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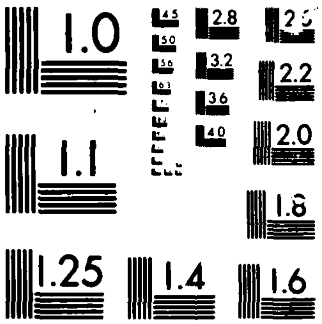

M'CROCOP' CHART

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FINAL SCIENTIFIC REPORT

Grant No. AF-AFOSR-83-0003

"Organosilicon Compounds and Organosilicon Polymer Intermediates"

Principal Investigator: Professor Dietmar Seyferth

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

December 9, 1985

A. Period Covered and Personnel

1. Period Covered

1 October 1982 - 30 June 1985

2. Personnel

(Personnel are listed whose salaries and/or research costs were covered totally or in part by this Grant.)

a. Senior Investigator:

Professor Dietmar Seyferth

b. Postdoctoral Investigators:

W.-L. Wang (Chenguang Chemical Industry Res. Inst., P.R.C.)
Y.-F. Yu (Ohio State Univ.)
T.S. Targos (Pennsylvania State Univ.)

c. Predoctoral Investigators

(Those whose name is followed by (Ph.D.) obtained their Ph.D. during the grant period.)

R.M. Weinstein (Ph.D.)
T.G. Wood (Ph.D.)
R.C. Hui

B. Research Accomplishments

1. Organosilicon Preceramic Polymers

a. Polysilanes Derived From Methyldichlorosilane

The sodium condensation of CH_3SiHCl_2 yields relatively low molecular materials of type $[(CH_3SiH)_x(CH_3Si)_y]_n$ in which the (CH_3Si) units represent silicon atoms whose H substituents have reacted with Na (in addition to the Cl substituents). (Hence these Si atoms are cross-linking sites). Use of hexane/THF as solvent gives a liquid product ($x \sim 0.8$; $y \sim 0.2$), while use of THF as solvent gives a solid ($x \sim 0.4$; $y \sim 0.6$). Neither are good SiC precursors. The former gives a

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low (∿20%) ceramic yield on pyrolysis. The ceramic products from both contain substantial amounts of free silicon in addition to SiC. Some attempts were made to crosslink the liquid product (photolysis; chlorination of SiH bonds followed by reaction with ammonia), but these were not successful.

b. Base-Catalyzed Reorganization of Liquid $[(CH_3SiH)_x(CH_3Si)_y]_n$

In a continuation of this work, it was found that a catalytic quantity of CH_3Li (and, later, other RLi) caused a bond reorganization of still unknown type, giving a solid product whose pyrolysis gave a ceramic yield of over 60%. It was discovered that similar "upgrading" could be achieved with catalytic amounts of lithium amides, R_2NLi, and even more effectively, with silylamides. This essentially solved the ceramic yield problem, but not the elemental composition problem.

c. Hybrid Polymers Based on $[(CH_3SiH)_x(CH_3Si)_y]_n$ and $[PhSiH]_n$

Since silylamides were effective in the conversion of $[(CH_3SiH)_x(CH_3Si)_y]_n$ to useful preceramic polymers, we carried out similar reactions with <u>polymeric</u> silylamides of the type $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]_m$ which we had developed earlier. In terms of silylamide functions, a catalytic quantity was used, but on a weight basis, comparable weights of the polysilane and polymeric silylamide were used. This "hybrid polymer approach" solved not only the ceramic yield problem, but also the elemental composition problem: the polysilane pyrolysis gives free Si in addition to SiC; the polysilazane pyrolysis gives free C in addition to SiC and Si_3N_4, so the Si and C can be balanced by reaction stoichiometry.

This approach was applied to another polysilane, $[PhSiH]_n$, obtained by Cp_2TiMe_2-catalyzed decomposition of Ph_2SiH_2 (method of Harrod et al).

d. "Up-grading" the Yajima Polycarbosilane

The Yajima polycarbosilane, which is the basis of the commercial SiC ceramic fibers, gives ceramic yields of ∿55-60% on pyrolysis of the uncured polymer. Since the main repeat unit of this polymer is $[CH_3Si(H)CH_2]$, the "hybrid polymer" approach is applicable. Reaction of the Yajima polycarbosilane with the polymeric silylamides, $[(CH_3SiHNH)_a(CH_3SiN)_b\text{-}CH_3SiHNK)_c]_m$, gives, after quenching with a reactive electrophile, new polymers which give much higher ceramic yields (75-85%) on pyrolysis.

e. Another Method of "Upgrading" Polysilanes

The polysilanes which we had studied as described above all contain Si-H bonds which should, under the appropriate conditions, add to C=C bonds. This basic reaction was used as a crosslinking process in AIBN-catalyzed reactions of $[(CH_3SiH)_x(CH_3\text{-}Si)_y]_n$, of $[PhSiH]_n$ (and also of the Yajima polycarbosilane) with various poly(vinyl) compounds. Of the latter, the cyclosilazane $[(CH_2{=}CH)CH_3SiNH]_3$ proved to be particularly effective in giving new polymers whose pyrolysis gave very markedly enhanced ceramic yields.

