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A summary of research leading to 1) The discovery and characterization of formable polysilane high polymers, copolymers of phenylmethylsilane and dimethylsilanes units; 2) Investigations leading to the synthesis of tetramesityldisilene, the first compound containing a silicon-silicon double bond; and 3) Various advances in the chemistry of polysilanes.

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Final Technical Report

CHEMICAL REACTIONS AND PROPERTIES OF ORGANOSILICON COMPOUNDS RELATED TO NEW MATERIALS

Grant No. [illegible]-AFOSR-78-3570
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Principal Investigator and
Author of Report:

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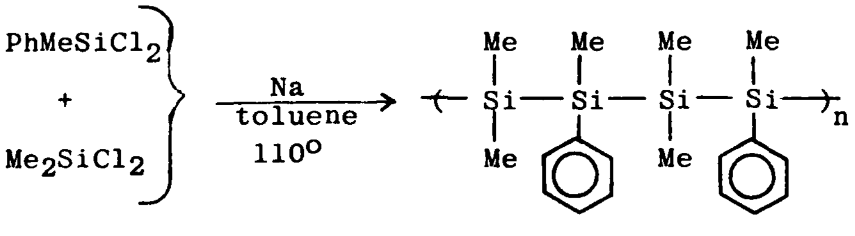
I. INTRODUCTION

Two developments in the research under this grant are particularly noteworthy. First, formable polysilane polymers such as "polysilastyrene" have been developed, which have important potential applications in ceramic technology and in the semiconductor industry. Secondly, a major scientific advance has been accomplished: The synthesis of the first compound containing a silicon-silicon double bond. These two advances are covered in parts A. and B. of the Research Progress section of this report. In Part C, the findings in our continuing research on polysilanes will be reported; this work is fundamental to that in parts A and B.

II. RESEARCH PROGRESS

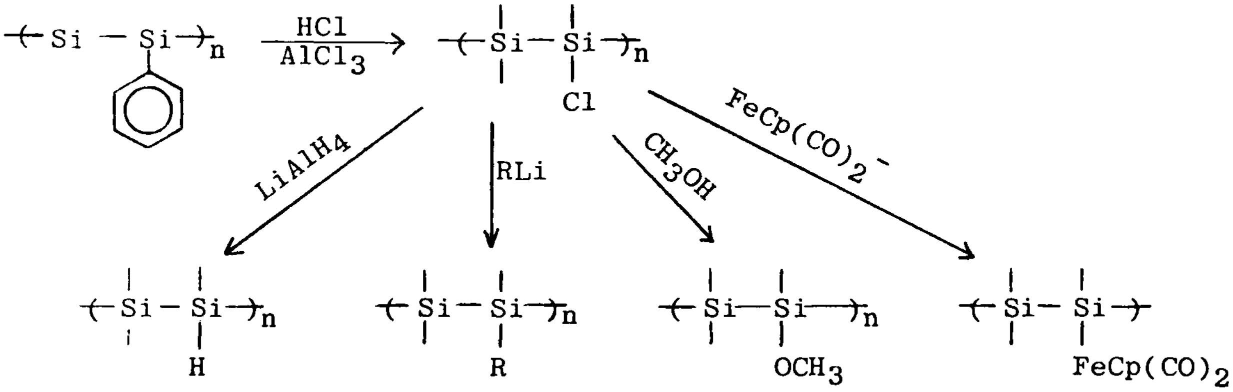
A. Polysilane High Polymers

Discovered under this grant was the silane polymer "polysilastyrene". This material is a high polymer consisting of chains of silicon atoms, with about equal numbers of dimethylsilyl and phenylmethylsilyl groups.[1] It can be made by co-condensation of two different dichlorosilanes:



Molecular weights ($\bar{M}_n$) from 8,000 to 400,000 can be achieved. Polysilastyrene is much easier to form and use than were earlier silane polymers. It is highly soluble in most organic solvents, and melts at about 200°C. Thus it can easily be cast into films, molded, and spun or drawn into fibers.

