
 73.90          8.3                 124.90         1.0               217.00         2.7
 74.90          3.8                 126.90         9.5               218.00         1.5
```

FIGURE 2

MASS SPECTRUM OF $(CH_2{=}CHSiMeSiMe_3)_2$

```
** Spectrum #  78.011 **  Sample #   9388   Retention Time = 14.3 minutes
Scanned from  20 to 600 amu  Number of Peaks Detected =  156
File type = linear
Base Peak =  72.90  Base Peak Abundance =     1368  Total Abundance =   18352
```

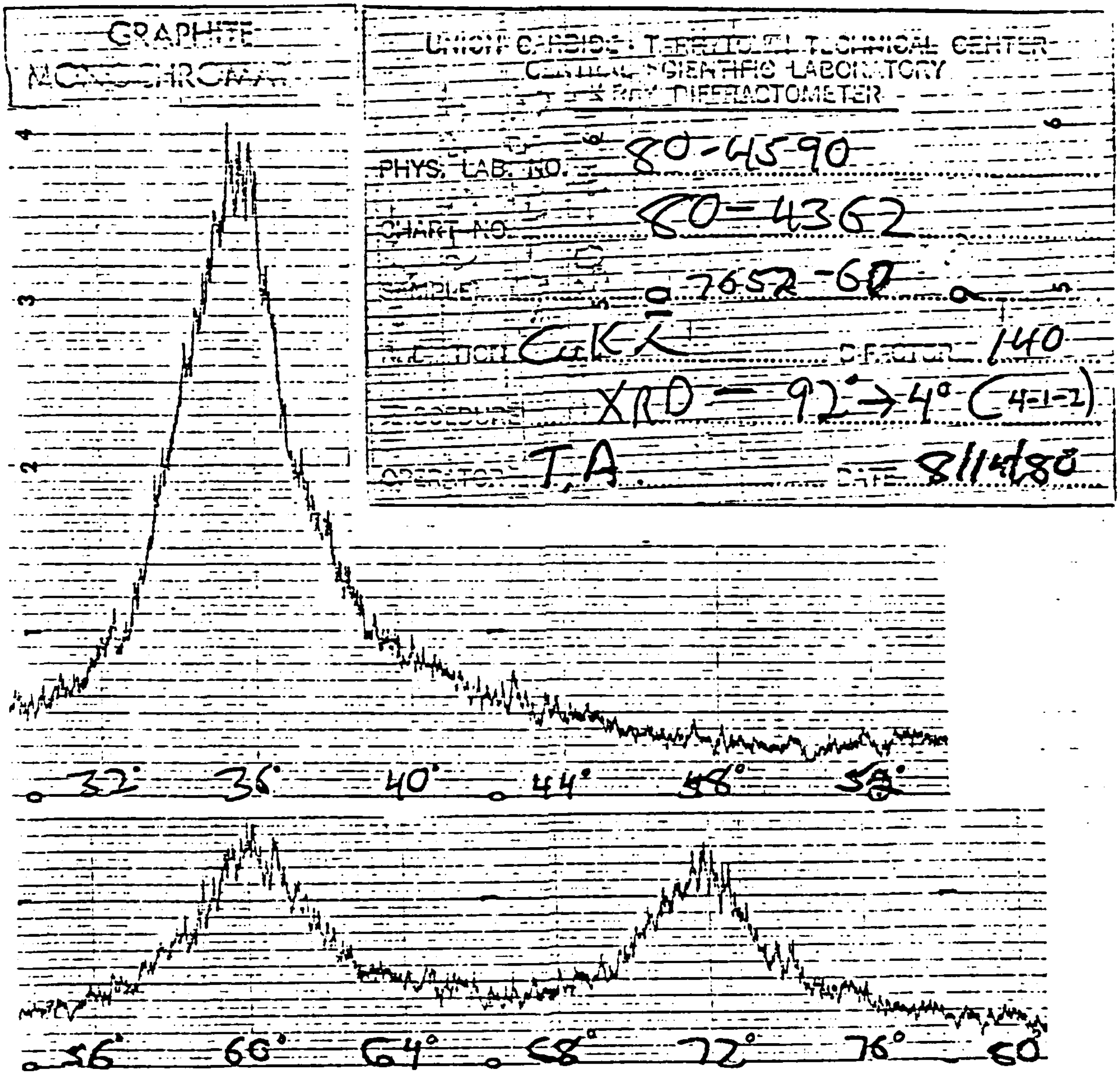


Lower Abundance Cutoff Level =   1.0%

MASS	ABUNDANCE (%)	MASS	ABUNDANCE (%)	MASS	ABUNDANCE
27.90	1.5	100.00	1.6	156.90	2.3
28.90	3.7	101.00	4.5	157.90	1.8
30.90	5.8	102.00	1.8	158.90	3.4
42.90	20.5	102.90	1.5	168.90	2.5
44.00	4.3	108.90	1.1	170.90	44.8
45.00	40.7	110.90	3.7	171.90	9.7
