

The Second International Topical Workshop

AD-A257 939



# *Advances in Silicon-Based Polymer Science*

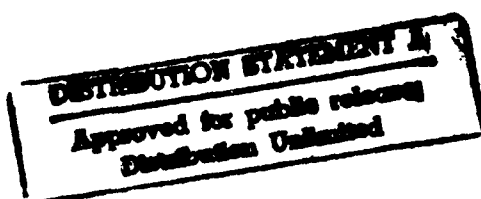
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*Makaha, Oahu, Hawaii  
December 16-20, 1990*

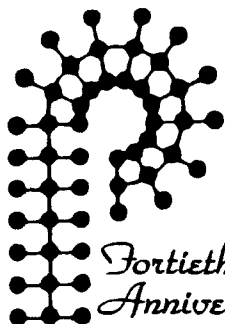


Sponsored by the Division of Polymer Chemistry  
American Chemical Society



Organizer:  
Dr. John M. Zeigler  
SiLCHEMY, Inc.  
2208 Lester Dr., NE  
Albuquerque, NM 87112-2640

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AMERICAN CHEMICAL SOCIETY



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*dist.*

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Please find enclosed a final report of the Second International Topical Workshop on Advances in Silicon-based Polymer Science that was held in Makaha, Oahu, Hawaii from December 16-20, 1990. The attached fulfills the reporting requirements of ONR Grant No. N00014-91-J-1571. Also included is a copy of the Silicon Notebook. Thank you for your support.

**TREASURER**

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March 22, 1991

ORGANIZER'S FINAL REPORT

The Second International Topical Workshop

ADVANCES IN SILICON-BASED POLYMER SCIENCE

Makaha, Oahu, Hawaii, December 16-20, 1990

Organizer:

Dr. John M. Zeigler  
Silchemy, Inc.  
2208 Lester Drive, NE  
Albuquerque, NM 87112

**Workshop Description:** The Workshop drew together current research in the areas of synthesis, properties, theory, chemistry, and applications of polymers with silicon-oxygen backbones (linear and ladder polysiloxanes, sol-gel type 3-D network structures), silicon-silicon backbones (polysilanes and related systems), preceramic polymers (polycarbosilanes, polysilazanes), and polymers with other types of silicon functionality in which the silicon plays a central role in determining the properties. The four day oral program had plenary sessions mainly in the mornings and evenings, with afternoons left open to allow ample time for informal discussions and in-depth viewing of posters.

**Program:** A total of 33 papers were presented in the oral sessions. In addition, 29 posters were also shown at the Workshop. Plenary critical overviews of emerging areas of silicon-based polymer science by world recognized experts, as well as shorter presentations on recent research results, made up the oral program.

The Workshop placed greater emphasis on current research than the 1987 Workshop; the critical overview talks made up only about 25% of the oral program and dealt with areas which have developed since 1987 or those in which progress has been particularly rapid. As in 1987, the program included speakers representing laboratories worldwide, making this Workshop truly international in scope and participation.

**Site:** The Sheraton Makaha Resort and Country Club at Waianae, Oahu, Hawaii again provided accommodations and served as the site of the Workshop. We found that the relative seclusion of this property was particularly valuable in establishing the close interaction among participants which is one of the major aims of this Workshop.

**Paper Publication:** Publication of papers from the Workshop is being done in a special issue of the Journal of Inorganic and Organometallic Polymers, to appear in the third or fourth quarter of this year.

**Funding:** Of the eighty participants at the Workshop, thirty-four authors were supported by fee waivers and/or travel assistance. Among the recipients of aid were 10 graduate students or post-doctorals. This aid was awarded on a competitive basis and at about half the level of established scientists in order to induce professors to make a commitment to the student as well. These expenses were paid from \$26,820 of gifts made or committed to the meeting by several organizations in the U.S., Japan, and Europe.

**Overall analysis:** Although there have been a number of recent competing meetings covering parts of the areas addressed by this Workshop, participants seemed very pleased with their attendance at the Workshop. Many specifically pointed out its unique "all-encompassing" approach to silicon polymer science as a strong point of the Workshop and the need for more meetings of this sort. For various reasons attendance was much lower than anticipated and the Polymer Division lost money on the project. However, the need for this type of Workshop remains real and its impact on the field highly significant.

Submitted by John M. Zeigler, Organizer

Edited by William H. Daly, Treasurer and Principal Investigator

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The Second International Topical Workshop

ADVANCES IN SILICON-BASED POLYMER SCIENCE

POCKET PROGRAM

SUNDAY DECEMBER 16, 1990 - ARRIVAL

12:00-20:00 Registration - Makaha Terrace

12:00 Welcome Gathering - Makaha Terrace

ORAL PROGRAM

Makaha Terrace

MONDAY DECEMBER 17, 1990 - FROM 1-D TO 3-D SILOXANES

12:00 Welcome and Announcements, J. ZEIGLER, Silchemy, Inc.

Session 1: Chairman - James E. McGrath

12:00 OS1-1 Kinetics of Ring-Opening Siloxane Polymerization, JULIAN CHOJNOWSKI, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences

12:00 OS1-2 Ring Opening Anionic Polymerization Kinetics of PDMS, RICARDO VERA, Jose Nunes, Filiberto Rivera, Universidad Nacional Autonoma de Mexico

12:30 Break/poster session 1

12:00 OS1-3 Synthesis and Properties of Liquid Crystalline Polysiloxanes, SYLVIE BOILEAU and D. Teyssie, College de France

12:00 OS1-4 Alkyl Substituted Siloxanes: Structure-Performance Relationships As Applied to Personal Care, E. B. Orler, H. A. A. Rasoul, E. T. LANCE-GOMEZ, Johnson Wax

12:30 Lunch

MONDAY P.M. - FROM 1-D TO 3-D SILOXANES

Session 2: Chairman - Geoffrey Swincer

12:00 OS2-1 Siloxane Containing High Performance Segmented Copolymer Systems, JAMES E. MCGRATH, Virginia Polytechnic Institute and State University

12:30 OS2-2 The Influence of Composition and Molecular Architecture on the Properties of Diphenylsiloxane Copolymers, DALE J. MEIER, Michigan Molecular Institute

12:00 OS2-3 Silicone Release Coatings: Network Structures and Properties, J. D. DeSorcie, J. STEIN, General Electric Company

12:00 Luau

TUESDAY A.M. DECEMBER 18, 1990 - FROM 1-D TO 3-D SILOXANES

Session 3: Chairman - Dietmar Seyferth

12:30 OS3-1 Some Novel Polysiloxane Elastomers and Inorganic-Organic Composites, J. E. MARK, University of Cincinnati

12:30 OS3-2 Recent Advances in the Rheo-optical Characterization of Si-containing Networks, VASILIOS GALIATSATOS, University of Akron

12:00 OS3-3 Microstructural Evolution of a Silicon Oxide Phase in a Perfluorosulfonic Acid Ionomer Via an In Situ Sol-Gel Reaction, KENNETH A. MAURITZ, I. D. Stefanithis, University of Southern Mississippi

12:30 Break/poster session 2

12:00 OS3-4 Sol-Gel Polymerization of the  $[Si_8O_{12}(OCH_3)_8]$  Cube, P. C. Cagle, W. G. KLEMPERER, C. A. Simmons, University of Illinois

11:30 OS3-5 Sheet and Tube Alkoxysiloxanes of Potential Use in Sol-Gel Ceramics, Bruce A. Harrington, Jesse Hefter, MALCOLM E. KENNEY, Case Western Reserve University

12:00 Lunch

TUESDAY P.M. - POLYSILANES AND RELATED POLYMERS

Session 4: Chairman - Thomas J. Barton

19:30 OS4-1 Synthesis and Degradation of Polysilylenes, KRZYSZTOF MATYJASZEWSKI, Carnegie Mellon University

20:30 OS4-2 Anionic Polymerization of the Masked Disilenes to High Molecular Weight Polysilylenes. Mechanism, Scope and Applications, HIDEKI SAKURAI, Tohoku University

21:00 OS4-3 Disilylene-ethynylene and Polysilylene-ethylene Alternating Copolymers, ROBERT WEST, Shuji Hayase, Takahisa Iwahara, University of Wisconsin

21:30 OS4-4 Theoretical Studies of the Energetics and Dynamics of Polysilane Model Compounds, WILLIAM WELSH, P. S. Ritter, S. Tersigni, W. Lin, University of Missouri-St. Louis

WEDNESDAY A.M. DECEMBER 19, 1990  
POLYSILANES AND RELATED POLYMERS

Session 5: Chairman - William Weber

8:30 OS5-1 Optical Properties and Ultrafast Dynamics of Excitations in Polysilanes, J. R. G. THORNE, J. M. Zeigler, R. M. Hochstrasser, University of Pennsylvania

9:00 OS5-2 Excited States of Polysilanes: High Resolution Low Temperature Spectroscopy and Molecular Modeling, A. TILGNER, H. Peter Trommsdorff, Universite Joseph Fourier Grenoble I

9:30 OS5-3 The Photochemistry of Substituted Silane High Polymers, R. D. MILLER, G. M. Wallraff, M. Baier, N. Clecak, IBM Almaden Research Center and J. Michl, T. Karatsu, Y.-P. Sun, University of Texas at Austin

10:00 OS5-4 Comparison of Radical Anions and Cations of Polygermane and Polysilanes, SEIICHI TAGAWA, University of Tokyo and Hiroshi Ban, Nippon Telegraph and Telephone

10:30 Break/poster session 3

11:00 OS5-5 Study of Third Order Optical Nonlinearities of Polysilanes by Self-focusing, D.V.G.L.N. RAO, University of Massachusetts

11:30 OS5-6 Electronic Structures of  $\sigma$ -Conjugated Polymers, NOBUO MATSUMOTO, Nippon Telegraph & Telephone Company

12:00 OS5-7 Time Resolved Studies of Electronic Transport in Si and Ge Polymer Dielectrics, M. ABKOWITZ, M. Stolka, Xerox Corporation

12:30 OS5-8 Transition Metal Oligosilane and Polysilane Activation, KEITH H. PANNELL, S. Vincenti, and Toshiaki Kobayashi, University of Texas at El Paso

13:00 Lunch

19:00 Workshop Banquet

THURSDAY A.M. DECEMBER 20, 1990  
SILANE NETWORK AND PRECERAMIC POLYMERS

Session 6: Chairman - Walter Klemperer

8:30 OS6-1 Silicon Network Polymers: Properties and Applications, PATRICIA BIANCONI, David A. Smith, Corie A. Freed, Michael S. Knapp, Pennsylvania State University and Rod R. Kunz, Mark W. Horn, Lincoln Laboratory

9:30 OS6-2 Preceramic Organosilicon Polymer/Metal Powder Composites: Their Pyrolytic Conversion to Ceramics, DIETMAR SEYFERTH, Nathan Bryson, Massachusetts Institute of Technology

1:00 OS6-3 *Thermal Sensitivity of Hydropolysilanes*, T. M. Hsu and S. P. SAWAN, University of Lowell

1:30 Break

1:00 OS6-4 *Ionic Ring-Opening Polymerization of Cyclosilazanes*, E. Duguet, M. Schappacher, A. SOUM, Universite de Bordeaux I

1:30 OS6-5 *Structure and Properties of Ceramic Fibers Prepared From Organosilicon Polymers*, JOHN LIPOWITZ, Dow Corning Corporation

1:00 Lunch

#### THURSDAY P.M. - SILICON CONTAINING POLYMERS

Session 7: Chairman - J. E. Mark

1:30 OS7-1 *Polymers from and of Silyl Acetylenes for Ceramic Fibers, Electrical and Optical Properties*, THOMAS J. BARTON, Iowa State University

1:00 OS7-2 *Synthesis, Microstructure, and Thermal Degradation of Poly(1-silapent-3-ene)s*, Young Tae Park, Young Hoon Ko, Stephen Q. Zhou, WILLIAM WEBER, University of Southern California

