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APPLICATIONS OF METHYLDICHLOROSILANE IN THE PREPARATION 1/1
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CAMBRIDGE DEPT OF CHEMISTRY D SEYFERTH ET AL.

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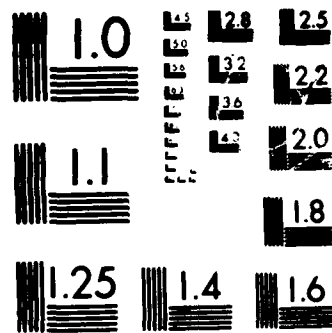
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APPLICATIONS OF METHYLDICHLOROSILANE IN THE PREPARATION OF
SILICON-CONTAINING CERAMICS

by

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APPLICATIONS OF METHYLDICHLOROSILANE
IN THE PREPARATION OF
SILICON-CONTAINING CERAMICS

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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.

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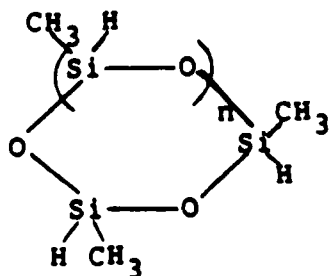


INTRODUCTION

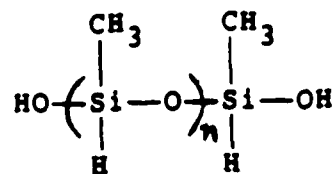
The Rochow-synthesis of methylchlorosilanes by the reaction of gaseous methyl chloride with a solid mass of silicon/copper alloy has been practised since the 1940's.¹ The major product of this reaction as practised industrially is dimethyldichlorosilane, $(\text{CH}_3)_2\text{SiCl}_2$, the workhorse of the silicones industry, but other products are formed as well, albeit in much lower yield. Among these are CH_3SiCl_3 , $(\text{CH}_3)_3\text{SiCl}$ and $\text{CH}_3\text{SiHCl}_2$. 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-CH₃ 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



1, $n = 1, 2, 3 \dots$



2, $n > 1$

For instance, hydrolysis of $\text{CH}_3\text{SiHCl}_2$ 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, 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 $\text{CH}_3\text{SiHCl}_2$ and $(\text{CH}_3)_2\text{SiCl}_2$, have found industrial application.²

The chemistry of $[\text{CH}_3\text{Si}(\text{H})\text{O}]$ -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-[CH₃Si(H)O]_n Mixtures Formed in the Hydrolysis of CH₃SiHCl₂

<u>n</u>	<u>mol %</u>	<u>n</u>	<u>mol %</u>
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

^aSome 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 $[\text{CH}_3\text{Si}(\text{H})\text{O}]_n$ cyclic oligomers have been used to introduce metal functionality. For instance, reactions of $[\text{CH}_3\text{Si}(\text{H})\text{O}]_n$ cyclics with $\text{Co}_2(\text{CO})_8$ and $[\eta\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ 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 $[\text{CH}_3\text{Si}(\text{H})\text{O}]_n$ 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 developed⁸, and we chose to approach this goal via metal alkoxide chemistry, using the reactivity of the $[\text{CH}_3\text{Si}(\text{H})\text{O}]_n$ oligomers and polymers to prepare the desired metal alkoxide-containing polymers.

Metal alkoxides containing alkenoxy groups, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{O}$, $n = 0, 1, 2 \dots$, can be prepared in

different ways. For our purposes we required two alkenoxy substituents on the metal for cross-linking hydrosilylation reactions with $[\text{CH}_3\text{Si}(\text{H})\text{O}]_n$. 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, $(\text{RO})_n\text{M}(\text{OCH}_2\text{CH}=\text{CH}_2)_{4-n}$ (when allyl alcohol was the unsaturated alcohol used), with n values of 0-4 possible, but with the average composition " $(\text{RO})_2\text{M}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$ ". An alternate designed synthesis of such a metal alkoxide uses the preformed $(\text{RO})_2\text{MCl}_2$ (a known, stable compound type) in a reaction with an unsaturated alkoxide reagent. The reaction of $(i\text{PrO})_2\text{TiCl}_2$ with two molar equivalents of $\text{CH}_2=\text{CHOLi}$ (prepared by the fragmentation reaction of tetrahydrofuran by n -butyllithium⁹) is an example of this approach. The reaction of alkoxide materials of average composition " $(i\text{PrO})_2\text{M}(\text{OCH}_2\text{CH}=\text{CH}_2)_2$ " ($\text{M} = \text{Hf}$ and Zr) with commercial $[\text{CH}_3\text{Si}(\text{H})\text{O}]_n$ PS-122 polysiloxane, using various reactant ratios and using as hydrosilylation catalyst $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, in toluene at $\sim 110^\circ\text{C}$ 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).

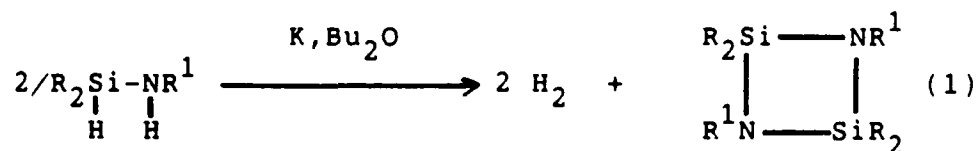
That the cross-linking involves hydrosilylation of allyloxy groups to build $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OM}(\text{OPr}^i)_2\text{OCH}_2\text{CH}_2\text{CH}_2-$ bridges between siloxane chains was demonstrated by the proton NMR spectra of the products. Since these products are initially soluble, 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 Methylchlorosilane.

