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               OF SILICON-CONTAI..(U) MASSACHUSETTS INST OF TECH
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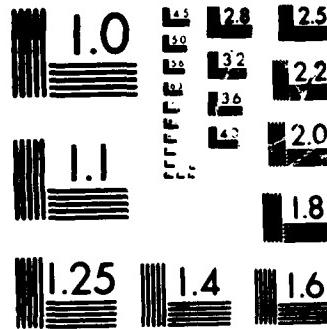
MICROCOPY RESOLUTION TEST CHART

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ORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS			
Unclassified				
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	Approved for public release Distribution unlimited.			
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)			
22				

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Massachusetts Institute of Technology		ONR
6c. ADDRESS (City. State and ZIP Code)		7b. ADDRESS (City. State and ZIP Code)
Department of Chemistry 77 Massachusetts Avenue Cambridge, MA 02139		Department of Navy Arlington, VA 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER			
ONR					
8c. ADDRESS (City. State and ZIP Code)		10. SOURCE OF FUNDING NOS.			
Department of Navy Arlington, VA 22217		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
		N-00014-82-K	NR631-618		

11. TITLE (Include Security Classification)
Applications of Methyldichlorosilane in the Preparation of Silicon-containing Ceramics

12. PERSONAL AUTHOR(S)
Dietmar Seyferth, G.H. Wiseman, Y.-F. Yu, T.S. Targos, C.A. Sobon, T.G. Wood, and G.E. Koppetsch

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Yr., Mo., Day)	15. PAGE COUNT
Preprint	FROM _____ TO _____		

16. SUPPLEMENTARY NOTATION
BOOK CHAPTER in Proceedings of Eighth International Conference on Organosilicon Chemistry

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	silicon nitride, silicon carbide, polysilanes,
			polysilazanes ceramics metal alkoxides

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Methyldichlorosilane is a useful starting material in the preparation of silicon-containing ceramics. Its hydrolysis, aminolysis and sodium condensation give products whose further polymerization or cross-linking yields useful preceramic polymers.

DTIC
SELECTED
AUG 2 1 1987

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION	
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐		
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code)	22c. OFFICE SYMBOL
Dr. Kenneth J. Wynne	(202)696-4410	NC
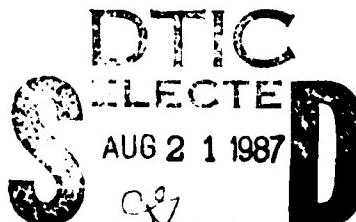
APPLICATIONS OF METHYLDICHLOROSILANE IN THE PREPARATION OF
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Dietmar Seyferth, G.H. Wiseman, Y.-F. Yu, T.S. Targos, C.A. Sobon, T.G. Wood and
G.E. Koppetsch

Department of Chemistry

Massachusetts Institute of Technology

Cambridge, MA 02139

August 14, 1987

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APPLICATIONS OF METHYLDICHLOROSILANE
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SILICON-CONTAINING CERAMICS

Dietmar Seyferth*, Gary H. Wiseman, Yuan-Fu Yu, Tom
S. Targos, Christine A. Sobon, Timothy G. Wood, and
Gundrun E. Koppetsch

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Mass. 02139

ABSTRACT

The hydrolysis, ammonolysis, sodium
condensation, and ethynylenation products of
methyldichlorosilane can be converted to useful
preceramic polymers. The chemistry involved in
these conversions is summarized.