1:30 OS7-3 *Synthesis and Reactions of Multifunctional Methacryl and Styryl Siloxane Macromonomers*, S. K. Duplock, A. G. SWINCER, and R. F. O. Warren, University of South Australia

1:00 OS7-4 *Side Chain Liquid Crystalline Polymers with Silphenylene-Siloxane Main Chains*, MAKI ITOH, Dow Corning Japan, Ltd., and Robert W. Lenz, University of Massachusetts

1:00 Closing Remarks

#### POSTER SESSION PROGRAMS

Makua Room

#### POSTER SESSION ONE - Monday December 17, 1990

11-1 BRUCE C. BERRIS, Ethyl Corporation, *Nickel-Catalyzed Silane Dehydrogenation Forming Cyclic and Bicyclic Oligomers*

11-2 ATSUSHI KURITA, Kohei Hamanishi, Michio Zembayashi, Toshiba Silicone Co., Ltd., *Synthesis and Photochemistry of (p-Vinylphenyl)methylpolysiloxane*

11-3 R. B. Jarayaman, G. Sinai-Zingde, J. S. RIFFLE, Virginia Polytechnic Institute and State University, *Synthetic Investigations of Aromatic Amine Functional Polydimethylsiloxane Oligomers*

11-4 Y. I. Lee, F. G. Wakim, SAMUEL P. SAWAN, University of Lowell, *Electrical Conductivity of Various Polysilanes*

11-5 H. J. Hsieh, J. Lavine, SAMUEL P. SAWAN, T. Hongsmatip, University of Lowell, *Photolithographic Studies of Polysilane Polymers in Reactive Ambients*

11-6 SEIICHI TAGAWA, University of Tokyo, *Relaxation Dynamics of Electronic Structure in Polygermane*

11-7 J. M. Yu, D. TEYSSIE, S. Boileau, College de France, *Hydrosilylation of Allyl Carbonates by Polymethylhydrosiloxane and Related Side-reactions*

11-8 G. WALLRAFF, M. Baier, P. Cotts, R. Miller, P. Shukla, F. DeSchryver, D. DeClerq, IBM Corporation, *Thermochromism of Dialkylsilanes*

11-9 WILLIAM J. WELSH, Samuel Tersigni, Peter Tersigni, Wangkan Lin, University of Missouri-St. Louis, *Conformational Analysis On a Series of Di-n-alkyl Polysilylene Model Compounds*

#### POSTER SESSION TWO - Tuesday December 18, 1990

12-1 TETSUO FUJIMOTO, Masahiro Terada, Toshiba Silicone Co., Ltd., *Anaerobic Silicone Adhesives*

PS2-2 T. M. Hsu, SAMUEL P. SAWAN, University of Lowell, *Synthesis and Photooxidation of Hydropolysilanes*

PS2-3 T. M. Hsu, SAMUEL P. SAWAN, University of Lowell, *Optical Properties and UV Photosensitivity of Hydropolysilanes*

PS2-4 J. G. Matisons and A. G. SWINCER, and D.R. Bennett, A. K. O. Netting, and R. St.C. Smart, University of South Australia, *The Bonding of Functionalised Silicones to Silica Surfaces*

PS2-5 SEIICHI TAGAWA, University of Tokyo, *Dynamics of Electron and Hole Pairs in Polysilanes*

PS2-6 Howard Shih-Jen Lee, WILLIAM P. WEBER, University of Southern California, *Addition of Dichloroketene to Poly(1-Sila-cis-pent-3-enes)*

PS2-7 Judith E. Durham, Joyce Y. Corey, WILLIAM J. WELSH, University of Missouri-St. Louis, *Theoretical and Experimental Investigation of a Non-Statistical Distribution of Stereoisomers in the Synthesis of Asymmetrically-Substituted Polysilane Precursors*

PS2-8 MASARU YOSHIDA, Kenkichi Sakamoto, Hideki Sakurai, Tohoku University, *Anionic Polymerization of the Masked Disilenes to High Molecular Weight Polysilylenes I. Structural Determination of Monomers and the Mechanism of Polymerization*

PS2-9 J. WILDEMAN, F. van Bolhuis, G. Hadziioannou, Groningen University, *Synthesis of Linear and Cyclic Copolymers of Silylthiophenes*

#### POSTER SESSION THREE - Wednesday December 19, 1990

PS3-1 PATRICIA A. BIANCONI, Walter J. Szymanski, Glenn Visscher, Pennsylvania State University, *Polygermynes: Synthesis and Properties of Germanium-Germanium Bonded Network Polymers*

PS3-2 MARK BAIER, R. Miller, G. Wallraff, IBM Corporation, *Fluorescence Quenching and Photodegradation in Solid Polysilanes*

PS3-3 YASUHIITO FUNADA, Kenkichi Sakamoto, Hideki Sakurai, Tohoku University, *Anionic Polymerization of the Masked Disilenes to High Molecular Weight Polysilylenes II. Block Copolymerizations*

PS3-4 KEITH PANNELL, Elvira Delgado, Francisco Cervantes-Lee, Sneha Sharma, Krishnan Raguvier, University of Texas at El Paso, *The Nature of the Silicon Germanium Bond*

PS3-5 T. M. Hsu, Y. T. Shieh, SAMUEL P. SAWAN, University of Lowell, *Differential Photocalorimetric Studies of Hydropolysilanes*

PS3-6 J. H. Su, J. Lavine, SAMUEL P. SAWAN, University of Lowell, *Hydropolysilanes as Negative Tone Photoresists*

PS3-7 SHUHEI SEKI, Seiichi Tagawa, Yoichi Yoshida, University of Tokyo, *Ion-beam Induced Changes of Molecular Structures and Solubilities of Polysilanes*

PS3-8 JUDITH STEIN, L. N. Lewis, K. A. Smith, GE Corporate Research and Development, *Kinetic and Mechanistic Studies of Platinum Catalyzed Hydrosilylation*

PS3-9 Liming Wang, Xiugao Liao, WILLIAM P. WEBER, University of Southern California, *Addition of Chlorofluorocarbene to Poly(1-Sila-Cis-Pent-3-Enes)*

PS3-10 JOHN M. ZEIGLER, Linda I. McLaughlin, Sandia National Laboratories, *Chain Transfer Processes In Dichlorosilane Reductive Polymerization And Their Control: A Simplified Route To High Molecular Weight Polysilylenes*

PS3-11 D. W. MCCARTHY, J. E. Mark, University of Cincinnati, *Properties of Poly(dimethylsiloxane) Elastomers Prepared From Aqueous Emulsion*

*Posters can be viewed from the start of the morning break to the end of the evening session or event.*

The Second International Topical Workshop  
**ADVANCES IN SILICON-BASED POLYMER SCIENCE**

**LAST MINUTE INFORMATION**

**Hawaiian Luau:** As indicated on the meeting agenda and oral program, a traditional Hawaiian luau, complete with entertainment, will be provided to participants at no extra cost. The luau will take place on Monday starting at 19:00 at the hotel luau grounds. Dress for the luau will be informal. Dress for the Workshop banquet, to be held Wednesday starting at 19:00 in the Makaha Terrace, will be coat and tie.

**Airport Transportation:** Airport transportation will be provided after the meeting to those departing on Thursday. Please indicate when you need to leave to the Workshop registration desk prior to Wednesday. Remember to allow an absolute minimum of two hours to get to Honolulu and check in for your flight.

**Paper Publication:** Authors should have received instructions for publication of their papers in a special issue of the *Journal of Inorganic and Organometallic Polymers*. If you need another copy of the instructions, it can be obtained at the registration table. Your manuscript must be received by the journal editor, Marty Zeldin, no later than February 1, 1991. This date is hard; manuscripts received after this date will be declined. Manuscripts will also be gratefully accepted during the Workshop. Participants in the Workshop who are not authors of papers at the Workshop may also submit a paper to the special issue on a space-available basis.

**Presentation Aids: ORAL:** To allow adequate time for questions, presentations scheduled for one hour should run for about 50 minutes, while nominal thirty minute presentations should occupy about 25 minutes. You may exceed these suggested times, but only to the limit of your total scheduled time and at the expense of time for questions. The Workshop provides standard 35mm slide and overhead projectors, pointers, microphones, etc. If you need something outside these items for an oral presentation, please contact the registration desk immediately. **POSTER:** Poster boards are set up in the Makua Room (ground floor of the Makaha Terrace building). Posters should be set up prior to the start of the morning session, so that they will be ready for viewing starting with the morning coffee break. Authors should be present with their posters during the break and also a half hour prior to the start of the evening session. Each poster will remain available for viewing through the afternoon and evening until the end of the evening session. Please take down your poster at the end of the evening session, so that the space will be available for the next day's poster session. Each poster is allotted an area 4 feet high by 8 feet wide (122 cm high by 244 cm wide). Use thumbtacks, double-sided adhesive tape, Velcro, or any other temporary adhesive material needed to attach your posters and present them properly. Do not attempt to use glue to secure the posters.

**Contact Numbers:** The Sheraton switchboard number is 808-695-9511; the hotel fax number is 808-695-5806. Messages can be passed to you directly or through the Workshop registration desk.

**Problems?:** If you need help with some aspect of your presentation or participation in the Workshop proper, please direct your questions to the Workshop registration desk. If you have a problem with your room, meals, etc., contact the hotel staff directly. Going through the Workshop registration desk with hotel-related issues will only delay their resolution.

**The Second International Topical Workshop**  
***ADVANCES IN SILICON-BASED POLYMER SCIENCE***

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**ACKNOWLEDGEMENT**

The organizer and sponsors of the Workshop gratefully acknowledge the financial assistance provided by the following organizations:

**Dow Corning Corporation**

**Huls America, Inc.**

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**Shin-Etsu Chemical Co., Ltd.**

**Toshiba Silicone Co., Ltd.**

**Wacker-Chemie GmbH**

The Second International Topical Workshop  
**ADVANCES IN SILICON-BASED POLYMER SCIENCE**

ORAL PROGRAM

**SUNDAY DECEMBER 16, 1990 - ARRIVAL**

15:00 - 21:00      Registration - Makaha Terrace

20:00      Welcome Gathering - Makaha Terrace

**MONDAY A.M. DECEMBER 17, 1990 - FROM 1-D TO 3-D SILOXANES**

8:50      *Welcome and Announcements*, J. ZEIGLER, Silchemy, Inc.