The polymeric silanes constitute an entirely new class of polymers, with possibilities for extensive structural modification. Polysilastyrene is a useful starting material because the phenyl groups can be exchanged for chlorines, which can subsequently be replaced by a variety of other nucleophilic reagents:[2]

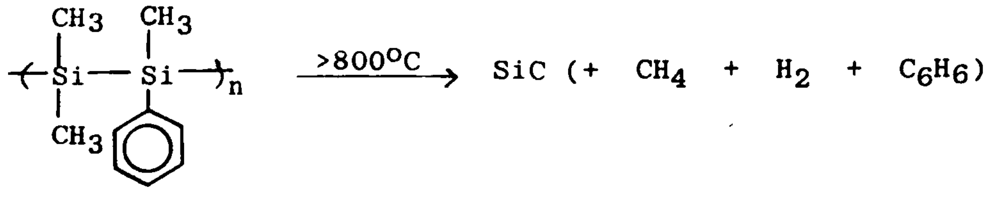


R = alkyl, aryl

An important feature of polysilastyrene is its photoreactivity. When irradiated with ultraviolet light in the presence of solvent, polysilastyrene is degraded to short fragments; but in solid form, irradiation of polysilastyrene leads to crosslinking, making the polymer more rigid and less soluble.

Two potential industrial uses for polysilastyrene are being developed. First, the material may be useful in making photo resist masks for the construction of microchips and other semiconductor devices. Here the ability to create crosslinks by irradiation is highly important. Improved photoresist technology is crucial to the development of smaller, faster microcomputers and microprocessors, which are now so important in aerospace technology.

Second, like other silane polymers polysilastyrene undergoes conversion at high temperature to silicon carbide:[3]



In this technology polysilastyrene enjoys great advantages over earlier materials, first because it can be formed by the ordinary methods of polymer technology, and secondly because it can be rigidified by photocrosslinking. Crosslinked fibers of polysilastyrene, mounted vertically at the bottom and fired to form silicon carbide, maintained their original shape throughout heating to 1000°C. Silicon carbide fibers are important as reinforcing materials for high-strength metals used in airframe construction, and silicon carbide is one of the materials which is under consideration for construction of advanced, high temperature power plants, for instance turbine engines. Polysilastyrene can also be converted to bulk silicon carbide for turbine blades, etc., or to silicon carbide high-temperature resistant coatings for metals or ceramics.

B. Silylenes and Disilenes: the Si=Si Double Bond

The most striking scientific discovery under this grant was undoubtedly the synthesis of a stable compound containing a double bond between two silicon atoms (a disilene).[4] This finding arose from research on silylenes, divalent organosilicon species.

We have found that ultraviolet photolysis of various polysilane precursors in rigid matrices (argon, at 8°K, or hydrocarbons, at 77°K) leads to silylenes, which are stable as long as they are confined in the matrix.[4,5] Some examples, with their colors, are shown below:

$(Me_2Si)_6 \xrightarrow{h\nu} (Me_2Si)_5 + Me_2Si:$ (yellow)

$(Et_2Si)_5 \xrightarrow{h\nu} (Et_2Si)_4 + Et_2Si:$ (yellow)

$Me_3Si\text{-}SiMePh\text{-}SiMe_3 \xrightarrow{h\nu} (Me_3Si)_2 + PhMeSi:$ (red)

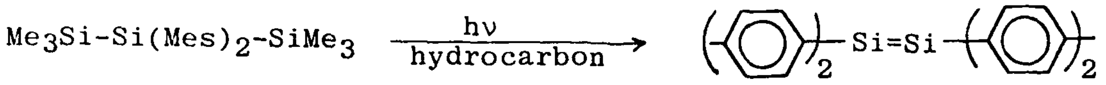
$Me_3Si\text{-}SiPh_2\text{-}SiMe_3 \xrightarrow{h\nu} (Me_3Si)_2 + Ph_2Si:$ (red)

$(\underline{t}BuMeSi)_4O \xrightarrow{h\nu} (\underline{t}BuMeSi)_3O + \underline{t}BuMeSi:$ (yellow)