45.90	2.7	111.90	3.1	172.90	7.2
47.00	1.4	112.90	15.3	173.90	4.1
52.80	1.8	113.90	3.1	175.00	1.1
54.90	4.8	114.90	7.2	182.90	7.7
56.90	2.2	115.90	6.6	184.00	2.5
58.90	56.9	116.90	5.2	185.00	10.0
59.90	4.0	122.90	1.5	186.00	3.5
60.90	1.7	124.90	5.4	187.00	3.2
66.90	1.3	125.90	1.8	197.00	19.6
68.80	5.1	126.90	10.7	198.00	5.0
69.90	1.2	128.00	2.6	199.00	2.9
70.90	5.6	129.00	10.5	201.00	1.6
72.90	100.0	129.90	1.9	211.00	5.8
73.90	8.3	131.00	3.4	212.00	6.9
74.90	3.9	138.90	8.0	213.00	18.2
80.90	1.4	140.00	1.8	214.00	4.8
82.90	12.1	141.00	8.4	215.00	2.1
84.00	2.3	142.00	2.0	227.00	4.4
84.90	14.5	143.00	4.2	228.00	1.3
85.90	2.2	145.00	1.0	242.95	1.5
86.90	1.8	153.00	5.6	270.95	10.9
94.90	2.9	154.00	1.2	271.95	3.5
96.90	3.6	154.90	3.9	272.95	2.0
98.90	6.8				

FIGURE 3

X-Ray Diffraction Scan of