Session 1: Chairman - James E. McGrath

9:00      OS1-1      *Kinetics of Ring-Opening Siloxane Polymerization*, JULIAN CHOJNOWSKI, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences

10:00      OS1-2      *Ring Opening Anionic Polymerization Kinetics of PDMS*, RICARDO VERA, Jose Nunes, Filiberto Rivera, Universidad National Autonoma de Mexico

10:30      Break/poster session 1

11:00      OS-3      *Synthesis and Properties of Liquid Crystalline Polysiloxanes*, SYLVIE BOILEAU and D. Teyssie, College de France

12:00      OS-4      *Alkyl Substituted Siloxanes: Structure-Performance Relationships As Applied to Personal Care*, E. B. Orlor, H. A. A. Rasoul, E. T. LANCE-GOMEZ, Johnson Wax

12:30      Lunch

**MONDAY P.M. - FROM 1-D TO 3-D SILOXANES**

Session 2: Chairman - Geoffrey Swincer

16:00      OS2-1      *Siloxane Containing High Performance Segmented Copolymer Systems*, JAMES E. MCGRATH, Virginia Polytechnic Institute and State University

16:30      OS2-2      *The Influence of Composition and Molecular Architecture on the Properties of Diphenylsiloxane Copolymers*, DALE J. MEIER, Michigan Molecular Institute

17:00      OS2-3      *Silicone Release Coatings: Network Structures and Properties*, J. D. DeSorcie, J. STEIN, General Electric Company

19:00      Luau

**TUESDAY A.M. DECEMBER 18, 1990 - FROM 1-D TO 3-D SILOXANES**

**Session 3: Chairman - Dietmar Seyferth**

- 8:30 OS3-1 *Some Novel Polysiloxane Elastomers and Inorganic-Organic Composites*, J. E. MARK, University of Cincinnati
- 9:30 OS3-2 *Recent Advances in the Rheo-optical Characterization of Si-containing Networks*, VASILIOS GALIATSATOS, University of Akron
- 10:00 OS3-3 *Microstructural Evolution of a Silicon Oxide Phase in a Perfluorosulfonic Acid Ionomer Via an In Situ Sol-Gel Reaction*, KENNETH A. MAURITZ, I. D. Stefanithis, University of Southern Mississippi
- 10:30 Break/poster session 2
- 11:00 OS3-4 *Sol-Gel Polymerization of the  $[\text{Si}_8\text{O}_{12}](\text{OCH}_3)_8$  Cube*, P. C. Cagle, W. G. KLEMPERER, C. A. Simmons, University of Illinois
- 11:30 OS3-5 *Sheet and Tube Alkoxysiloxanes of Potential Use in Sol-Gel Ceramics*, Bruce A. Harrington, Jesse Heftner, MALCOLM E. KENNEY, Case Western Reserve University
- 12:00 Lunch

**TUESDAY P.M. - POLYSILANES AND RELATED POLYMERS**

**Session 4: Chairman - Thomas J. Barton**

- 19:30 OS4-1 *Synthesis and Degradation of Polysilylenes*, KRZYSZTOF MATYJASZEWSKI, Carnegie Mellon University
- 20:30 OS4-2 *Anionic Polymerization of the Masked Disilenes to High Molecular Weight Polysilylenes. Mechanism, Scope and Applications*, HIDEKI SAKURAI, Tohoku University
- 21:00 OS4-3 *Disilylene-ethynylene and Polysilylene-ethylene Alternating Copolymers*, ROBERT WEST, Shuji Hayase, Takahisa Iwahara, University of Wisconsin
- 21:30 OS4-4 *Theoretical Studies of the Energetics and Dynamics of Polysilane Model Compounds*, WILLIAM WELSH, P. S. Ritter, S. Tersigni, W. Lin, University of Missouri-St. Louis

**WEDNESDAY A.M. DECEMBER 19, 1990 - POLYSILANES AND RELATED POLYMERS**

**Session 5: Chairman - William Weber**

- 8:30 OS5-1 *Optical Properties and Ultrafast Dynamics of Excitations in Polysilanes*, J. R. G. Thorne, J. M. Zeigler, R. M. HOCHSTRASSER, University of Pennsylvania
- 9:00 OS5-2 *Excited States of Polysilanes: High Resolution Low Temperature Spectroscopy and Molecular Modeling*, H. PETER TROMMSDORFF, Universite Joseph Fourier Grenoble I

- 9:30 OS5-3 *The Photochemistry of Substituted Silane High Polymers*, R. D. MILLER, G. M. Wallraff, M. Baier, N. Clecak, IBM Almaden Research Center and J. Michl, T. Karatsu, Y.-P. Sun, University of Texas at Austin
- 10:00 OS5-4 *Comparison of Radical Anions and Cations of Polygermane and Polysilanes*, SEIICHI TAGAWA, University of Tokyo and Hiroshi Ban, Nippon Telegraph and Telephone
- 10:30 Break/poster session 3
- 11:00 OS5-5 *Study of Third Order Optical Nonlinearities of Polysilanes by Self-focusing*, D.V.G.L.N. RAO, University of Massachusetts
- 11:30 OS5-6 *Electronic Structures of  $\sigma$ -Conjugated Polymers*, NOBUO MATSUMOTO, Nippon Telegraph & Telephone Company
- 12:00 OS5-7 *Time Resolved Studies of Electronic Transport in Si and Ge Polymer Dielectrics*, M. ABKOWITZ, M. Stolka, Xerox Corporation
- 12:30 OS5-8 *Transition Metal Oligosilane and Polysilane Activation*, KEITH H. PANNELL, S. Vincenti, and Toshiaki Kobayashi, University of Texas at El Paso
- 1:00 Lunch

**WEDNESDAY P.M. DECEMBER 19, 1990**

- 7:00 Workshop Banquet

**THURSDAY A.M. DECEMBER 20, 1990 - SILANE NETWORK AND PRECERAMIC POLYMERS**

**Session 6: Chairman - Walter Klemperer**

- 8:30 OS6-1 *Silicon Network Polymers: Properties and Applications*, PATRICIA BIANCONI, David A. Smith, Corie A. Freed, Michael S. Knapp, Pennsylvania State University and Rod R. Kunz, Mark W. Horn, Lincoln Laboratory
- 9:30 OS6-2 *Preceramic Organosilicon Polymer/Metal Powder Composites: Their Pyrolytic Conversion to Ceramics*, DIETMAR SEYFERTH, Nathan Bryson, Massachusetts Institute of Technology
- 10:00 OS6-3 *Thermal Sensitivity of Hydropolysilanes*, T. M. Hsu and S. P. SAWAN, University of Lowell
- 10:30 Break
- 11:00 OS6-4 *Ionic Ring-Opening Polymerization of Cyclosilazanes*, E. Duguet, M. Schappacher, A. SOUM, Universite de Bordeaux I

11:30 OS6-5 *Structure and Properties of Ceramic Fibers Prepared From Organosilicon Polymers*, JOHN LIPOWITZ, Dow Corning Corporation

12:00 Lunch

**THURSDAY P.M. - SILICON CONTAINING POLYMERS**

Session 7: Chairman - J. E. Mark

13:30 OS7-1 *Polymers from and of Silyl Acetylenes for Ceramic Fibers, Electrical and Optical Properties*, THOMAS J. BARTON, Iowa State University

14:00 OS7-2 *Synthesis, Microstructure, and Thermal Degradation of Poly(1-silapent-3-ene)s*, Young Tae Park, Young Hoon Ko, Stephen Q. Zhou, WILLIAM WEBER, University of Southern California

14:30 OS7-3 *Synthesis and Reactions of Multifunctional Methacryl and Styryl Siloxane Macromonomers*, S. K. Duplock, A. G. SWINCER, and R. F. O. Warren, University of South Australia

15:00 OS7-4 *Side Chain Liquid Crystalline Polymers with Silphenylene-Siloxane Main Chains*, MAKI ITOH, Dow Corning Japan, Ltd., and Robert W. Lenz, University of Massachusetts

16:00 Closing Remarks

**Oral sessions will be held in the Makaha Terrace**

**Poster sessions will take place in the Makua Room**

The Second International Topical Workshop  
**ADVANCES IN SILICON-BASED POLYMER SCIENCE**

**POSTER SESSION 1**

Makua Room

**Monday December 17, 1990**

- PS1-1     **BRUCE C. BERRIS**, Ethyl Corporation, *Nickel-Catalyzed Silane Dehydrogenation Forming Cyclic and Bicyclic Oligomers*
- PS1-2     **ATSUSHI KURITA**, Kohei Hamanishi, Michio Zembayashi, Toshiba Silicone Co., Ltd., *Synthesis and Photochemistry of (p-Vinylphenyl)methylpolysiloxane*
- PS1-3     **R. B. Jarayaman**, G. Sinai-Zingde, J. S. RIFFLE, Virginia Polytechnic Institute and State University, *Synthetic Investigations of Aromatic Amine Functional Polydimethylsiloxane Oligomers*
- PS1-4     **Y. I. Lee**, F. G. Wakim, **SAMUEL P. SAWAN**, University of Lowell, *Electrical Conductivity of Various Polysilanes*
- PS1-5     **H. J. Hsieh**, J. Lavine, **SAMUEL P. SAWAN**, T. Hongsmatip, University of Lowell,, *Photolithographic Studies of Polysilane Polymers in Reactive Ambients*
- PS1-6     **SEIICHI TAGAWA**, University of Tokyo, *Relaxation Dynamics of Electronic Structure in Polygermane*
- PS1-7     **J. M. Yu**, D. TEYSSIE, S. Boileau, College de France, *Hydrosilylation of Allyl Carbonates by Poly methyl hydrosiloxane and Related Side-reactions*
- PS1-8     **G. WALLRAFF**, M. Baier, P. Cotts, R. Miller, P. Shukla, F. DeSchryver, D. DeClerq, IBM Corporation, *Thermochromism of Dialkylsilanes*
- PS1-9     **WILLIAM J. WELSH**, Samuel Tersigni, Peter Tersigni, Wangkan Lin, University of Missouri-St. Louis, *Conformational Analysis On a Series of Di-n-alkyl Polysilylene model Compounds*

Posters can be viewed from the start of the morning break to the end of the evening session or event.

The Second International Topical Workshop  
**ADVANCES IN SILICON-BASED POLYMER SCIENCE**

**POSTER SESSION 2**

Makua Room

Tuesday December 18, 1990

- PS2-1      TETSUO FUJIMOTO, Masahiro Terada, Toshiba Silicone Co., Ltd., *Anaerobic Silicone Adhesives*
- PS2-2      T. M. Hsu, SAMUEL P. SAWAN, University of Lowell, *Synthesis and Photooxidation of Hydropolysilanes*
- PS2-3      T. M. Hsu, SAMUEL P. SAWAN, University of Lowell, *Optical Properties and UV Photosensitivity of Hydropolysilanes*
- PS2-4      J. G. Matisons and A. G. SWINCER, and D.R. Bennett, A. K. O. Netting, and R. St.C. Smart, University of South Australia, *The Bonding of Functionalised Silicones to Silica Surfaces*
- PS2-5      SEIICHI TAGAWA, University of Tokyo, *Dynamics of Electron and Hole Pairs in Polysilanes*
- PS2-6      Howard Shih-Jen Lee, WILLIAM P. WEBER, University of Southern California, *Addition of Dichloroketene to Poly(1-Sila-cis-pent-3-enes)*
- PS2-7      Judith E. Durham, Joyce Y. Corey, WILLIAM J. WELSH, University of Missouri-St. Louis, *Theoretical and Experimental Investigation of a Non-Statistical Distribution of Stereoisomers in the Synthesis of Asymmetrically-Substituted Polysilane Precursors*
- PS2-8      MASARU YOSHIDA, Kenkichi Sakamoto, Hideki Sakurai, Tohoku University, *Anionic Polymerization of the Masked Disilenes to High Molecular Weight Polysilylenes I. Structural Determination of Monomers and the Mechanism of Polymerization*
- PS2-9      J. WILDEMANN, F. van Bolhuis, G. Hadziioannou, Groningen University, *Synthesis of Linear and Cyclic Copolymers of Silylthiophenes*

Posters can be viewed from the start of the morning break to the end of the evening session or event.

The Second International Topical Workshop  
**ADVANCES IN SILICON-BASED POLYMER SCIENCE**

**POSTER SESSION 3**

Makua Room

Wednesday December 19, 1990

- PS3-1     PATRICIA A. BIANCONI, Walter J. Szymanski, Glenn Visscher, Pennsylvania State University, *Polygermynes: Synthesis and Properties of Germanium-Germanium Bonded Network Polymers*
- PS3-2     MARK BAIER, R. Miller, G. Wallraff, IBM Corporation, *Fluorescence Quenching and Photodegradation in Solid Polysilanes*
- PS3-3     YASUHITO FUNADA, Kenkichi Sakamoto, Hideki Sakurai, Tohoku University, *Anionic Polymerization of the Masked Disilenes to High Molecular Weight Polysilylenes II. Block Copolymerizations*
- PS3-4     KEITH PANNELL, Elvira Delgado, Francisco Cervantes-Lee, Sneha Sharma, Krishnan Raguveer, University of Texas at El Paso, *The Nature of the Silicon Germanium Bond*
- PS3-5     T. M. Hsu, Y. T. Shieh, SAMUEL P. SAWAN, University of Lowell, *Differential Photocalorimetric Studies of Hydropolysilanes*
- PS3-6     J. H. Su, J. Lavine, SAMUEL P. SAWAN, University of Lowell, *Hydropolysilanes as Negative Tone Photoresists*
- PS3-7     SHUHEI SEKI, Seiichi Tagawa, Yoichi Yoshida, University of Tokyo, *Ion-beam Induced Changes of Molecular Structures and Solubilities of Polysilanes*
- PS3-8     JUDITH STEIN, L. N. Lewis, K. A. Smith, GE Corporate Research and Development, *Kinetic and Mechanistic Studies of Platinum Catalyzed Hydrosilylation*
- PS3-9     Liming Wang, Xiugao Liao, WILLIAM P. WEBER, University of Southern California, *Addition of Chlorofluorocarbene to Poly(1-Sila-Cis-Pent-3-Enes)*
- PS3-10    JOHN M. ZEIGLER, Linda I. McLaughlin, Sandia National Laboratories, *Chain Transfer Processes In Dichlorosilane Reductive Polymerization And Their Control: A Simplified Route To High Molecular Weight Polysilylenes*
- PS3-11    D. W. MCCARTHY, J. E. Mark, University of Cincinnati, *Properties of Poly(dimethylsiloxane) Elastomers Prepared From Aqueous Emulsion*

Posters can be viewed from the start of the morning break to the end of the evening session or event.