INTRODUCTION

The Rochow-synthesis of methylchlorosilanes by the reaction of gaseous methyl chloride with a solid mass of silicon/copper alloy has been practised since the 1940's.[1] The major product of this reaction as practised industrially is dimethyldichlorosilane, $(CH_3)_2SiCl_2$, the workhorse of the silicones industry, but other products are formed as well, albeit in much lower yield. Among these are CH_3SiCl_3, $(CH_3)_3SiCl$ and CH_3SiHCl_2. The latter, methyldichlorosilane, has some commercial applications.[2,3] It presents interesting options for further chemical conversion: in addition to its two very reactive Si-Cl bonds, it has a reactive Si-H bond.[2,4] (The Si-CH$_3$ bond, on the other hand, is kinetically quite stable). In some cases, exclusive reactions of the Si-Cl bonds are possible. In other cases, exclusive reactions of the Si-H bond can be effected. Toward some reagents, both the Si-Cl and Si-H bonds are reactive, but usually at different rates. Thus the chemistry of methyldichlorosilane is potentially rich and variable. We have found it to be an excellent precursor for a number of different preceramic polymer systems which we shall discuss below.

The Hydrolysis of Methyldichlorosilane

The hydrolysis of methyldichlorosilane can be carried out in such a manner that a high yield of cyclic oligomers, 1, is obtained, in addition to linear polysiloxanes, 2.[5]
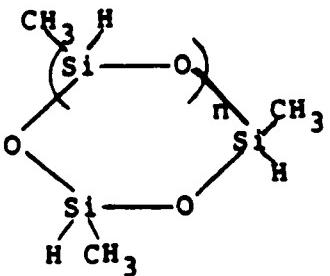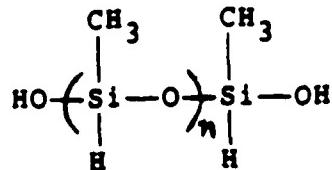
$\underline{1}$, n = 1, 2, 3 . . . $\underline{2}$, n > 1

For instance, hydrolysis of CH_3SiHCl_2 in dichloromethane solution at room temperature by slow addition of bulk water gave the distribution of cyclic oligomers shown in Table I.[5b] Since the Si atoms contain CH_3 and H substituents, cis and trans isomers of the cyclic oligomers will be possible. Mostly linear polysiloxanes, $\underline{2}$, also can be prepared. One such polymeric product, a liquid of molecular weight 2000-5000 (vendor data), is sold under the designation PS-122 by the Silanes and Silicones Group of Dynamit Nobel (formerly Petrarch Systems). Such linear polysiloxanes, as well as polysiloxanes obtained by cohydrolysis of CH_3SiHCl_2 and $(CH_3)_2SiCl_2$, have found industrial application.[2]

The chemistry of $[CH_3Si(H)O]$-containing polysiloxanes, both the cyclic oligomers and the linear polymers, has been investigated. The reactions studied have involved in the main

Table I. Composition of cyclo-$[CH_3Si(H)O]_n$ Mixtures
Formed in the Hydrolysis of CH_3SiHCl_2

n	mol %	n	mol %
3	trace[a]	11	1.57
4	36.97	12	1.34
5	26.43	13	1.21
6	13.80	14	1.04
7	6.95	15	0.87
8	3.72	16	0.68
9	2.46	17	0.51
10	1.88	18	0.38
		19	0.22
		20-22	trace

[a]Some of the cyclic trimer may have been lost on
concentration of the solution.

hydrosilylation,[4] the catalyzed additions of their
Si-H bonds to C=C bonds of diverse olefinic
substrates, although other Si-H reactions are
possible. Thus, for instance, conversion of the Si-
H linkages of the linear polymer to reactive Si-Cl
bonds has been carried out using allyl or benzyl
chloride with Pd/C catalyst as the chlorination
reagent.[6] Other reactions of $[CH_3Si(H)O]_n$ cyclic
oligomers have been used to introduce metal
functionality. For instance, reactions of
$[CH_3Si(H)O]_n$ cyclics with $Co_2(CO)_8$ and $[\eta$-
$C_5H_5Fe(CO)_2]_2$ gave interesting cobalt- and iron-
containing cyclosiloxanes with Si-Co and Si-Fe
bonds.[7]

In our own research we have used reactions of
both the cyclic $[CH_3Si(H)O]_n$ oligomers and the
linear polysiloxanes containing this repeat unit to
prepare polymers containing metal alkoxide side
groups. The impetus for preparing such materials
was given by a need for coating materials for
carbon/carbon composites that would serve to protect
them from high temperature oxidative degradation.
Current thinking suggested that hafnium or zirconium
containing materials might be suitable in this
application, so our focus was on the preparation of
polymeric systems containing these elements.