2. Highly-reactive Elemental Silicon

In our previous AFOSR Grant (AFOSR-79-0007) we had initiated research on "highly reactive silicon" as prepared from $CaSi_2$ by "reacting away" the calcium. This work turned out to be totally unproductive, the main reason, in our estimation, being that the commercial "$CaSi_2$" is grossly impure. In various private communications I have since heard that much of the published work on this subject is essentially unreproducible.

C. Publication List

1. Cyclic Polysiloxanes from the Hydrolysis of Dichlorosilane.
   Inorg. Chem., 22, 2163 (1983)
   D. Seyferth, C. Prud'homme and G.H. Wiseman
2. 1,1,12,12-Tetra-n-butyl[1.1]stannaferrocenophane: Preparation and Crystal and Molecular Structure.
   Inorg. Chim. Acta, 75, 139 (1983). A. Clearfield, C.J. Simmons, H.P. Withers, Jr. and D. Seyferth
3. Hexamethylsilirane. IV. Nucleophilic Ring Opening by Alkyllithium Reagents.
   J. Organometal. Chem., 264, 149 (1984).
   D. Seyferth, G.H. Wiseman, D.C. Annarelli and M.L. Shannon

4. Hexamethylsilirane. 5. Conversion to Five-Membered Ring Silicon Compounds by "Two-Atom" Insertion Reactions of Aryl Olefins, 1,3-Dienes and Conjugated Acetylenes.
   Organometallics, 3, 574 (1984).
   D. Seyferth, D.P. Duncan, M.L. Shannon and E.W. Goldman

5. Hexamethylsilirane. 6. Conversion to 1-Oxa-2-silacyclopentanes by "Two-Atom" Insertion Reactions of Aldehydes and Ketones.
   Organometallics, 3, 579 (1984).
   D. Seyferth, D.P. Duncan and M.L. Shannon

6. The Chemistry of Octamethyl-1,2-disilacyclobutane. Some Si-Si Cleavage and Insertion Reactions.
   J. Organometal. Chem., 271, 337 (1984).
   D. Seyferth, E.W. Goldman and J. Escudie

7. Direct Nucleophilic Acylation with Acyllithium Reagents: Acyl Anion Synthons Unmasked.
   Israel J. Chem., 24, 167 (1984).
   D. Seyferth, R.M. Weinstein, W.-L. Wang, R.C. Hui and C.M. Archer

8. Silacyclopropenes. I. Synthesis and Properties of Some Silacyclopropenes.
   J. Organometal. Chem., 272, 123 (1984).
   D. Seyferth, D.C. Annarelli and S.C. Vick

9. Silacyclopropenes. 2. "Two-Atom" Insertion Reactions of

1,1-Dimethyl-2,3-bis(trimethylsilyl)silirene.
Organometallics 3 (1984) 1897.
D. Seyferth, S.C. Vick and M.L. Shannon

10. 1,1,1,5,5,5-Hexamethyltrisiloxane: Preparation and Some Reactions.
J. Organometal. Chem., 277, 203 (1984)
D. Seyferth, C.C. Prud'homme and W.-L. Wang

11. Linear Polysiloxanes from Dichlorosilane.
Inorg. Chem., 23 (1984) 4412.
D. Seyferth and C.C. Prud'homme

12. Silacyclopropenes. 3. Palladium-Catalyzed Insertion Reactions.
Organometallics, 4 (1985) 57.
D. Seyferth, Mark L. Shannon, S.C. Vick and T.F.O. Lim

D. Patents

Three applications for patents have been submitted to the U.S. Patent Office on the work described in Sections B.1.b, B.1.c. and B.1.d. Another is being evaluated by the M.I.T. Patent Office.