The Second International Topical Workshop  
*ADVANCES IN SILICON-BASED POLYMER SCIENCE*

# *ORAL SESSION ABSTRACTS*

Kinetics of siloxane ring  
opening polymerization

Julian Chojnowski

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of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland

Studies on kinetics and mechanism of the anionic and cationic ring opening polymerization of cyclic siloxanes will be reviewed. The main purpose of this presentation will be to give a general idea on the state of knowledge in this field and to discuss problems which are essential for a better understanding of these processes in connection with their practical application. The emphasis will be put on the polymerization of cyclic trisiloxanes. Due to the strain in their ring, the kinetically controlled polymerization of these monomers gives a possibility of tailoring structure of the polymer.

Much attention will be devoted to the association phenomena in the polymerization systems as they strongly affect the course of the reactions and the character of their products. In particular three types of the interaction of active propagation centers in the anionic polymerization will be discussed, i.e., formation of ionic aggregates, interactions with monomer and polymer and complexes with nucleophilic additives. In the cationic polymerization of cyclic siloxanes the hydrogen bonding association is of a great importance as it determines to a large extent the kinetic pattern of the process.

The second major discussed problem will be kinetics and mechanism of the formation of oligomers in the polymerization processes. The formation of the cyclic oligomers reduces the yield of the polymer and may affect the size and the microstructure of the polymer chain. On the other hand, the kinetics of the oligomer formation gives valuable information about mechanism of the chain formation.

The third general discussed question will be the interconnection of some mechanistic features of the polymerizations with the character of the polymer products in particular with their molecular weight, molecular weight distribution, end groups, and also the microstructure of the chain related to the problem of chemo-, regio- and stereoselectivity of the process.

## Ring Opening Anionic Polymerization Kinetics of PDMS

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Universidad Nacional Autonoma de Mexico, UNAM  
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Polydimethylsiloxane (PDMS) properties and applications depend upon molecular structure and purity. In turn they are mainly defined by the selected intermediate, polymerization mechanism and reaction conditions. Here we report the polymerization of octamethylcyclotetrasiloxane,  $D_4$ , by an anionic mechanism using a potassium siloxanolate as initiator. The effects of temperature and initiator concentration on reaction kinetics and on molecular structure are discussed. An FTIR spectroscopy technic combined with GPC were used to follow reaction kinetics, molecular structure and molecular weight distribution. The applicability of these technics for the studied system are also discussed.

Total reaction yields above 80% were obtained under proper reaction conditions. According to the kinetic study polymerization reaction with respect to  $D_4$  conversion is first order.

## SYNTHESIS AND PROPERTIES OF LIQUID CRYSTALLINE POLYSILOXANES

S. BOILEAU and D. TEYSSIE

Collège de France\*, Place Marcelin Berthelot, 11,  
75231 PARIS CEDEX 05, FRANCE.

Most studies on the structure-properties relationships of liquid crystalline polysiloxanes are focused on the side-chain type polymers, bearing calamitic (sometimes laterally attached) or discotic side groups decoupled from the backbone via a flexible spacer. However main-chain liquid crystalline polymers were also obtained by combining flexible siloxane segments with rigid rod type mesogens. These two main types of liquid crystalline polysiloxanes will be examined and compared with other liquid crystalline polymers with backbones of different flexibility.

One of the most widely used methods for the preparation of liquid crystalline polysiloxanes is the hydrosilylation of unsaturated compounds. However this reaction is not always as clean and clear-cut as it would be necessary for the obtention of polymers with reproducible characteristics. This point will also be emphasized with specific examples of side-reactions.

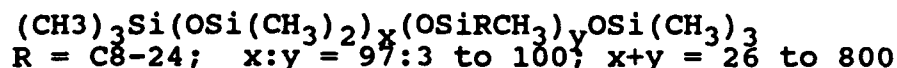
The basis for the interest in polysiloxanes as liquid crystals is of course the flexibility of the backbone but also the possibility of obtaining liquid crystalline elastomers. Potential applications of liquid crystalline polysiloxanes and future developments will be discussed.

\* Laboratoire de Chimie Macromoléculaire associé au CNRS: URA 24.

# Alkyl Substituted Siloxanes: Structure-Performance Relationships as Applied to Personal Care

E.B. Orler, H.A.A. Rasoul, E.T. Lance-Gomez

A series of alkyl-methyl, dimethyl siloxane copolymers of formula:



were prepared. Thermal and rheological properties were measured by differential scanning calorimetry (DSC) and steady shear rheology, respectively. These copolymers were developed as hair treatment additives.

For lower degrees of alkyl substitution the DSC profiles show a glass transition for the siloxane main chain and a separate melting transition ( $T_m$ ) for the alkyl side chains randomly attached to the siloxane backbone. At higher degrees of substitution the glass transition is not resolvable due to the high degree of crystallinity. This melting transition increases in temperature and is related to alkyl chain length and percent substitution. The melting transitions were taken as the minimum in the melting point endotherm and ranged from  $-22^\circ\text{C}$  to  $45^\circ\text{C}$ .

The side-chain  $T_m$  and degree of substitution determines whether the copolymer is a gel or waxy solid below the side chain  $T_m$ . Rheologically, below  $T_m$  the gels undergo shear thinning; above the  $T_m$  the copolymers are Newtonian fluids. Both thermal and rheological properties have an impact on their performance as hair care additives.

Positive performance on hair fibers was shown to correlate to molecular structure. Some of the benefits found were unexpected and superior to those found for related dimethylsiloxanes. The benefits include:

1. lubricity for combing;
2. improved apparent volume of the hair assembly; (fullness and body)
3. improved fiber resiliency (bounce);
4. and, ease of orienting/reorienting fibers. (manageability and restyling)
5. no unfavorable coating of the hair.

The effect of the molecular structure of the copolymer on the above performance benefits will be described.

## Silicon in Polymer Science Workshop

December 16, 1990

## LOW DIELECTRIC, HYDROPHOBIC POLY(SILOXANE IMIDE) SEGMENTED COPOLYMERS FOR ELECTRONIC AND ADHESIVE APPLICATIONS

J. E. McGrath, T. Yoon, M. E. Rogers, H. Grubbs, A. Gungor, S. Smith, G. York,  
and C. A. Arnold

National Science Foundation Science & Technology Center:  
High Performance Polymeric Adhesives and Composites  
Virginia Polytechnic Institute & State University  
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Polyimides generally possess excellent thermal and mechanical properties, making them attractive candidates for high performance applications. To be useful for microelectronic applications, however, these materials must also be good insulators, as well as be readily processable.

The incorporation of flexible polysiloxane segments into the polyimide backbone structure has been shown to yield soluble, processable copolyimides with good thermal and mechanical properties. In addition, the siloxane component imparts a number of other significant benefits for electronic applications. These include reduced water sorption, surface modification, good thermal and ultraviolet stability, and resistance to degradation in oxygen plasma environments. For polar polyimide systems, siloxane incorporation will also reduce the dielectric constant. The use of other less polar, more hydrophobic monomers will consistently yield soluble systems with low dielectric constants as well.

In this work, a series of high molecular weight, soluble polyimide are randomly coupled and perfectly alternating segmented polysiloxane-polyimide copolymers were synthesized by a solution technique. The solution procedure, conducted at lower temperatures ( $\sim 170^\circ\text{C}$ ) than the classical bulk thermal imidization ( $300^\circ\text{C}$ ), has been shown to yield polyimides of enhanced solubility. In order to further enhance processability, molecular weight was controlled through the incorporation of monofunctional reagents such as phthalic anhydride and maleic anhydride, yielding nonreactive or potentially reactive endgroups, respectively. Particular advantages for electronic applications include thermal and dimensional stability over a wide temperature range, good mechanical properties, and chemical resistance. Structure-property characterization, including water sorption, dielectric constants, solubility behavior and thermal/mechanical properties will be reported. In particular, the adhesion behavior to metals such as titanium 6/4 and PEEK graphite composites in excellent and will be discussed.

The Influence of Composition and Molecular Architecture  
on the Properties of Diphenylsiloxane Copolymers

Dale J. Meier  
Michigan Molecular Institute  
Midland, Michigan 48640

We have prepared a variety of siloxane polymers of controlled composition, molecular architecture and molecular weight by anionic polymerization techniques. Of greatest interest have been those containing diphenylsiloxane. Polydiphenylsiloxane is stable at high-temperatures, highly crystalline, and, as a result of it being a rigid-rod molecule, it melts to a liquid-crystalline state at about 260°C. It is soluble at high temperatures in a few selected solvents. We are investigating substitution reactions on diphenylsiloxane polymers, with a view of lowering the melting point but with retention of the liquid crystalline state.

A variety of copolymers of diphenylsiloxane (P) with dimethylsiloxane (M) or methylphenylsiloxane (P/M) have been prepared. Depending on molecular architecture, the properties vary from tough elastomers (P-M-P tri-blocks) to elastic solids (random P<sub>3</sub>-M<sub>3</sub> triads) to viscous liquids (random P-M or P-P/M copolymers).

The preparation, characterization and properties of various polymers containing diphenylsiloxane will be described.

**SILICONE RELEASE COATINGS:  
NETWORK STRUCTURES AND PROPERTIES**

J.D. Desorcie, J. Stein

GE Research & Development  
Schenectady, NY 12301

**ABSTRACT**

Silicone Release Coatings are used by the Pressure Sensitive Adhesive industry for labelling applications. A background discussion of thermally and photolytically cured coatings will be provided. The determination of the network structure and the effect of chain transfer agents on network structure of photolytically prepared silicone coatings will be discussed. Additionally, a degradation procedure for the determination of the network structure and residual functionality of addition cured coatings (thermal) has been developed.



## **SOME NOVEL POLYSILOXANE ELASTOMERS AND INORGANIC-ORGANIC COMPOSITES**

**J. E. Mark**

**Department of Chemistry and the Polymer Research Center  
The University of Cincinnati**

The elastomers were prepared so as to have unusual network chain length distributions, thereby improving their ultimate properties. The technique involved end linking mixtures of very short and relatively long functionally-terminated chains of poly(dimethylsiloxane) to give bimodal networks. Such (unfilled) elastomers show very large increases in reduced stress or modulus at high elongations because of the very limited extensibility of the short chains present in the networks. This non-Gaussian behavior also appears in compression or biaxial extension, as obtained by inflation of sheets of the material. Non-Gaussian theories taking into account this limited chain extensibility were found to be in good agreement with experiment. It is pointed out that some types of elastomeric networks described in the literature may be bimodal, albeit inadvertently.