The chemistry of zirconium and hafnium alkoxides
is well developed[8], and we chose to approach this
goal via metal alkoxide chemistry, using the
reactivity of the $[CH_3Si(H)O]_n$ oligomers and
polymers to prepare the desired metal alkoxide-
containing polymers.

Metal alkoxides containing alkenoxy groups,
$CH_2=CH(CH_2)_nO$, n = 0, 1, 2 . . . ., can be prepared in

different ways. For our purposes we required two
alkenoxy substituents on the metal for cross-linking
hydrosilylation reactions with $[CH_3Si(H)O]_n$. The
simplest approach to such alkoxides of hafnium and
zirconium involves the reaction of two molar
equivalents each of a saturated alcohol and an
unsaturated alcohol with one equivalent of the
hafnium or zirconium tetrachloride, using ammonia as
HCl acceptor. This would be expected to give a
mixture of species, $(RO)_nM(OCH_2CH=CH_2)_{4-n}$ (when
allyl alcohol was the unsaturated alcohol used),
with n values of 0-4 possible, but with the average
composition "$(RO)_2M(OCH_2CH=CH_2)_2$". An alternate
designed synthesis of such a metal alkoxide uses the
preformed $(RO)_2MCl_2$ (a known, stable compound type)
in a reaction with an unsaturated alkoxide reagent.
The reaction of $(iPrO)_2TiCl_2$ with two molar
equivalents of $CH_2=CHOLi$ (prepared by the
fragmentation reaction of tetrahydrofuran by n–
butyllithium[9]) is an example of this approach. The
reaction of alkoxide materials of average
composition "$(iPrO)_2M(OCH_2CH=CH_2)_2$" (M = Hf and Zr)
with commercial $[CH_3Si(H)O]_n$ PS-122 polysiloxane,
using various reactant ratios and using as
hydrosilylation catalyst $H_2PtCl_6 \cdot 6H_2O$, in toluene at
~110°C gave glassy solids which were initially
soluble in organic solvents such as benzene, toluene
and THF. However, once these products were isolated
from solution they tended to become insoluble on
storage under nitrogen at room temperature. The
cross-linking process must have been effective in
forming a network structure since the pyrolysis of
these materials (to 1000°C in a stream of argon)
left a residue in 80 weight % yield (ceramic yield).

That the cross-linking involves hydrosilylation of allyloxy groups to build $-CH_2CH_2CH_2OM(OPr^i)_2OCH_2CH_2CH_2-$ bridges between siloxane chains was demonstrated by the proton NMR spectra of the products. Since these products are initially soluble, their solutions may be used in vacuum dip-coating of carbon/carbon composite substrates. A testing program of the oxidation resistance of carbon/carbon composites treated with these zirconium- and hafnium-containing products is in progress. It is clear that polysiloxane-anchored metal alkoxides of many other metals can be made by this procedure and we are examining further possibilities.

The Ammonolysis of Methyldichlorosilane.