E. *Lectures Presented on AFOSR Research During the Grant Period.*

Union Carbide Corp., Tarrytown, N.Y.
Wayne State University
University of Virginia
Corning Glass Works
CRD, du Pont
University of Montpellier
University of Toulouse
University of Bordeaux
University of Poitiers
St. Fons Laboratories, Rhône-Poulenc Co.
Princeton University
Rensselaer Polytechnic Institute
Technical University Munich
University of Dortmund
Max-Planck-Institut für Kohlenforschung, Mülheim
BASF, Ludwigshafen
Technische Hochschule, Darmstadt
University of Karlsruhe
University of Kaiserslautern
University of Frankfurt
University of Marburg
University of Oldenburg
Vrije Universiteit Amsterdam
University of Erlangen

University of Colorado, Denver
Rutgers University, Newark
University of Minnesota
University of North Carolina, Greensboro
Ciba-Geigy, Ardsley, N.Y.
Int. Conf. on Ultrastructure in Organic and Inorganic Polymers, Univ. of Mass., Amherst
University of Oklahoma
Drew University
Basic Sciences Div., Am. Ceramic Society, Baltimore
Dow Chemical Co., Wayland, Mass.

F. Special Recognition of (in part) AFOSR-Sponsored Research

a) Alexander von Humboldt Prize, 1984

b) R.N. Keller Memorial Lecturer, Univ. of Colorado, Boulder

c) H. Martin Friedman Lecturer, Rutgers University

d) J. Clarence Karcher Lecturer, Univ. of Oklahoma

e) Research Scholar Lecturer, Drew University

COMPLETED PROJECT SUMMARY

1. TITLE: Organosilicon Compounds and Organosilicon Polymer Intermediates

2. PRINCIPAL INVESTIGATOR: Prof. Dietmar Seyferth
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Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

3. INCLUSIVE DATES: 1 October 1982 - 30 June 1985

4. Grant No.: AF-AFOSR-83-0003

5. COST AND FY SOURCE:

6. SENIOR RESEARCH PERSONNEL: W.-L. Wang
Y.-F. Yu
T.S. Targos

7. JUNIOR RESEARCH PERSONNEL: R.M. Weinstein (Ph.D.)
T.G. Wood (Ph.D.)
R.C. Hui

8. PUBLICATIONS:

"Cyclic Polysiloxanes from the Hydrolysis of Dichlorosilane", D. Seyferth, C. Prud'homme and G.H. Wiseman, Inorg. Chem., 22, 2163 (1983).

"1,1,12,12-Tetra-n-butyl[1.1]stannaferrocenophane: Preparation and Crystal and Molecular Structure", A. Clearfield, C.J. Simmons, H.P. Withers, Jr. and D. Seyferth, Inorg. Chim. Acta, 75, 139 (1983).

"Hexamethylsilirane. IV. Nucleophilic Ring Opening by Alkyllithium Reagents", D. Seyferth, G.H. Wiseman, D.C. Annarelli and M.L. Shannon, J. Organometal. Chem., 264, 149 (1984).

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"Silacyclopropenes. I. Synthesis and Properties of Some Silacyclopropenes", D. Seyferth, D.C. Annarelli and S.C. Vick, J. Organometal. Chem., 272, 123 (1984).

"Silacyclopropenes. 2. "Two-Atom" Insertion Reactions of 1,1-Dimethyl-2,3-bis(trimethylsilyl)silirene", D. Seyferth, S.C. Vick and M.L. Shannon, Organometallics 3 (1984) 1897.

"1,1,1,5,5,5-Hexamethyltrisiloxane: Preparation and Some Reactions", D. Seyferth, C.C. Prud'homme and W.-L. Wang, J. Organometal. Chem., 277, 203 (1984).

"Linear Polysiloxanes from Dichlorosilane", D. Seyferth and C.C. Prud'homme, Inorg. Chem., 23 (1984) 4412.

"Silacyclopropenes. 3. Palladium-Catalyzed Insertion Reactions", D. Seyferth, Mark L. Shannon, S.C. Vick and T.F.O. Lim, Organometallics 4 (1985) 57.

9. ABSTRACT AND OBJECTIVES AND ACCOMPLISHMENTS

a. The sodium condensation of CH_3SiHCl_2 has been studied. It gives products of type $[(CH_3SiH)_x(CH_3Si)_y]_n$ which are not useful precursors for Si-C.

b. Base-catalyzed reorganization of the polysilanes in (a) gives new materials whose pyrolysis gives markedly higher ceramic yields.

c. Useful preceramic hybrid polymers are obtained by the reaction of the polysilanes in (a) with a poly(silylamide) of type $[(CH_3SiHNH)_a(CH_3SiN)_b(CH_3SiHNK)_c]_m$

d. This "hybrid polymer approach" also is useful in upgrading the Yajima polycarbosilane.

e. The polysilanes of (a) also may be converted to useful preceramic materials by reaction with poly(vinyl) compounds, notably cyclo-$[(CH_2{=}CH)CH_3SiNH]_3$.

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