The composites were prepared using techniques very similar to those employed in the new sol-gel approach to ceramics. Alkoxysilanes and related metalo-organic materials were hydrolyzed in the presence of polymer chains, for example polysiloxanes and polyoxides, that have end groups such as hydroxyls. The end groups bond the polymer chains into the silica or related ceramic material formed in the hydrolysis, thus forming inorganic-organic composites. When the polymer chains are in excess, they constitute the continuous phase, with ceramic-type material appearing as reinforcing domains. When present in smaller amounts, the polymer is dispersed in the continuous phase, to give a polymer-modified ceramic. Under some conditions, bicontinuous systems are obtained. The composites thus prepared were characterized by stress-strain measurements, density determinations, x-ray and neutron scattering, and electron microscopy.

Recent Advances in the Rheo-optical Characterization  
of Si-containing Networks

Vassilios Galiatsatos  
Institute of Polymer Science  
The University of Akron  
Akron, OH 44325

The advancement of the theories of Rubberlike Elasticity has allowed the development of *molecular* theories of strain-birefringence. These theories are invaluable in the rheo-optical characterization of certain types of elastomers. Si-containing networks such as poly(dimethylsiloxanes) (PDMS) are ideal materials for this type of experiments because of their optical transparency. The paper will cover the various theories of strain-birefringence, including enough background, present the latest developments in the field and show how the rheo-optical behavior of Si-containing elastomers can be characterized by parameters related to the topology of the networks and the molecular structure of the chains.

MICROSTRUCTURAL EVOLUTION OF A SILICON OXIDE PHASE IN  
NAFION MEMBRANES BY AN *IN SITU* SOL-GEL REACTION

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Microcomposite membranes were produced via the *in situ* diffusion controlled and acid-catalyzed sol/gel reaction for tetraethoxysilane in pre-hydrated and methanol-swollen Nafion perfluorosulfonic acid films. The storage and loss components of the complex dielectric constants of these microcomposites were determined as a function of invasive silicon oxide content and temperature. A parameter  $n$  which is extracted from isothermal loss component vs. frequency spectra is reflective of the degree of connectivity of charge pathway networks.  $n$  vs. temperature or silicon oxide content curves are viewed as coarsely indicative of the evolution of morphological texture with variance of these two factors. The thermal behavior of these microcomposites was investigated using TGA and DSC. Two strong thermal transitions, identified with the polar cluster and microcrystalline domains, at pre-degradative temperatures, were identified for all microcomposite and unfilled membranes. Upon annealing at a temperature just below the "cluster transition temperature" and then quenching, this transition becomes suppressed for all membranes.

SOL-GEL POLYMERIZATION OF THE  
[Si<sub>8</sub>O<sub>12</sub>](OCH<sub>3</sub>)<sub>8</sub> CUBE

P. C. Cagle, W. G. Klemperer,<sup>\*</sup> and C. A. Simmons

Department of Chemistry and Materials Research Laboratory  
University of Illinois  
Urbana, Illinois 61801

In contrast with polymeric materials, ceramic materials are generally prepared from structurally simple starting materials and therefore cannot be engineered on a molecular level. We have addressed the problem of manipulating the structure of silica on the molecule size scale through the sol-gel polymerization of the cubic octasilicate ester [Si<sub>8</sub>O<sub>12</sub>](OCH<sub>3</sub>)<sub>8</sub>. Comparative studies of Si(OCH<sub>3</sub>)<sub>4</sub>- and [Si<sub>8</sub>O<sub>12</sub>](OCH<sub>3</sub>)<sub>8</sub>-derived gels and glasses have been performed employing pycnometry, gas adsorption measurements, and electron microscopy. These studies demonstrate that the molecular building block approach to ceramic materials syntheses can be used to control structure on a molecular level and in this fashion influence bulk materials properties.

SHEET AND TUBE ALKOXYSILOXANES OF USE FOR THE  
PREPARATION OF CERAMICS BY THE SOL-GEL TECHNIQUE

Bruce A. Harrington<sup>1</sup>, Jesse Hefter<sup>2</sup>, and Malcolm E. Kenney<sup>1</sup>

<sup>1</sup>Department of Chemistry, Case Western Reserve University,  
Cleveland, OH 44106, <sup>2</sup>GTE Laboratories, Inc., Waltham, MA 02254

Recently we reported the synthesis of monomeric alkoxy silanes and oligomeric alkoxy siloxanes from metal silicates by a procedure that involves extraction and grafting. This procedure preserves or essentially preserves the silicate framework of the parent metal silicate. The procedure has now been applied to the synthesis of polymeric alkoxy siloxanes from two polymeric metal silicates. One of these silicates is the sheet silicate apophyllite,  $\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{F},\text{OH}) \cdot 8\text{H}_2\text{O}$ . The alkoxy sheet polymers obtained from it have been characterized by hydrolysis-gas chromatography, infrared,  $^{29}\text{Si}$  MAS-NMR, X-ray diffraction, and transmission electron microscopy techniques. The results from this characterization work show that the sheets are thin ( $\sim 11 \text{ \AA}$  in the ethoxy case), very broad, and fairly flexible. They also show that the sheets stack like pieces of paper and that their alkoxy groups are fairly readily cleaved off by hydrolysis. The second silicate to which the technique has been applied is the tube silicate  $\text{K}_2\text{CuSi}_4\text{O}_{10}$ . The alkoxy tube polymers obtained have been characterized by the same group of techniques. The results of this work show that the tubes have small diameters ( $\sim 17 \text{ \AA}$  in *n*-propoxy-methoxy case), are very long, and are moderately flexible. They also show that the tubes pack in bundles and that their alkoxy groups are fairly readily cleaved off by hydrolysis. Both the tube alkoxy polymers and the sheet alkoxy polymers appear to be promising candidates for use in the preparation of ceramics by the sol-gel technique.

## Synthesis and Degradation of Polysilanes

Krzysztof Matyjaszewski

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4400 Fifth Avenue, Pittsburgh PA 15213

Mechanistic aspects of synthesis and degradation of polysilanes will be discussed. Reductive coupling of disubstituted dichlorosilanes at ambient temperatures in the presence of ultrasound leads to monomodal polymers with relatively narrow molecular weight distributions ( $M_w/M_n$  from 1.2 to 1.5) and relatively high molecular weights ( $M_n$  from 50,000 to 100,000). Ring-opening polymerization of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane initiated with carbanions and silyl anions provides polymers with molecular weights from 10,000 to 100,000 and gives potential possibility of the microstructure control. The dearylation of phenyl containing polysilanes with triflic acid provides polymers with strong electrophilic silyl triflate moieties. They can react with any nucleophiles such as alcohols, amines, carbanions, organometallics, etc. This opens a new synthetic avenue towards various functional polysilanes. The reactivity of silyl triflates is so high that they can initiate cationic polymerization of some alkenes and heterocyclics to form graft copolymers. Synthesis and characterization of random copolysilanes will be covered. Model studies based on well-defined oligosilanes will be presented. Other synthetic routes will also be discussed. Thermal, mechanical, and chemical degradation of polysilanes will be described.

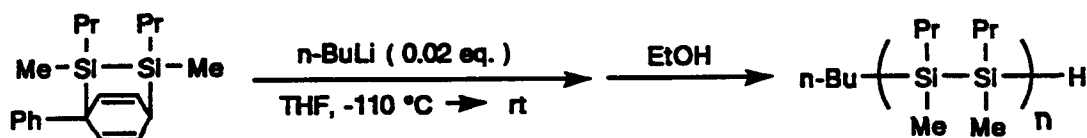
# Anionic Polymerization of the Masked Disilenes to High Molecular Weight Polysilylenes. Mechanism, Scope, and Applications

Hideki Sakurai

*Department of Chemistry, Faculty of Science, Tohoku University,  
Aoba-ku, Sendai 980, Japan*

In spite of recent development of the chemistry of polysilylenes, synthetic method is quite limited. To date, polysilylenes are prepared mostly by the Wurtz-type coupling of dichlorodialkylsilanes with sodium in refluxing toluene. However, the method has several difficulties such as the poor control of molecular weight and polydispersity. Yields of polymers are also generally low.

Very recently we have found an entirely new method of preparing polysilylenes based on anionic polymerization of masked disilenes<sup>1)</sup> and have prepared several polysilylene homopolymers (SiMeR-SiMeR)<sub>n</sub> and alternating copolymers (SiMe<sub>2</sub>-SiMeR)<sub>n</sub> of highly ordered structure.



The mechanism of the polymerization should involve repetitive attack of the polysilylenyl anions to a silicon atom of the monomer resulting in the formation of the new propagating polymer anion and biphenyl.

The new method has several interesting and useful features as demonstrated by the preparation of poly(1,1-dihexyl-2,2-dimethyldisilene) (SiHex<sub>2</sub>-SiMe<sub>2</sub>)<sub>n</sub> which demonstrated remarkable differences in structure and properties from poly[(dihexylsilylene)-co-(dimethylsilylene)] prepared by conventional methods.<sup>2</sup> In this lecture, the latest results on the anionic polymerization of masked disilenes will be presented.

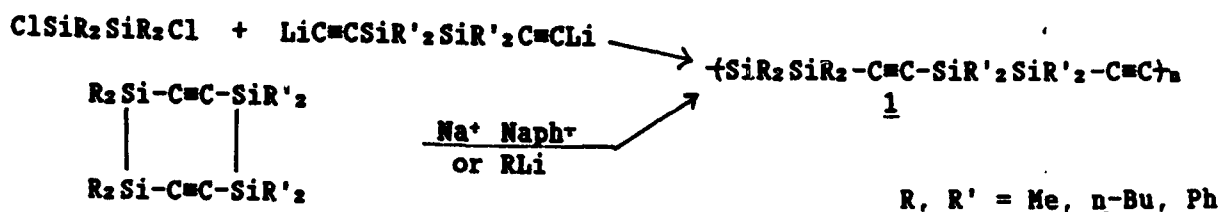
1) Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 7641.

2) Sakamoto, K.; Yoshida, M.; Sakurai, H. *Macromolecules* **1990**, in press.

## ETHYNYLENE-DISILYLENE ALTERNATING COPOLYMERS

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Polymers (1) in which ethynylene units  $-C\equiv C-$  alternate with disilylene units  $-SiR_2SiR'_2-$  have been prepared by two routes: A. Condensation of dichlorodisilanes with dilithium derivative of 1,2-dieithynyldisilanes, and B. Ring-opening polymerization of strained cyclic disilanylene-actylenes. The polymers display UV absorption near 240 nm indicative



of  $\sigma-\pi$  conjugation between the  $Si_2$  and  $C\equiv C$  moieties. Polymers with  $R = R' = n-Bu$ , or  $R = n-Bu, R' = Ph$  undergo solid-state transitions to form liquid crystalline mesophases resembling those observed for many poly(silylenes). Single crystals were obtained for the polymer with  $R = R' = CH_3$ , by precipitation from dilute cyclohexene solution. The solid-state properties and structures of this family of polymers will be discussed.



THEORETICAL STUDIES OF THE ENERGETICS AND DYNAMICS OF POLYSILANE MODEL COMPOUNDS. W.J. Welsh, P.S. Ritter, S. Tersigni, and W. Lin, Department of Chemistry, University of Missouri-St. Louis, St. Louis, MO 63121.

The polysilanes  $[-Si(RR')-]$ , with R and R' representing various organic groups, exhibit unusual electronic spectra and in some cases thermochromism. This behavior may be due to conformational transformations along the Si-Si backbone. We have carried out conformational energy calculations on model symmetrically-substituted polysilanes for the series  $R=R'=\text{methyl} \rightarrow \text{hexyl}$  using the MM3 force field with full geometry optimization. The conformational energy maps so generated were employed to ascribe conformational preferences as a function of the size and nature of the R substituent. Molecular dynamics simulations have also been performed on these model polysilanes to monitor the trajectories for possible conformational transformations. This research is supported by a grant to WJW from the Donors of the Petroleum Research Fund, administered by the American Chemical Society.