The reaction of ammonia with methyldichlorosilane was reported first by Brewer and Haber in 1948.[10] They obtained a viscous oil which decomposed on attempted vacuum distillation with release of ammonia. An insoluble gel remained as residue. Sememova, Zhinkin and Andrianov[11] studied the same reaction and reported obtaining by vacuum distillation a 25% yield of $[CH_3SiNHN]_4$ and a 10% yield of a bicyclic compound formulated as $(CH_3SiHNH)_3[(CH_3SiH)_{1.5}N]_2$. In our hands, the ammonolysis of CH_3SiHCl_2 proceeded smoothly in diethyl ether or THF at 0° C. Very little insoluble polysilazane precipitated with the ammonium chloride. Removal of solvent in vacuum from the filtrate left a mobile oil in high yield. Its proton NMR spectrum was in agreement with the formulation $[CH_3SiHNH]_n$, and a cryoscopic molecular

weight determination gave values of n between 4.7 and 5.4. This ammonolysis product, probably a mixture of cyclic oligomers and, perhaps, also some linear species was not a useful silicon carbonitride precursor. Its pyrolysis to 1000°C gave a ceramic yield of only 20%. Application of the ammonium salt-induced thermal polymerization of Rochow and Krüger to the CH_3SiHCl_2 ammonolysis resulted in evolution of ammonia and formation of a very viscous polysilazane oil ($SiCH_3$:NH:SiH = 3:0.55:1 vs 3:1:1 for $[CH_3SiHNH]_n$). Pyrolysis of this material, however, gave a ceramic yield of only 36%.

In a search for better ways of converting the CH_3SiHCl_2 ammonolysis product to a useful silicon carbonitride precursor, we applied the dehydrocyclodimerization reaction which had been reported by Fink in 1965 (eq.1)[13].

$$2/R_2\underset{\substack{| \\ H}}{Si}-\underset{\substack{| \\ H}}{NR^1} \xrightarrow{K,Bu_2O} 2\ H_2 + \begin{array}{c} R_2Si\text{——}NR^1 \\ |\qquad\quad| \\ R^1N\text{——}SiR_2 \end{array} \quad (1)$$
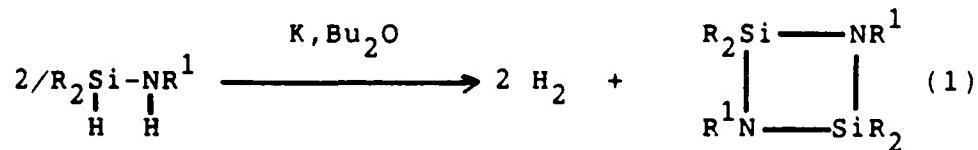
In each cyclic $[CH_3SiHNH]_n$ oligomer there are "n" sets of adjacent Si-H and N-H bonds. If the process shown in eq.1 could be induced, then a polymer consisting in good part of fused cyclosilazane rings would result. (No doubt, the process would be more complicated, since base-induced in' .molecular Si-H/ N-H reactions (to give an Si-N bond and H_2) also were known.

Since the potassium in eq.1 would quickly be converted to KH, we used KH as the basic catalyst. The hoped-for dehydrocyclopolymerization did indeed

take place and we obtained organic-soluble low polymers (MW between 800 and ca. 2000, depending on experimental condition).[14] These still retained unreacted N^-K^+ functionality and, therefore, had to be treated with a suitable electrophile to obtain the "neutral" polymer. (Usually, CH_3I or $(CH_3)_2SiHCl$ was the electrophile used). Sufficient Si(H)-N(H) functionality was present in the neutral polymer (a typical formulation, after a CH_3I quench, was $(CH_3SiHNH)_{0.39}(CH_3-SiN)_{0.57}(CH_3SiHNCH_3)_{0.04}$), so that on pyrolysis to 1000°C further efficient thermal cross-linking occurred and the ceramic yields obtained are high: almost 85%. The volatiles released during the pyrolysis consist of H_2, CH_4 and a trace of NH_3. The silicon carbonitride ceramic residue, based on elemental analysis contains about 67% by weight of Si_3N_4 equivalent, 27% by weight of SiC equivalent and 5% by weight of excess carbon. This material is amorphous and crystallizes only above 1400°C. At this point, distinct β-Si_3N_4 and α-SiC phases can be observed by X-ray diffraction. Our studies of this useful system and its applications (production of ceramic fibers and coatings, use as a binder for ceramic powders and in the "up-grading" of Si-H containing polymers which by themselves are poor or only moderately good preceramic materials[15]) are continuing.