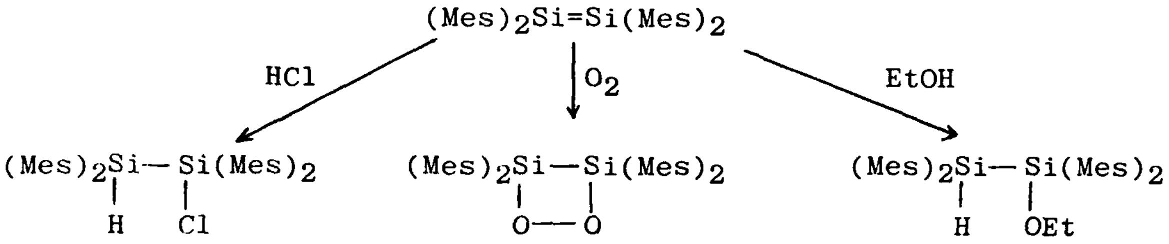
$Me_3Si\text{-}Si(Mes)_2\text{-}SiMe_3 \xrightarrow{h\nu} (Me_3Si)_2 + Mes_2Si:$ (blue)

(Mes = mesityl, 2,4,6-trimethylphenyl)

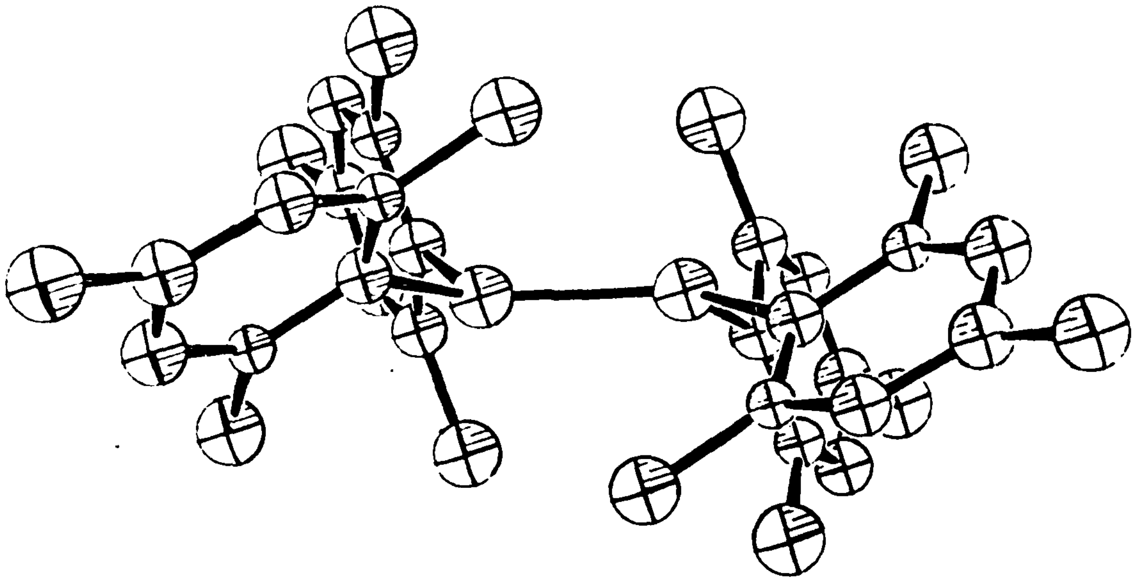
When the matrices are warmed to the softening point, the silylenes disappear and yellow intermediates formed, which we believe to be disilenes, $R_2Si=SiR_2$. Complete melting of the matrices leads in most cases to the formation of a colorless polysilane polymer. Dimesitylsilylene behaves abnormally, however. When the matrix containing it is melted, the silylene dimerizes cleanly to the disilene, which remains stable up to room temperature. Tetramesityldisilene can be generated more simply by photolyzing the trisilane precursor in solution, either at room temperature or below:



The disilene is a yellow solid, which is strongly thermochromic; it turns orange when heated and melts reversibly to a red liquid at 178°C. It undergoes addition reactions, some of which are similar to those of carbon-carbon doubly-bonded compounds (alkenes) and some of which are unique:



X-ray crystal structure investigation shows that the silicon atoms are slightly pyramidalized, and that the bond length is 2.17Å, *significantly* shorter than the 2.34Å length for Si-Si single bonds.[6] An ORTEP diagram of the molecules from the x-ray crystallographic study is shown below.



The properties of tetramesityldisilene are under continuing study, and experiments to synthesize other disilenes are under way. The discovery of this first disilene seems likely to lead to an important new field of multiply-bonded silicon chemistry.