**Optical Properties and Ultrafast Dynamics of Excitations  
in Polysilanes**

J. R. G. Thorne  
J. M. Zeigler  
and  
R. M. Hochstrasser

A survey of recent work on polysilanes will be presented. The superfast radiative rates of the UV excitations are consistent with extensively delocalized excitations observed in optical saturation. Femtosecond time resolved excited state absorption spectra are used to reveal new excited states, some of which are also seen in two-photon spectroscopy. A discussion of excited state dynamics following the femtosecond optical excitation is focused on the nature of the extended excitations on the linear chains.

The Second International Workshop  
"Advances in Silicon-Based Polymer Science"  
Makaha, Oahu, Hawaii, December 16-20 1990

EXCITED STATES OF POLYSILANES: HIGH RESOLUTION LOW  
TEMPERATURE SPECTROSCOPY AND THEORETICAL MODELLING

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The excited electronic states of poly-di-n-hexyl-silane (PDHS) have been characterized in glassy solutions at liquid helium temperatures by high resolution absorption, emission, as well as holeburning spectroscopy.

The excitations of the polymer chain are described by a model which regards the polymer as a weakly disordered chain, in which the excitation is treated as a Frenkel exciton. This model was successfully used to numerically simulate the absorption spectra, to explain the observed holeburning spectra as a function of excitation wavelength, and to predict the position of the maximum and the width of the emission spectra.

From the confrontation of the experimental data with the predictions of the model the rates and ranges of energy transfer are evaluated and definite predictions about the dispersion of the spectral properties of the excited states are made. The model also suggests explanations for the behavior of polysilanes in general.

**THE PHOTOCHEMISTRY OF SUBSTITUTED SILANE HIGH POLYMERS**

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**ABSTRACT:** The unusual spectroscopic properties of high molecular weight substituted silane polymers have been discussed in terms of a variable length, chromophore segment model. The segments, which we have previously suggested may be trans or nearly trans segments, are partially electronically decoupled by conformational defects, but communicate by rapid energy transfer. Exhaustive irradiation at short wavelengths in the presence of trapping reagents produces evidence for the formation of substituted silylenes and chain cleaved silyl radicals. The photochemistry is wavelength dependent and while silylene extrusion occurs only at wavelengths below 300 nm, polymer chain scission apparently proceeds at all wavelengths absorbed by the polymer.

The radiation sensitivity of polysilane derivatives drops markedly in the solid state relative to solution. We have addressed this problem both by the

synthesis of more photosensitive polysilanes and by the incorporation of sensitizing additives. While many additives efficiently quench the fluorescence of photoexcited polysilanes, relatively few also accelerate the rate of photo bleaching and hence chain scission. We will discuss our studies on the mechanism of fluorescence quenching and the role that it plays in the photochemistry of polysilane derivatives. In addition, we will describe our recent deep UV lithographic studies on polysilane-sensitizer photoresist combinations.

COMPARISON OF RADICAL ANIONS AND CATIONS OF  
POLYGERMANE AND POLYSILANES

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University of Tokyo

and

Hiroshi Ban  
NTT

The present paper describes the comparison of radical anions and cations of polygermane and polysilanes.

The transient absorption spectra of the radical cation of poly(dibutylgermane) have been observed by using pulse radiolysis techniques. The maximum wavelength and the band width of the absorption due to the radical cation of poly(dibutylgermane) are very different from those of the radical anion of poly(dibutylgermane)<sup>1</sup>. These results are very different from results observed for transient optical absorption spectra due to polysilane radical anions and cations, which have very good pairing properties, that is, very similar absorption spectra<sup>2</sup>.

The stabilities and reactivities of radical anions and cations of polysilanes and polygermane have been studied by using pulse radiolysis techniques. The radical cations of polysilanes and polygermane are more stabilized and less reactive than the radical anions of them. The radical ions of polygermane are more stabilized and less reactive than the radical ions of polysilanes.

The transition energies from ground states to excited states of polysilane and polygermane radical ions are compared with those of neutral molecules. These results are discussed on the basis of electronic structures of polysilanes and polygermanes.

References

1. H.Ban, A.Tanaka, N.Hayashi, S.Tagawa and Y.Tabata, Radiat. Phys. Chem. 1989, 34, 587
2. S.Tagawa, 200th ACS Meeting, Washington, Symposium on Sigma-Conjugated Polymers, Polymer Preprint 1990, 31, 242

## Study of Third Order Optical Nonlinearities of Polysilanes by self-focusing

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Organic polymers with large and fast nonlinearities are currently receiving lot of attention in view of potential applications in information processing. Polysilane polymers offer the advantages of being transparent in the entire visible region and forming thin films of good optical quality. Third harmonic generation and four wave mixing techniques are widely used to measure the third order susceptibility  $\chi^{(3)}$ . We describe a method of studying third order nonlinear optics of polymers from measurements of self-focusing in solutions. Self-focusing of laser beams is an interesting third order nonlinear effect which results from wave front distortion of a single mode laser beam with a gaussian profile. It occurs when the refractive index  $n$  of the nonlinear medium increases with beam intensity as per equation  $n = n_0 + n_2 \langle E^2 \rangle$  where  $n_0$  is the field independent index,  $\langle E^2 \rangle$  is the time averaged square of the electric field and  $n_2$  is the nonlinear coefficient related to  $\chi^{(3)}$ . For  $Q$  switched laser pulses in liquids the pulse width of order nanoseconds is much larger than the picosecond response time of the medium. One could then apply the quasi steady state theory to derive the critical power  $P_{cr}$  from observations of self-focusing threshold powers. Our group carried out measurements of the threshold power for self-focusing using a ruby laser with different sample lengths by monitoring the beam diameter at the exit window as a function of incident laser power. The critical power for self-focusing is obtained and  $n_2$  calculated from the relation  $P_{cr} = 3.77\lambda^2 c / 32\pi^2 n_2$ . For linearly polarized light in isotropic materials  $\chi^{(3)}$  is related to  $n_2$  by the equation  $n_2 = \frac{12\pi}{n_0} \chi^{(3)}$ . We studied several polysilane polymers in n-hexane and tetrahydrofuran solutions. The values obtained for  $\chi^{(3)}$  are in the range of  $10^{-12}$  esu. The method is shown to be sensitive and can be successfully used for study of conformational transitions of conjugated polymer chains. For some of the samples  $\chi^{(3)}$  is also measured by degenerate four wave mixing which give somewhat lower values. The advantages as well as the limitations of the technique are discussed.

## Electronic structures of $\sigma$ -conjugated polymers

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Results of the band theory for  $\sigma$ -conjugated polymers, such as polysilanes, polygermanes, their hetero-copolymers and 2-dimensional silicon network polymers, are discussed. The calculations for the electronic structures of the parent polysilanes whose unit cell consists of  $n$  trans links and a gauche link, and alternated copolymers  $\text{Si}_n\text{Ge}_m$  show that the  $\sigma$ -conjugation along a backbone chain is hardly disturbed by the existence of gauche defects and hetero-atoms. The electronic structure of polysilane with multiple phases, on the other hand, corresponds to the hetero-junction between one-dimensional semiconductors with different band gaps. The carrier is localized in the smaller gap region by the potential barrier. The barrier height for electrons is much larger than that for holes. It is the origin of the large mobility difference between electrons and holes. Silicon network polymers exhibit quite different optical properties from linear polysilanes. Their absorption spectra have completely different profiles, and they have broad photoluminescence spectra in the visible light region. These optical properties are attributed to a silicon network structure with a high dimensionality close to that of a 2-dimensional structure.



## **Time resolved studies of electronic transport in Si and Ge backbone polymers**

**M.A. Abkowitz and M. Stolka**  
**Xerox Corporation, 800 Phillips Road, Webster, N.Y. 14580**

Time resolved transport studies in alkyl and aryl substituted Si and Ge polymers together with xerographic discharge measurements clearly demonstrate the ability of a wide variety of these polymers to transit holes, photo-generated (or photoinjected) at one surface under an applied field, through the film bulk to the opposite surface with negligible loss of these carriers to deep traps. Average carrier velocity per unit field (i.e., the drift mobility  $\mu$ ) is measured by the small signal current mode time-of-flight technique (TOF). Carrier range (average distance an injected carrier travels before being immobilized in a deep trap) is xerographically determined. Three results will be discussed in detail as follows: (1) The mechanism of electronic transport in the glassy state which is established to be hopping among energetically inequivalent sites on the polymer main chain<sup>1</sup> (rather than band motion); (2) Elucidation of the mechanism by which drift mobility in a given polymer can be modified by chemical doping; and (3) The effect on transport behavior of the glass transition process (general) and side chain melting (specific to only certain alkyl substituted species<sup>2</sup>).

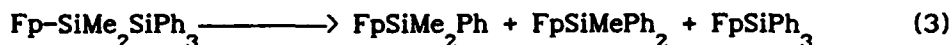
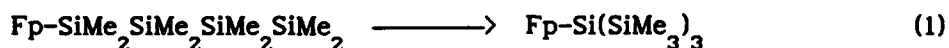
1. See M.A. Abkowitz, M.J. Rice and M. Stolka, *Philos. Mag* **B 61** 25-57 (1990).
2. F.C. Schilling, F.A. Bovey, A.J. Lovinger and J.M. Zeigler, Chapter 21 in *Silicon Based Polymer Science*, Edited by J.M. Zeigler and F.W.G. Fearon, *Adv. in Chem. Series*, vol 224 (ACS, Washington, D.C., 1990).

## Transition Metal Oligosilane and Polysilane Activation

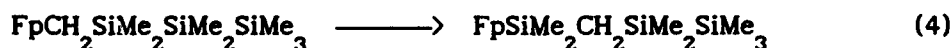
Keith H. Pannell, S. Vincenti, and Toshiaki Kobayashi

University of Texas at El Paso, El Paso, TX. 79968

The effect of transition metals upon oligo- and polysilane photochemistry is profound. In the case of oligosilane chemistry certain transition metal substituents e.g.,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$ , Fp, and  $(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2^-$ , IFp, affect a major activation and create new photochemical transformations leading to skeletal isomerizations, eq. 1, 2, and deoligomerizations, eq.3



Other substituents effectively shut down photochemical reactions of oligosilanes, for example ferrocenyl substituents,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)$ , Fc. Separation of the oligosilane moiety from the metal atom by a methylene group changes the nature of the photochemistry exhibited by the Fp and IFp complexes, but is also dependant upon the position of metal substitution. Two examples are provided for 1- and 2-substituted trisilanes, eq. 4 and 5



Extension of such metal substituents to high molecular weight polysilanes has in general a stabilizing influence upon the photochemistry. Thus, as previously reported, placement of Fc units into a high molecular weight polysilanes retards the depolymerization reactions. Similar retardations are observed for the Fp substituents, but most markedly we find that  $\text{Cr}(\text{CO})_3$  substituents are very good at protecting the integrity of polysilanes under photolytic conditions. Since this group is readily removed to "reactivate" the polysilane, it has certain interesting potential applications.

Such chemical systems will be described, detailed and discussed.

**Silicon Network Polymers: Properties and Applications\***

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Michael S. Knapp  
The Pennsylvania State University  
University Park, PA; and  
Rod R. Kunz and Mark W. Horn  
Lincoln Laboratory  
Massachusetts Institute of Technology  
Lexington, MA**

The synthesis of a new class of inorganic network materials, the polysilynes  $[\text{RSi}]_n$ , has been accomplished by reductive condensation of alkyl and aryltrichlorosilanes. The important parameters necessary for the synthesis of soluble, stable, high molecular weight polymers of this structure will be discussed. Synthesis of copolymers, including both all-silicon materials and backbones containing heteroatoms, can be used to tailor the chemical and physical properties of the polymers. Tailoring the reactivity and surface characteristics of the silicon network backbone can be accomplished by functionalization of a precursor polymer with a variety of groups. The polysilyne polymers contain all silicon bonds in the polymer backbone, and although stoichiometrically analogous to polyacetylenes, exist as amorphous networks of linked alkylsilicon fragments. They therefore display many of the optical and electronic properties of soluble semiconductor clusters. Actual and potential applications of the new materials as deep UV photoresists, waveguides, photopatternable abrasion-resistant coatings, and precursors to ceramic films will be described.