The Sodium Condensation of Methyldichlorosilane

Linear polysilylenes (or polysilanes), $[RR'Si]_n$, whose backbone is a chain of silicon atoms, have received much attention in recent years. As such[16] and as precursors to polycarbosilanes,[17] they have

attained considerable importance in the materials chemistry of silicon. Most of the polysilanes prepared to date bear two organic substituents on the silicon atoms. They generally are prepared by the action of an alkali metal on the respective diorganodichlorosilane.[16]

The action of alkali metals on methyldichlorosilane has been examined in these laboratories[18] and also by Wensley-Brown and Sinclair at 3M.[19] In this reaction, attack at the Si-Cl linkages is preferred, but reaction can also occur at the Si-H bond. To what extent such attack at Si-H occurs is very dependent on the reaction conditions used. For instance, a reaction of CH_3SiHCl_2 with an excess of sodium carried out in 7:1 (by volume) hexane/THF gives liquid products of composition (by NMR) $[(CH_3SiH)_x(CH_3Si)_y]_n$, with $x = 0.75-0.9$ and $y = 0.25-0.1$ and $n = 14-16$. Thus, between 10 and 25% of the Si-H bonds have reacted. This leads to some cross-linking since hydrogen loss generates trifunctional silicon atoms. These polysilanes are not good ceramic precursors. On pyrolysis to 1000°C the ceramic yield obtained from them ranged between 12 and 27% and the composition of the ceramic product (on the basis of elemental analysis) was 1.0 mole SiC + 0.42 g atom Si. A better product, at least in terms of ceramic yield on pyrolysis, was obtained when the sodium condensation of CH_3SiHCl_2 was carried out in THF alone. As might be expected, the extent of reaction of the Si-H bond was considerably greater and the composition of the product was, on the average, $[(CH_3SiH)_{0.4}(CH_3Si)_{0.6}]_n$. That is, 60% of the Si-H bonds had reacted. As a result, the polymeric

product was much less soluble in hydrocarbon solvents, but it was soluble in THF. The greater cross-linking also had as a useful consequence that the ceramic yield on pyrolysis to 1000°C was increased to 60%. However, the problem of the elemental composition of the ceramic residue remained, the composition being (on the basis of elemental analysis) 1.0 SiC + 0.49 Si. Such an excess of silicon (mp 1414°C) would be expected to compromise the high temperature applications of this ceramic material.

The $[(CH_3SiH)_x(CH_3Si)_y]_n$ compositions contain reactive Si-H and Si-Si functionality which should provide the basis for further chemical conversions which might serve to convert the at first sight unpromising polymers to useful preceramic materials. The hydrosilylation reaction has already been mentioned and we have used this reaction to good advantage in the present instance.[20] Reactions of $[(CH_3SiH)_x(CH_3Si)_y]_n$ (both of 7 hexane/1 THF and THF preparations) with various compounds and polymers containing two or more vinyl groups were examined. Best results were obtained with the ammonolysis product of $CH_3(CH_2=CH)SiCl_2$. In this ammonolysis reaction mostly cyclic species are formed, $[CH_3(CH_2=CH)SiNH]_n$, and in our hydrosilylation experiments we used the cyclic trimer $[CH_3(CH_2=CH)SiNH]_3$ which was separated by distillation. Although the hydrosilylation reaction can be catalyzed by free radical initiators as well as by low valent, coordinatively unsaturated transition metal species,[4] we chose to use as catalyst a member of the former class, azobisisobutyronitrile, $(CH_3)_2(CN)CN=NC(CN)(CH_3)_2$