Typical SiC Composition



GRAPHITE MONOCHROMATOR

UNION CARBIDE TARRYTOWN TECHNICAL CENTER
CENTRAL SCIENTIFIC LABORATORY
X-RAY DIFFRACTOMETER

PHYS. LAB. NO. 80-4590
CHART NO. 80-4362
SAMPLE 7652-60
RADIATION CuKα D FACTOR 140
PROCEDURE XRD 92°→4° (4-1-2)
OPERATOR T.A. DATE 8/14/80

FIGURE 4 Thermogravimetric Analysis, Typical Soluble Solid

T-4788	**T-AXIS**	**DTA-DSC**	**TGA •**	**TMA**	80-1133
RUN NO ___ DATE 3/5/80	SCALE, °C/in 50	SCALE, °C/in ______	SCALE, mg/in 1.00	SCALE, mils/in ______	He Atmosphere
OPERATOR [illegible]	PROG. RATE, °C/min 10	(mcal/sec)/in ______	SUPPRESSION, mg 0.2	MODE ______	20 min purge
SAMPLE 7480-42, 43	HEAT X COOL ___ ISO ___	WEIGHT, mg ______	WEIGHT, mg 8.2 mg	SAMPLE SIZE ______	Red = Δ wg.
ATM He	SHIFT, in 0	REFERENCE ______	TIME CONST., sec ______	LOAD, g ______	Blue = dy