\*The Penn State portion of this work was sponsored by the National Science Foundation Divisions of Polymer Chemistry and Solid State Chemistry. The Lincoln Laboratory portion was sponsored by the Defense Advanced Research Project Agency.

## PRECERAMIC ORGANOSILICON POLYMER/METAL POWDER COMPOSITES: THEIR PYROLYTIC CONVERSION TO CERAMICS.

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Massachusetts Institute of Technology  
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The pyrolysis of ceramic/metal systems is a known preparative route to ceramics composed of the metallic element as well as elements contained in the original ceramic (e.g.,  $\text{SiC} + \text{Ti} \longrightarrow \text{TiC} + \text{TiSi}_2$ ). We have found that preceramic organosilicon polymer/metal powder composites (which are easily prepared) when pyrolyzed in a stream of argon to 1500°C give crystalline ceramics. These are either single phases or two or more phases and are derived from the elements brought into reaction: the metal, silicon, carbon and, in some cases, nitrogen. Carbon-free ceramics usually are obtained when the pyrolysis is carried out in a stream of ammonia. Among the organosilicon polymers used in this research are the Ethyl polysilazane, the Nippon Carbon polycarbosilane, the 3M/MIT  $[(\text{CH}_3\text{SiH})_{0.4}(\text{CH}_3\text{Si})_{0.6}]_n$  polysilane and Ti, Zr and Hf-containing polysilanes. The transition metals used were mostly those of Periodic Groups 4, 5 and 6. In general, carbides, silicides and nitrides were formed in the pyrolysis of such organosilicon polymer/metal powder composites.

## **Thermal Sensitivity of Hydropolysilanes**

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The thermal sensitivity and degradation of hydropolysilanes have been investigated by thermogravimetric analysis in both nitrogen and air at temperatures up to 900 °C. Hydropolysilanes containing Si-H bonds are easily crosslinked in air at elevated temperature and gain weight by reacting with oxygen up to 490 °C. High residual weight is noted in these materials up to 900 °C and especially when the hydropolysilane contains branch sites. Pyrolysis of these polymers in nitrogen reveals decomposition temperatures between 240 °C and 280 °C with residuals substantially less than those in air. The residual weight was observed to increase as the content of Si-H or/and silicon branch sites increase. For the copolymer prepared from the methylhydrodichlorosilane and methyltrichlorosilane monomers, the residue at 900 °C in nitrogen was approximately 63% of the starting mass. This type of polymer appears to show significant potential as a silicon-carbide precursor material.

# IONIC RING-OPENING POLYMERIZATION OF CYCLOSILAZANES

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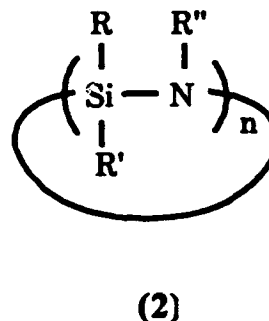
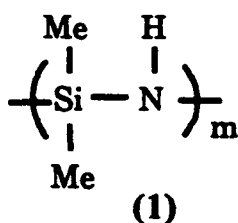
E. DUGUET, M. SCHAPPACHER, A. SOUM

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Polysilazanes (1) are potential macromolecular precursors to silicon nitride and silicon carbonitride ceramics. However the usual synthesis by ammonolysis or aminolysis of dihalosilanes leads to low molar mass volatile oligomers.



In order to increase the chain length of the polysilazanes and, therefore, to provide suitable ceramic synthons, the ring-opening polymerization of cyclosilazane monomers (2) has been investigated.

Various cyclosilazanes have been reacted with both cationic and anionic initiators. These reactions give two main products : larger size cyclosilazanes and linear oligomers. The respective amount of cyclic and linear compounds, the kinetic of their formation and their molar mass, highly depend on both the size of the initial cyclic monomer and the nature of the nitrogen substituent.

These results are explained on the base of the electronic structure of the initial monomers.

STRUCTURE AND PROPERTIES OF CERAMIC FIBERS  
PREPARED FROM ORGANOSILICON POLYMERS

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Midland, MI 48686-0995

Ceramic fibers are prepared from organosilicon polymers by melt-spinning, cross-linking, and pyrolysis. Fibers in the Si-C-O or Si-C-N-O systems display a rich nanostructure consisting of some or all of the following metastable phases: (1) An amorphous, continuous siliconoxycarbide or siliconoxycarbonitride phase; (2) dispersed carbon nanocrystallites; (3) dispersed  $\beta$ -SiC or  $\text{Si}_3\text{N}_4$  nanocrystallites; and (4) closed, globular nanopores. The crystalline phases increase in volume fraction and crystallite size as stoichiometry approaches the crystalline composition and as pyrolysis temperature increases. Pore size increases and total pore volume decreases with increasing pyrolysis temperature. Considerable variation in ceramic fiber composition can be achieved by varying pyrolysis atmosphere. Polycrystalline SiC fibers can be produced by pyrolysis above 1600°C.

Fiber diameters range from 7 to 20  $\mu\text{m}$ . Elastic moduli vary from 140 to >420 GPa (20 to >60 Msi) and are controlled by composition, nanostructure and fiber density. Fiber densities range from ~2.2 to >3.1 g/cm<sup>3</sup>. Tensile strengths range up to ~5 GPa (700 ksi) and are Griffith flaw-controlled.

Use of ceramic fibers in ceramic matrix composites at high temperature and some of the unsolved problems in fiber/matrix interactions will be discussed.

**Polymers from and of Silyl Acetylenes for Ceramic Fibers,  
Electrical and Optical Properties**

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Ames Laboratory  
Iowa State University  
Ames, Iowa 50011

Simple, efficient syntheses of silylene (and disilylene) -ethynylene,  $\left[ \text{R}_2\text{Si}-\text{C}\equiv\text{C} \right]_n$ , silylene-diethynylene,  $\left[ \text{R}_2\text{Si}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C} \right]_n$ , and silylene-ethylene,  $\left[ \text{R}_2\text{Si}-\text{CH}=\text{CH} \right]_n$ , will be described along with various methods for crosslinking, transformation into ceramic fibers and use as densification and scintering agents.

The catalytic polymerization of diethynylsilanes and -germanes produces novel polymers which when doped are electrically conducting. By far the most interesting properties of these new conjugated polymers are their optical properties which make them promising candidates for optoelectric devices. The question of the nature(s) of the electronic states produced upon doping and photomodulation will be probed.



## SYNTHESIS, MICROSTRUCTURE, AND THERMAL DEGRADATION OF POLY(1-SILAPENT-3-ENES)

**YOUNG TAE PARK, YOUNG HOON KO, STEPHEN Q. ZHOU**

**AND**

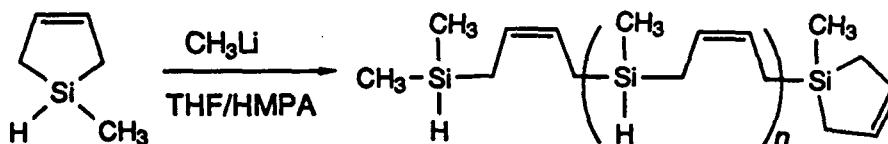
**WILLIAM P. WEBER**

Department of Chemistry

Department of Chemistry  
University of Wisconsin

**Madison, WI 53706**

Anionic ring opening polymerization of 1-methyl-1-silacyclopent-3-ene, 1-silacyclopent-3-ene, 3,4-benzo-1-methyl-1-silacyclopentene, 3,4-benzo-1-silacyclopentene, and 3,4-benzo-1-phenyl-1-silacyclopentene have been carried out. The low molecular weight of these polymers permits end groups analysis by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR. This information provides insights into the mechanism of these polymerization reactions. Such difunctional polymers which possess both reactive Si-H and C+ C bonds may undergo catalyzed crosslinking reactions. The formation of relatively high char yields on thermal degradation of these polymers and the composition of these chars will be discussed.



## **SYNTHESIS AND REACTIONS OF MULTIFUNCTIONAL METHACRYL AND STYRYL SILOXANE MACROMERS**

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G.A. George and M.S. O'Shea

University of Queensland  
St. Lucia, Queensland, Australia

The copolymerization of silicones with other polymer systems has many potential advantages, but there are also difficulties associated with the very different natures of the two polymer systems. A study has been made using styrene as a model reaction system.

Difunctional and Multifunctional siloxane macromers of molecular weights ranging from 1600 g/mole to 100000 g/mole and containing between two and ten methacryl or styryl groups were synthesized.

The copolymerization of some of these macromers with styrene (10-50% wt macromers) in bulk at 60°C using AIBN as an initiator was studied and the resultant copolymers analysed by UV, HNMR, GPC and DMA.

Cloud point measurements showed that phase separation during copolymerization occurred in all cases.

The time to phase separation was decreased by;

- increase in the macromer molecular weight
- a decrease in the functionality of the macromer
- an increase in the weight % feed of macromer.

Unlike monofunctional macromers of similar weights (1,2) these polyfunctional macromers show a high degree of conversion of the methacryl functional groups compared to styrene and a high inclusion of the macromer in the resultant copolymer with styrene.

The copolymers formed from the multifunctional macromer (Mol Wt 16000 g/mole Functionality = 6) varied from being moderately crosslinked siloxane rich materials (low conversion time, high wt% macromer feed) to highly crosslinked brittle materials (high conversion times).

Dynamic mechanical analysis revealed that all the copolymers containing significant amounts of the other component (i.e. > 2 wt%) possessed phase separated morphologies.

### **References:**

- 1 - Cameron, G.G. and Chisholm, M.S., Polymer, 1985, V26, 437.
- 2 - Tsukahara, Y., Hayashi, N., Jiang, X., and Yamashita, Y., Polym. J., 1989, 5, 377.

## Side Chain Liquid Crystalline Polymers with Silphenylene-Siloxane Main Chains

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### Abstract

Side chain liquid crystalline polymers (SCLCP) with silphenylene-siloxane backbone have been synthesized and characterized.

First, silphenylene-siloxane polymers containing hydrosilane, Si-H, groups were prepared. Both polymerizations in a basic media using 1,4-bis(hydroxydimethylsilyl)benzene and bis(1-pyrrolidinyl)-methylsilane and in a neutral condition using bis(1,1-tetramethylene-3-phenylureido)methylsilane as a comonomer formed crosslinked polymers. However, a soluble polymer could be successfully synthesized in an acidic condition using methyldichlorosilane as the comonomer.

SCLCPs were prepared by hydrosilylation reaction between a backbone polymer and a terminal-olefinic side chain mesogenic monomer. When biphenyl group was used as a mesogenic core, presence of mesophase was only indicated by the isotropization peak appeared on the shoulder of the melting peak in the DSC thermogram. By changing the mesogenic core from biphenyl to phenylbenzoate moiety, however, melting temperatures were greatly reduced to form a stable nematic phase.

In contrast to this backbone, polymethylsiloxanes with the same side chains exhibited smectic phases in wider temperature ranges. The less stability of the mesophases in silphenylene-siloxane polymers can be attributed to the rigidity of the backbone and the larger distance between the side chain along with the main chain.

### Acknowledgment

The support provided by Sumitomo Metal Industries, Ltd. for Maki Itoh to work at the University of Massachusetts is gratefully acknowledged.