(AIBN). The thermal decomposition of this compound is relatively rapid at 80°C and provides the initiating radicals, $(CH_3)_2(CN)C\cdot$, and molecular nitrogen. In one such experiment, a mixture of $[(CH_3SiH)_{0.91}(CH_3Si)_{0.09}]_n$ and $[CH_3(CH_2=CH)SiNH]_3$ (Si-H:Si-Vi ratio ~6) in benzene was heated briefly in the presence of a catalytic amount of AIBN. The soluble product (MW 2100) had the composition (NMR and analysis) $[(CH_3SiH)_{0.73}(CH_3Si)_{0.1}(CH_3SiCH_2CH_2Si(CH_3)(CH=CH_2)-NH)_{0.17}]$. Its pyrolysis (to 1000°C) under argon gave a black ceramic product in 77% yield. Elemental analysis of the ceramic allowed the calculation of the composition as 1.0 SiC + 0.03 Si_3N_4 + 0.04 C, which is equivalent to 1 weight % of free carbon.

The hydrosilylation reaction of $[(CH_3SiH)_{0.91}(CH_3Si)_{0.09}]_n$ with the trifunctional $[CH_3(CH_2=CH)SiNH]_3$ thus appears to have produced a network polymer. This is indicated by the good pyrolysis yield of ceramic residue. Furthermore, the chemical composition of the ceramic produced is now quite satisfactory. This improved preceramic polymer was found to be applicable to the preparation of ceramic fibers and ceramic bars and served well as a binder for β-SiC powder.

The hydrosilylation of unsaturated metal alkoxides, for instance, "$Hf(OPr^i)_2(OCH_2CH=CH_2)_2$" with $[(CH_3SiH)_{0.8}(CH_3Si)_{0.2}]_n$ using $H_2PtCl_6\cdot6H_2O$ as catalyst (SiH/SiVi molar ratio = 5) in toluene also was examined. A white, glassy solid was produced (MW ~1630) whose pyrolysis to 1000°C left a black ceramic residue in 86% yield. It would appear that these systems also may be applicable to the

protection of carbon/carbon composites toward
oxidation.

It is also possible to convert the $[(CH_3SiH)_x-(CH_3Si)_y]_n$ polymers to useful hybrid polymers[15a] by
reaction with major amounts of the $[(CH_3SiHNH)_a]_n$
species which is the product of the KH-induced
dehydrocyclopolymerization of the CH_3SiHCl_2
amomonolysis product before quenching with an
electrophile[14b] (see previous section). After a
CH_3I quench, a new polymer can be isolated which on
pyrolysis gives a ceramic yield in the 75-85% range.
Furthermore, the excess silicon which usually
results in the pyrolysis of the $[(CH_3SiH)_x(CH_3Si)_y]_n$
materials does not form if the appropriate
polysilazane/polysilane ratio is used.

The Alkynylenation of Methyldichlorsilane

We have studied the reactions of CH_3SiHCl_2 and
other dichlorosilanes with magnesium acetylide.
The latter reagent, easily prepared in THF medium by
reaction of commercial dibutylmagnesium with gaseous
acetylene, reacts readily with chlorosilanes. Its
reaction with CH_3SiHCl_2 produces the expected
$[CH_3Si(H)C\equiv C]_n$, but the molecular weight is low
(~900). Nevertheless, pyrolysis of this material
(under argon to 1000°C) results in an 82% yield of a
black ceramic residue. Its composition (by
elemental analysis) is 1.0 SiC + 0.5C, which is an
unacceptably high carbon content. Similar low
polymer products were obtained using $(CH_3)_2SiCl_2$ and
$(CH_3)(CH_2=CH)SiCl_2$ as starting materials:
$[(CH_3)_2SiC\equiv C]_n$, a poorly soluble powder, and
$[(CH_3)(CH_2=CH)SiC\equiv C]_n$, a soluble wax, MW 1100. The

latter on pyrolysis under argon to 1000°C gave 1.0 SiC + 1.0C (83% ceramic yield). However, hydrosilylation of this product with $[(CH_3SiH)_{0.4}(CH_3Si)_{0.6}]_n$ resulted in a new preceramic polymer whose pyrolysis also gave a good ceramic yield. If appropriate stoichiometry was used, the excess C and excess Si of the respective starting materials were balanced out and elemental analysis showed a nearly 1:1 Si/C ratio.