FLOW RATE 0.08 ft³/hr.			dY, (mg/min)/in 0.1	dY, (10X), (mils/min)/in ______	

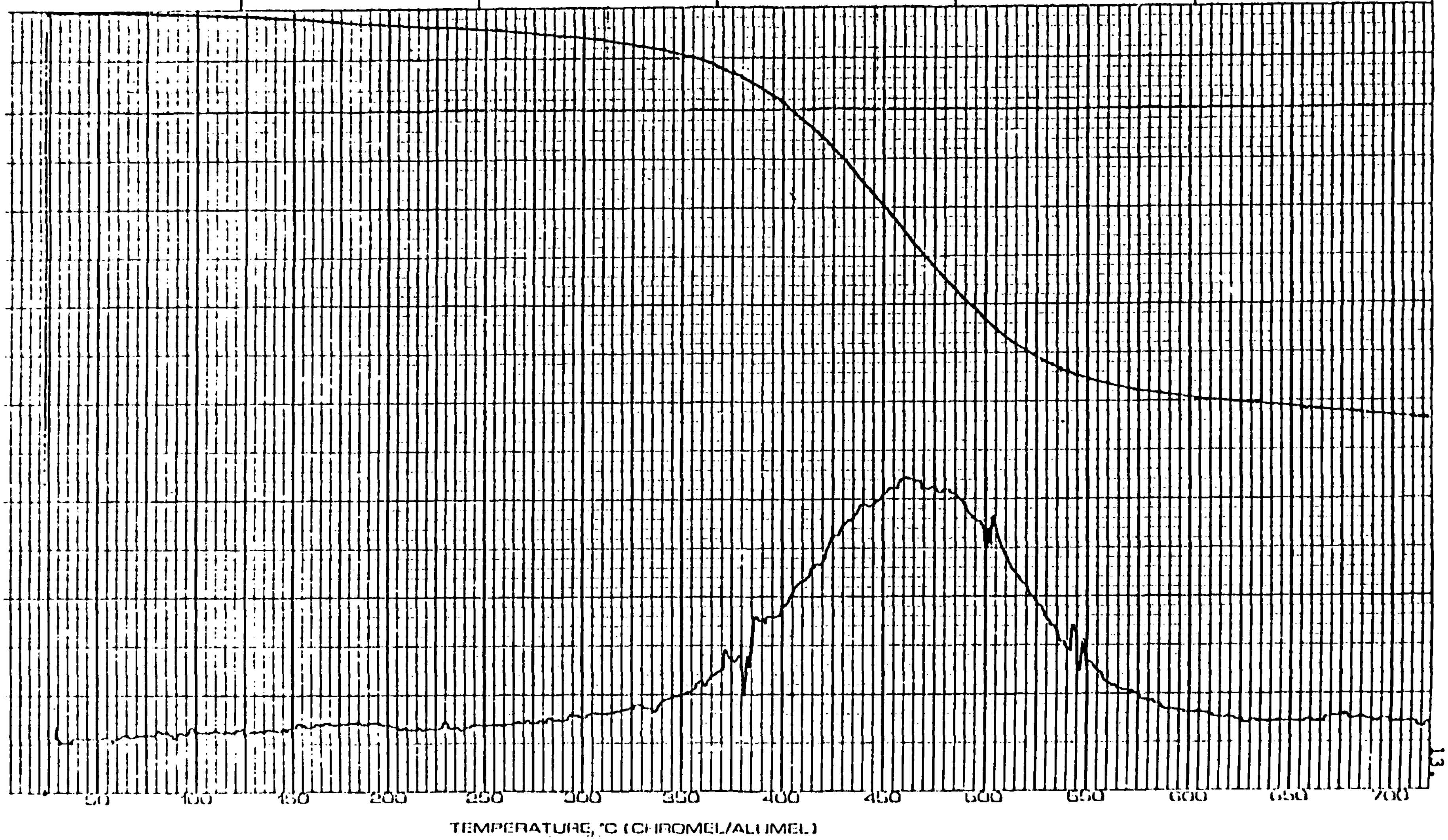
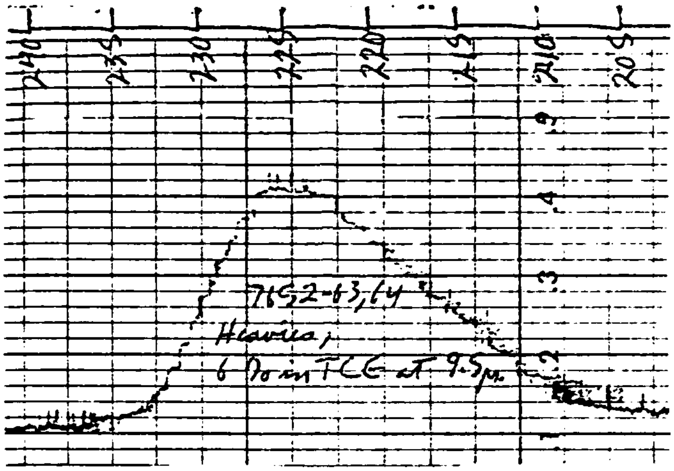
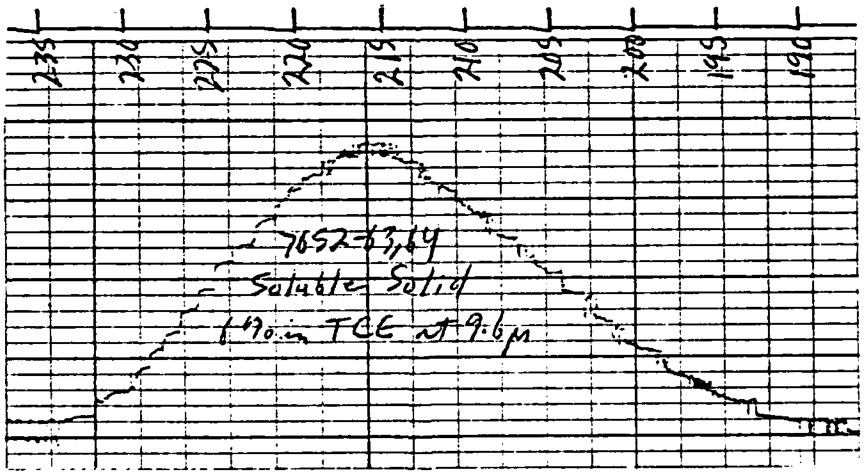


FIGURE 5

GEL PERMEATION CHROMATOGRAPHY OF LIQUID AND SOLID FRACTIONS OF POLYCARBOSILANE PREPARED FROM 3/1.2 $ClCH_2SiMe_2Cl/CH_2=CHSiMeCl_2$



SOLUBLE LIQUID SAMPLE (9.5 µ)



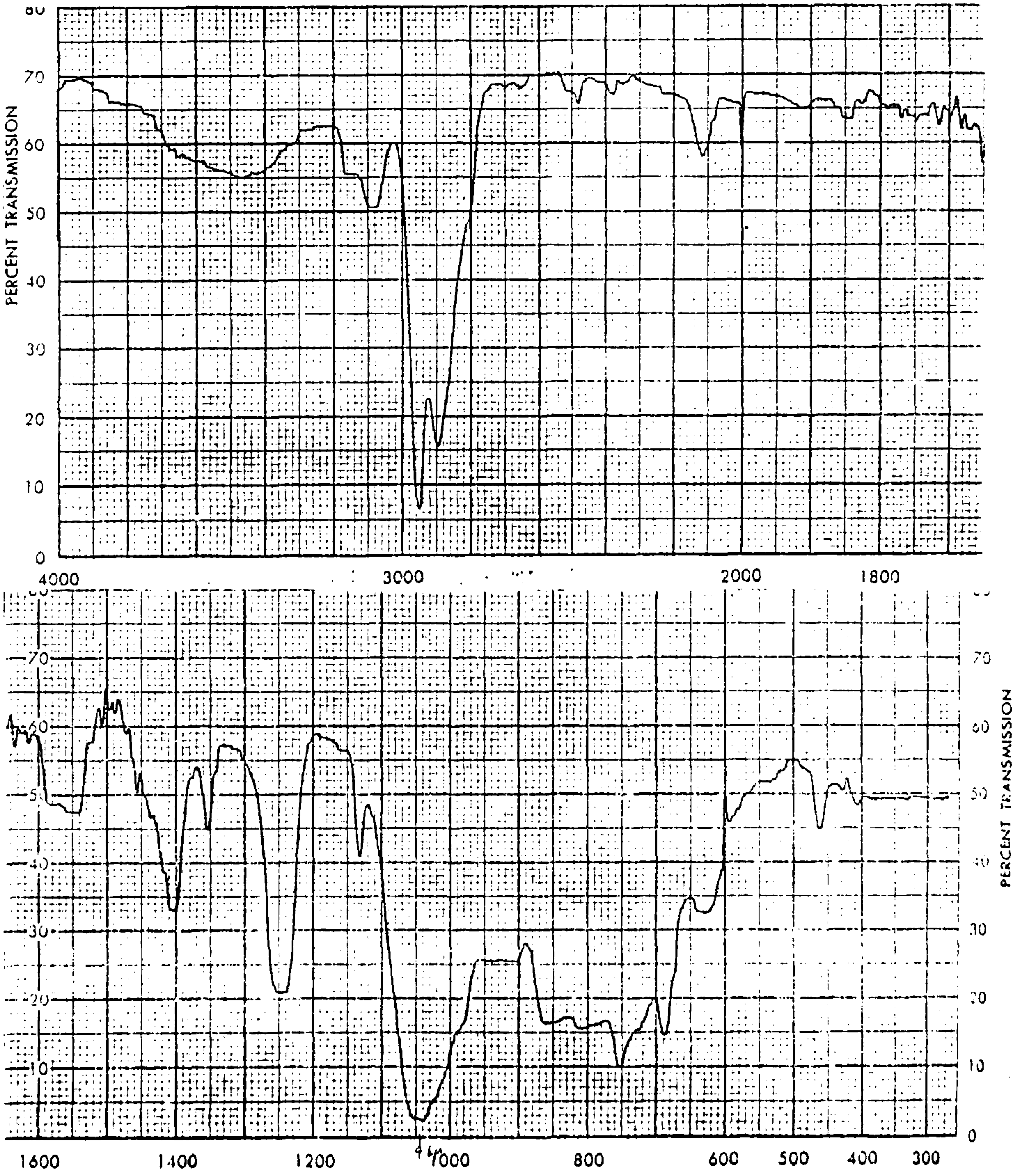
SOLUBLE SOLID SAMPLE (9.6 µ)

Analyses were run at 6 wt-% concentrations in trichloroethylene solvent on a custom-built low-pressure instrument using infrared detection at 9.5 or 9.6 µ.

FIGURE 6

INFRARED SCAN OF SOLUBLE SOLID POLYCARBOSILANE

PREPARED FROM 3/1.2 $ClCH_2SiMe_2Cl/CH_2=CHSiMeCl_2$



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