The reaction of ammonia with methylchlorosilane 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 Andrianov¹¹ studied the same reaction and reported obtaining by vacuum distillation a 25% yield of $[\text{CH}_3\text{SiNH}_2]_4$ and a 10% yield of a bicyclic compound formulated as $(\text{CH}_3\text{SiNH})_3[(\text{CH}_3\text{SiH})_{1.5}\text{N}]_2$. In our hands, the ammonolysis of $\text{CH}_3\text{SiHCl}_2$ 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 $[\text{CH}_3\text{SiNH}]_n$, 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 $\text{CH}_3\text{SiHCl}_2$ ammonolysis resulted in evolution of ammonia and formation of a very viscous polysilazane oil ($\text{SiCH}_3\text{:NH:SiH} = 3:0.55:1$ vs $3:1:1$ for $[\text{CH}_3\text{SiHNNH}]_n$). Pyrolysis of this material, however, gave a ceramic yield of only 36%.

In a search for better ways of converting the $\text{CH}_3\text{SiHCl}_2$ ammonolysis product to a useful silicon carbonitride precursor, we applied the dehydrocyclocondimerization reaction which had been reported by Fink in 1965 (eq.1)¹³.



In each cyclic $[\text{CH}_3\text{SiHNNH}]_n$ 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 intramolecular 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 dehydrocyclocondimerization 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 $1000^\circ C$ 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 $1400^\circ C$. At this point, distinct $\beta-Si_3N_4$ and $\alpha-SiC$ 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 materials¹⁵) are continuing.

The Sodium Condensation of Methylchlorosilane

Linear polysilylenes (or polysilanes), $[RR'Si]_n$, whose backbone is a chain of silicon atoms, have received much attention in recent years. As such¹⁶ 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 methylchlorosilane has been examined in these laboratories¹⁸ 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 $\text{CH}_3\text{SiHCl}_2$ with an excess of sodium carried out in 7:1 (by volume) hexane/THF gives liquid products of composition (by NMR) $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$, 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 $\text{CH}_3\text{SiHCl}_2$ 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, $[(\text{CH}_3\text{SiH})_{0.4}(\text{CH}_3\text{Si})_{0.6}]_n$. 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 $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ 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 $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ (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 $\text{CH}_3(\text{CH}_2=\text{CH})\text{SiCl}_2$. In this ammonolysis reaction mostly cyclic species are formed, $[\text{CH}_3(\text{CH}_2=\text{CH})\text{SiNH}]_n$, and in our hydrosilylation experiments we used the cyclic trimer $[\text{CH}_3(\text{CH}_2=\text{CH})\text{SiNH}]_3$ 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, $(\text{CH}_3)_2(\text{CN})\text{CN}=\text{NC}(\text{CN})(\text{CH}_3)_2$

(AIBN). The thermal decomposition of this compound is relatively rapid at 80°C and provides the initiating radicals, $(\text{CH}_3)_2(\text{CN})\text{C}\cdot$, and molecular nitrogen. In one such experiment, a mixture of $[(\text{CH}_3\text{SiH})_{0.91}(\text{CH}_3\text{Si})_{0.09}]_n$ and $[\text{CH}_3(\text{CH}_2=\text{CH})\text{SiNH}]_3$ (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)

$[(\text{CH}_3\text{SiH})_{0.73}(\text{CH}_3\text{Si})_{0.1}(\text{CH}_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)(\text{CH}=\text{CH}_2)-\text{NH})_{0.17}]$. 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 $[(\text{CH}_3\text{SiH})_{0.91}(\text{CH}_3\text{Si})_{0.09}]_n$ with the trifunctional $[\text{CH}_3(\text{CH}_2=\text{CH})\text{SiNH}]_3$ 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, " $\text{Hf}(\text{OPr}^i)_2(\text{OCH}_2\text{CH}=\text{CH}_2)_2$ " with $[(\text{CH}_3\text{SiH})_{0.8}(\text{CH}_3\text{Si})_{0.2}]_n$ using $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ 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 $[(\text{CH}_3\text{SiH})_x - (\text{CH}_3\text{Si})_y]_n$ polymers to useful hybrid polymers^{15a} by reaction with major amounts of the $[(\text{CH}_3\text{SiHNNH})_a]_n$ species which is the product of the KH-induced dehydrocyclopolymerization of the $\text{CH}_3\text{SiHCl}_2$ amonomolysis 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 $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$ materials does not form if the appropriate polysilazane/polysilane ratio is used.

The Alkynylenation of Methylchlorosilane

We have studied the reactions of $\text{CH}_3\text{SiHCl}_2$ 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 $\text{CH}_3\text{SiHCl}_2$ produces the expected $[(\text{CH}_3\text{Si}(\text{H})\text{C}\equiv\text{C})_n]$, 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 $(\text{CH}_3)_2\text{SiCl}_2$ and $(\text{CH}_3)(\text{CH}_2=\text{CH})\text{SiCl}_2$ as starting materials: $[(\text{CH}_3)_2\text{SiC}\equiv\text{C}]_n$, a poorly soluble powder, and $[(\text{CH}_3)(\text{CH}_2=\text{CH})\text{SiC}\equiv\text{C}]_n$, 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 $[(\text{CH}_3\text{SiH})_{0.4}(\text{CH}_3\text{Si})_{0.6}]_n$ 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.

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