Conclusions.

Methyldichlorosine has proved to be a very useful starting material for the preparation of preceramic polymer systems. Its Si-Cl bonds provide the means for forming the initial oligomers or polymers which often in themselves are not useful in the preparation of ceramic materials. However, the reactivity of the Si-H bond then can be brought into play to convert these polymers to useful preceramic materials. Its commercial availability and relatively low cost make it a very attractive starting material for silicon-based materials.

REFERENCES

1.   (a) Rochow, E.G., "An Introduction to the
      Chemistry of the Silicones", 2nd edition,
      1951, Wiley: New York, Chapter 2.

      (b)Zuckerman, J.J. Advan. Inorg. Chem. Radio
      chem., 6 (1964) 383.

2.   Noll, W. "Chemistry and Technology of
      Silicones", Academic Press: New York, 1968,
      pp. 589-591.

3.   Fox, H.W.; Taylor, P.W.; Zisman, W.A. Ind. Eng.
      Chem. (Industr.), 39 (1947) 1401.

4.   Lukevics, E.; Belyakova, Z.V.; Pomerantseva,
      M.G., Voronkov, M.G. J. Organomet. Chem.
      Library, 5 (1977) 1.

5.   (a) Sokolov, N.N.; Andrianov, K.A.; Akomova,
      S.M., J. Gen. Chem. USSR, 26 (1956) 933.

      (b) Seyferth, D.; Prud'homme, C.; Wiseman,
      G.H., Inorg. Chem., 22 (1983) 2163.

6.   Pai, Y.-M.; Servis, K.L.; Weber, W.P.,
      Organometallics, 5 (1986) 683.

7.   Harrod, J.F.; Pelletier, E., Organometallics, 3
      (1984) 1064.

8.   Bradley, D.C.; Mehrotra, R.C.; Gaur, D.P.
      "Metal Alkoxides", Academic Press, New York,
      1978.

9.   Bates, R.B.; Kroposki, L.M.; Potter, D.E., _J._
     Org. Chem. 37 (1972) 560.

10. Brewer, S.D.; Haber, C.P., _J. Am. Chem. Soc.,_
     70 (1948) 3888.

11. Semenova, E.A.; Zhinkin, D.Ya.; Andrianov,
     K.A., _Izv. Akad. Nauk SSSR, Otd. Khim. Nauk._
     (1962) 2036.

12. Krüger, C.R.; Rochow, E.G., _J. Polym. Sci._ _Part_
     _A,_ 2 (1964) 3179.

13. Monsanto Co., Neth. Appl. 6,507,996 (23 Dec.
     1965); _Chem. Abstract.,_ 64 (1966) 19677d.

14. (a) Seyferth, D.; Wiseman, G.H., _J. Amer._
     Ceram. Soc., 67 (1984) C-132.

     (b) Seyferth, D.; Wiseman, G.H., U.S. Patent
     4,482,669 (1984).

     (c) Seyferth, D.; Wiseman, G.H., Chapter 38 in
     "Science of Ceramic Chemical Processing," L.L.
     Hench and D.R. Ulrich, editors, Wiley: New
     York, 1986.

15. (a) Seyferth, D.; Yu, Y-F., Proceedings of the
     Fourth Annual IUCCP Symposium, "Design of New
     Materials," Texas A&M University, March 25,
     1986.

     (b) Seyferth, D.; Yu, Y-F., U.S. Patent
     4,645,807 (1987).

(c) Seyferth, D.; Yu, Y-F., U.S. Patent 4,650,837 (1987).