Work in this area was done in collaboration with Prof. Josef Michl of the University of Utah.

C. Synthesis and Electronic Properties of Polysilanes

Our exploration of the chemistry of polysilanes and their electronic behavior, begun more than ten years ago, has continued under this grant. These molecules show evidence for electron mobility of the σ-electrons in the silicon-silicon bonds.

Nearly all of modern electronics is based on the mobility of electrons in elemental silicon, which is fabricated into transistors, microchips, etc. The polysilanes are important because they provide molecular analogs for elemental silicon. In the cyclic polysilanes, electron mobility may be studied by spectroscopic techniques which cannot be applied to the much more complex system present in solid silicon.

Several noteworthy advances have been made in the study of polysilanes under this grant:

1. The equilibration of the cyclosilanes $(Me_2Si)_5$, $(Me_2Si)_6$ and $(Me_2Si)_7$ was studied using potassium metal as the equilibrating catalyst.[7] The six-membered ring is the most stable in this series but the preference for the six-membered ring is much less than in the cycloalkane series.

2. By condensing dimethyldichlorosilane with sodium-potassium alloy under nonequilibrating conditions, we found that the entire sequence of permethylcyclosilanes, $(Me_2Si)_5$ through $(Me_2Si)_{35}$ is formed.[8,9] These compounds with ring sizes from $(Me_2Si)_5$ up to $(Me_2Si)_{19}$ have been separated and investigated spectroscopically.

3. Radical-cations have been observed from cyclosilanes, when oxidized by aluminum chloride in dichloromethane:[10]

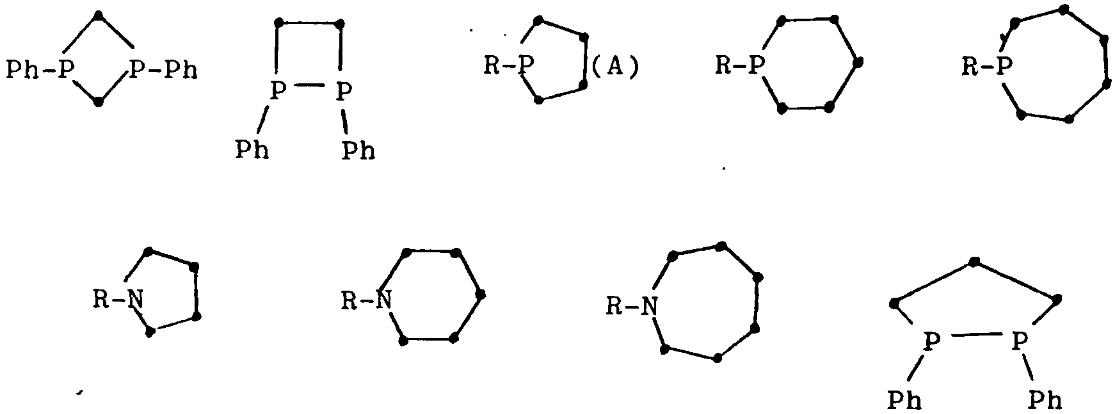
$$(Me_2Si)_6 \xrightarrow[CH_2Cl_2]{AlCl_3} (Me_2Si)_6^{+\cdot}$$

Study of the resulting cation-radicals by electron spin resonance spectroscopy indicated that the unpaired electron, and the positive charge, corresponding to a "hole" in solid-state technology, is delocalized over the entire polysilane ring.

4. The diethylcyclosilanes $(Et_2Si)_n$ where n = 4 to 9 have been synthesized and characterized.[11]

5. The solid-state phase transitions and especially the remarkable plastic crystalline behavior of $(Me_2Si)_5$ and $(Me_2Si)_6$ have been investigated.[12,13]

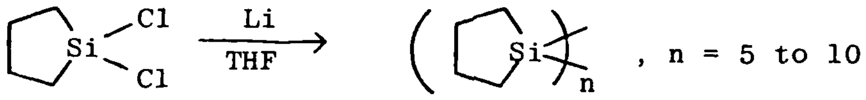
6. Phosphorus and nitrogen-containing cyclosilanes were synthesized;[14,15] examples are shown here with the dots representing silicon atoms bearing two methyl groups:



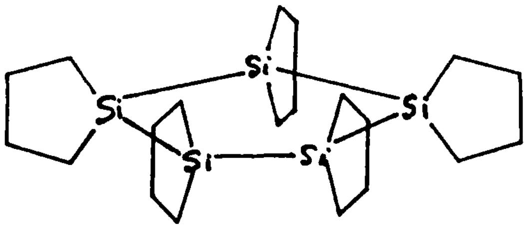
(R = Methyl or phenyl)

In these compounds, the nitrogen atoms appear to serve as "insulators" interrupting electron delocalization around the ring. The phosphorus atom, at least in compound (A), appears to participate in conjugation and electron delocalization.

7. Most recently, a series of organosilicon rotanes have been synthesized, starting from cyclo(tetramethylene)dichlorosilane:[16]



These molecules are "rings of rings", with unique polyspiro structures. A structural drawing of a typical organosilicon rotane is shown below:



8. Electron spin resonance spectroscopy has been employed to study electron delocalization in arylcyclopentasilanes and in perethylcyclopolysilanes.[17,18]

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14. Synthesis and Spectral Properties of Group V Heteroatom-permethylcyclopolysilanes, $MeN(SiMe_2)_n$ and $MeP(SiMe_2)_n$, T. H. Newman, R. West and R. T. Oakley, J. Organometal. Chem., 197, 159 (1980).

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III. ACTIVITIES OF PRINCIPAL INVESTIGATOR

During the period from 1979 to 1982, Professor West presented about 75 invited lectures in the U. S. and abroad, mostly on work done under this grant. He served as Lady Davis Visiting Professor at Hebrew University, Jerusalem, Israel during 1979, and as Visiting Professor at the University of Utah in 1981. In 1980 he participated in the China-Japan-U.S. Symposium on Organometallic Chemistry, the first International meeting in chemistry ever held in the People's Republic of China. In 1981 he was a plenary lecturer at the International Symposium on Inorganic Ring Systems in Austria and at the International Symposium on Novel Aromatic Compounds in Jerusalem.

Dr. West's continuing responsibilities include serving as Coeditor for "Advances in Organometallic Chemistry", now in its 20th volume, and for the monograph series on organometallic chemistry. He also serves on the Advisory Committee for International Symposia on Organosilicon Chemistry and Inorganic Ring Systems.

He is also active in environmental affairs, as adviser to the Wisconsin Legislature on environmental legislation and as a member of the National Board and Executive Committee of Zero Population Growth, Inc.

IV. PERSONNEL

The summary of persons supported under this grant can be found on the following page.

Summary of Persons Supported Under This Grant

Graduate Students	Degree Granted	Present Location
David Stanislawski	Ph.D.	University of Dayton
A. C. Buchanan III	Ph.D.	Oak Ridge National Labs
Lawrence Brough	Ph.D.	Iowa State University
Timothy Drahnak	Ph.D.	3M Corp. Research Labs
Thomas Newman	Ph.D.	University of Texas-Austin
Lawrence D. David	Ph.D.	Celanese Research Labs
Bradley Helmer	Ph.D.	University of Wisconsin
Corey Carlson	-	University of Wisconsin
Cynthia Wadsworth	-	University of Wisconsin
Mark Fink	-	University of Wisconsin
Mike Michalczyk	-	University of Wisconsin
Fathieh Shafiee	-	University of Wisconsin
Dennis Bean	-	University of Wisconsin
Douglas DeYoung	-	University of Wisconsin
Jonathan Rich	-	University of Wisconsin
Postdoctoral Associate		
Koichi Matsumura		Takeda Chem. Industries, Ltd. Osaka, Japan

V. CUMULATIVE LIST OF PUBLICATIONS UNDER THIS GRANT

1. Medium-Ring Cyclosilanes from the Reaction of Dimethyldichlorosilane with Lithium, K. Matsumura, L. F. Brough and R. West, J.C.S. Chem. Commun., 1092 (1978).

2. Pulsed ^{1}H NMR Studies of Molecular Motion and Plastic Crystallinity in Dodecamethylcyclohexasilane, D. W. Larsen, B. A. Soltz, F. E. Stary and R. West, J.C.S. Chem. Commun., 1093 (1978).

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