16. West, R., J. Organomet. Chem., 300 (1986) 327.

17. Yajima, S., Am. Ceram. Soc. Bull.., 62 (1983) 893.

18. Wood, T.G., Ph.D. Dissertation, M.I.T., 1984.

19. Brown-Wensley, K.A.; Sinclair, R.A., U.S. patent 4,537,942 (1985).

20. Seyferth, D.; Yu, Y.-F., U.S. patent 4,639,501 (1987).

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ABSTRACTS DISTRIBUTION LIST, 356B

Professor T. Marks
Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Dr. Kurt Baum
Fluorochem, Inc.
630 S. Ayon Avenue
Azuza, California 91702

Dr. Ulrich W. Suter
Department of Chemical and Engineering
Massachusetts Institute of Technologies
Room E19-628
Cambridge, MA 02139-4309

Dr. William Bailey
Department of Chemistry
University of Maryland
College Park, Maryland 20742

Dr. J.C.H. Chien
Department of Polymer Science and
    Engineering
University of Massachusetts
Amherst, MA 01003

Professor G. Whitesides
Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

Dr. K. Paciorek
Ultrasystems, Inc.
P.O. Box 19605
Irvine, California 92715

Dr. Ronald Archer
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002

Professor D. Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Professor J. Moore
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. V. Percec
Department of Macromolecular
Science
Case Western Reserve University
Cleveland, Ohio 44106

Dr. Gregory Girolami
Department of Chemistry
University of Illinois
Urbana-Champagne, IL 61801

Dr. Ted Walton
Chemistry Division
Code 6120
Naval Research Lab
Washington D.C. 20375-5000

Professor Warren T. Ford
Department of Chemistry
Oklahoma State University
Stillwater, OK 74078

Professor H. K. Hall, Jr.
Department of Chemistry
The University Arizona
Tucson, Arizona 85721

Dr. Fred Wudl
Department of Chemistry
University of California
Santa Barbara, CA 93106

Professor Kris Matjaszewski
Department of Chemistry
Carnegie-Mellon University
4400 Fifth Avenue
Pittsburgh, PA 15213

Professor Richard Schrock
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

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Professor A. G. MacDiarmid
Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania 19174

Dr. Richard M. Laine
SRI International
333 Ravenswood Avenue
Menlo Park, California 94025

Dr. E. Fischer, Code 2853
Naval Ship Research and
    Development Center
Annapolis, Maryland 21402

Dr. L. Buckley
Naval Air Development Center
Code 6063
Warminster, Pennsylvania 18974

Professor H. Allcock
Department of Chemistry
Pennsylvania State University
University Park, Pennsylvania   16802

Dr. James McGrath
Department of Chemistry
Virginia Polytechnic Institute
Blacksburg, Virginia 24061

Professor R. Lenz
Department of Chemistry
University of Massachusetts
Amherst, Massachusetts 01002

Dr. Geoffrey Lindsay
Chemistry Division
Naval Weapons Center
China Lake, California 93555

Professor G. Wnek
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, NY 12181

Professor J. Salamone
Department of Chemistry
University of Lowell
Lowell, Massachusetts 01854

Professor C. Allen
Department of Chemistry
University of Vermont
Burlington, Vermont 05401

Dr. J. Griffith
Naval Research Laboratory
Chemistry Section, Code 6120
Washington, D. C. 20375-5000

Dr. Ivan Caplan
DTNSRDC
Code 0125
Annapolis, MD 21401

Professor T. Katz
Department of Chemistry
Columbia University
New York, New York 10027

Dr. R. Miller
Almaden Research Center
650 Harry Road K91B801
San Jose, CA 95120

Dr. Christopher K. Ober
Department of Materials Science
  and Engineering
Cornell University
Ithaca, New York 14853-1501

Dr. William B. Moniz
Chemistry Division
Naval Research Laboratory
Washington, D.C. 20375-5000

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