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The Second International Topical Workshop  
*ADVANCES IN SILICON-BASED POLYMER SCIENCE*

# *POSTER SESSION ONE ABSTRACTS*

Nickel-Catalyzed Silane Dehydrogenation  
Forming Cyclic and Bicyclic Oligomers

PS1-1

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Baton Rouge, LA 70898

Abstract:

Two general groups of nickel catalysts for dehydrogenative coupling of silanes were discovered. Two specific members of these groups were highly active, converting alkyl- and phenyl-silanes to oligomeric mixtures of polysilanes by a classical condensation mechanism. When *n*-butylsilane was dehydrogenated in the presence of one such catalyst, bicyclic octa- and heptasilanes were identified by GCMS as the major products, in addition to monocyclic and linear oligomers. Integration of the <sup>1</sup>H-NMR spectrum confirmed that alkyl hydrogens and silicon hydrides were present in the expected ratio. Disubstituted silanes were efficiently converted to 1,1,2,2-tetrasubstituted disilanes. Other interesting characteristics of these reactions will be compared with those reported in the literature.

SYNTHESIS AND PHOTOCHEMISTRY OF  
(p-VINYLPHENYL)METHYLPOLYSILOXANE

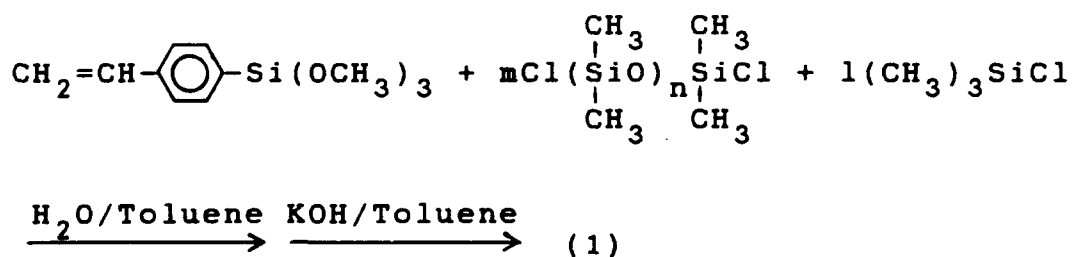
PSI-2

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Styrene monomer has been used for one of photopolymers.

In order to utilize the photopolymerization property of styrene,  
we synthesized (p-Vinylphenyl)methylpolysiloxane(1) as below.



$\lambda_{\text{max}}$  of (1) was 254.1nm and  $\lambda_s$  were 249.6 and 261.6nm.

And  $\epsilon$  measured by (p-Vinylphenyl)trimethoxysilane was 19500.

(1) showed excellent photosensitivity and the conversion  
after irradiation of  $400\text{mJ}/\text{cm}^2$  at 254nm was over 80%. It was  
excellent yeild compared with 63% of (p-Vinylphenyl)trimethoxy-  
silane.

**Synthetic Investigations of Aromatic Amine  
Functional Polydimethylsiloxane Oligomers**

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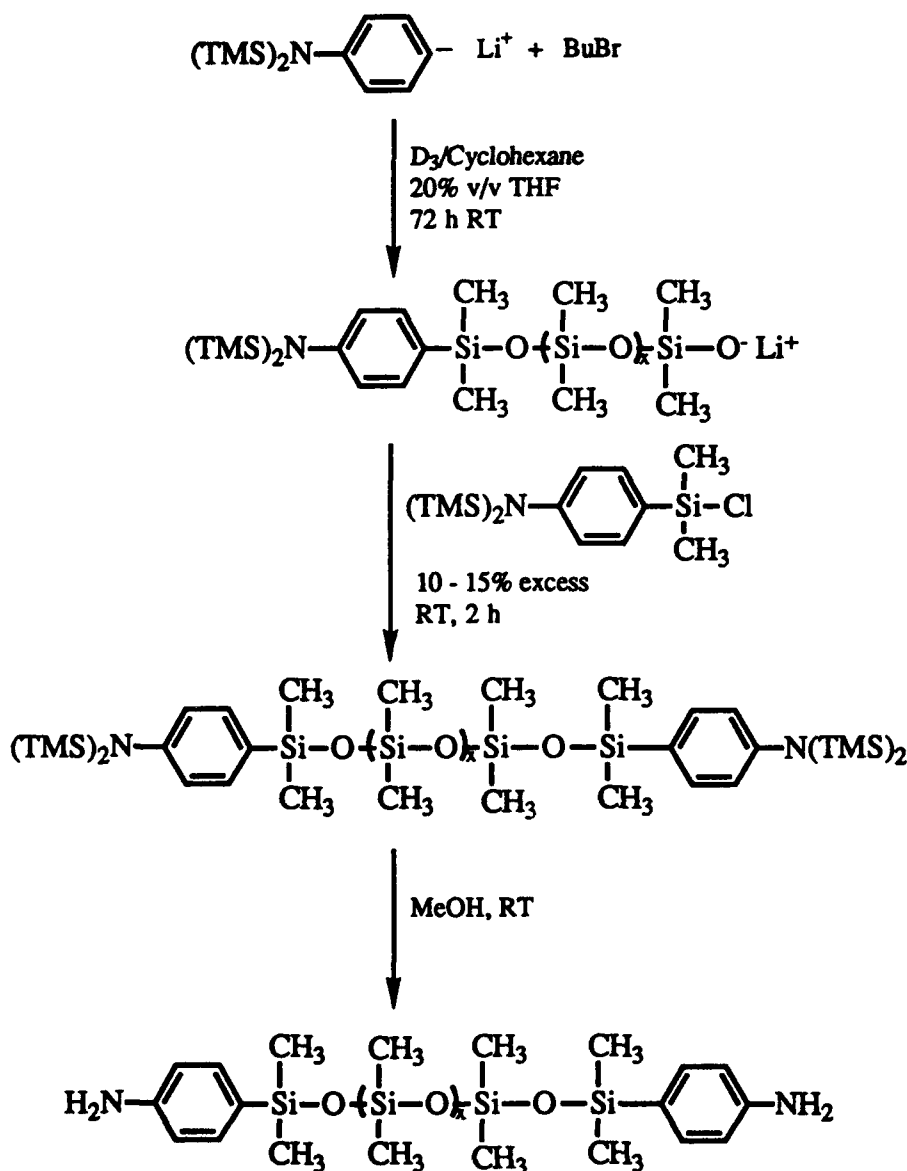
**Abstract**

**$\alpha,\omega$ -Arylamine Functional Polydimethylsiloxane Oligomers**

Over the past several years, a significant effort has been devoted to investigations of high performance polyimides containing thermo-oxidatively stable, flexible, block segments. Telechelic polydimethylsiloxane oligomers are almost unique among flexible components in possessing a combination of these properties. It has been demonstrated that incorporation of aminopropyl terminated polydimethylsiloxane oligomers into polyimides provides flexibility needed for high temperature adhesives and provides hydrophobicity which results in dramatically increased durability of structural adhesives to humid environments.

This particular work has focused on the preparation of telechelic amine functional oligomers with no aliphatic backbone character. It is anticipated that these will be more stable than the aminopropyl functionalized systems due to the absence of backbone aliphatic C—H bonds. These materials have now been prepared with narrow molecular weight distributions according to the procedure outlined in Scheme 1. Functionality and molecular weight have been characterized and confirmed using endgroup titrations,  $^{29}\text{Si}$  NMR,  $^1\text{H}$  NMR, and gel permeation chromatography against polydimethylsiloxane standards. The molecular weight of these narrow distribution

Scheme 1. Synthesis of Arylamine Terminated Polydimethylsiloxane



polymers can be controllably increased in redistribution reactions with octamethylcyclotetrasiloxane (D<sub>4</sub>) using anionic catalysts. Thus, this allows for a low molecular weight oligomer to be converted to any desired higher molecular weight in a facile reaction step. The redistribution step has been monitored and confirmed primarily using gel permeation chromatography.

We are now in the process of investigating the reactivity of these new oligomers in imidization and amidation reactions in order that they can be incorporated into high performance polyimides and aramids. Thermal and oxidative stability will be compared to the analogous polymers containing the previously utilized aminopropyl terminated polymers. A combination of techniques will be utilized for the analytical evaluation including TGA-MS and TGA-FTIR.



## Electrical Conductivity of Various Polysilanes

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Measurements of the electrical conductivity of different polysilanes have been carried out over an extended range of temperature and D.C. field. D.C. conductivities of these samples in a dry N<sub>2</sub> atmosphere were measured with a picoammeter. The I-V characteristics were obtained on polysilane films that were deposited on glass using aluminum contacts at applied voltages from 2 to 30 V. The conductivities were temperature dependent and ranged from 10<sup>-10</sup> to 10<sup>-11</sup> (Ω-cM)<sup>-1</sup> at room temperature. All polysilanes evaluated were unstable at high field strength. The temperature dependence of conductivity at constant field was linear in Arrhenius plots for these polymers with activation energies of the order of 0.78 eV. These experimental results suggest that electrical conductivities of polysilanes are associated with the Si-Si main chain backbone and not with the side groups.

## **Photolithographic Studies of Polysilane Polymers in Reactive Ambients**

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Several polymers prepared from n-propyl methyl and phenyl methyl silanes and from cyclohexyl methyl and n-propyl methyl silanes by a standard Wurtz condensation method were subsequently fractionated to yield polymers with molecular weight distributions less than 4. These materials were characterized by infrared and ultraviolet spectrophotometry, thermogravimetric analysis and gel permeation chromatography.

These materials degrade into lower molecular weight fragments under exposure to UV radiation but tend to plasticize in the presence of oxygen due to the formation of siloxanes. These polymers have been examined as self-developing resists using low intensity ( $< 15$  mW) broadband UV radiation (220-260 nm) in air and in controlled ambients of  $\text{NH}_3$  and  $\text{CF}_4$ . The photobleaching behavior of these materials in the same ambients has also been examined. The use of a controlled ambient significantly improves the photolithographic performance of these materials and allows for their utilization with low intensity sources.

## RELAXATION DYNAMICS OF ELECTRONIC STRUCTURE IN POLYGERMANE

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(University of Tokyo)

The present paper describes the relaxation dynamics of the electronic states of poly(dibutylgermane) by using the relaxation dynamics of transient absorption spectra of the radical anion.

Recently we have reported transient absorption spectra of radical anions and cations of polysilanes by using pulse radiolysis techniques<sup>1-5</sup>. Transient absorption spectrum of polygermane has also published very briefly<sup>4</sup>.

Relaxation dynamics in polysilanes due to the spatial energy transfer from the higher energy segments to the lower energy segments in polymer chains have been studied by time-resolved fluorescence depolarization<sup>6,7</sup>.

The time-resolved absorption spectra of the radical anion of poly(dibutylgermane) have been observed by pulse radiolysis techniques. The blue shift and the absorption band narrowing of the transient absorption of the radical anion of poly(dibutylgermane) have been observed very clearly on subnanosecond and nanosecond time scale. The relaxation dynamics are explained by both the spatial electron transfer between segments with different sigma-conjugated chain lengths and the difference of the most stable polymer structures of the neutral and the charged polygermane.

The reactivities of unrelaxed and relaxed states of the radical anions of poly(dibutylgermane) with some electron scavengers are very different and are explained mainly by the different stability of the radical anions with the different sigma-conjugated polymer segments.

## References

1. H.Ban, K.Sukegawa, and S.Tagawa, *Macromolecules* 1987, 20, 1775
2. H.Ban, K.Sukegawa, and S.Tagawa, *Macromolecules* 1988, 21, 45
3. S.Tagawa, M.Washio, Y.Tabata, H.Ban and S.Imamura, *J. Photopolymer Sci. Tech.* 1988, 1, 323
4. H.Ban, A.Tanaka, N.Hayashi, S.Tagawa, and Y.Tabata, *Radiat. Phys. Chem.* 1989, 34, 587
5. S.Tagawa, *Polym. Prep.* 1990, 31, 242
6. Y.R.Kim, M.Lee, J.R.G.Thorne, R.M.Hochstrasser and J.M.Zeigler, *Chem. Phys. Lett.* 1988, 145, 75
7. J.Michl, J.W.Downing, T.Karatu, K.A.Klingensmith, G.M.Wallraff and R.D.Miller, *Inorganic and Organometallic Polymers*, ACS Symposium Series 360, Zeldin, Wvnnne, Allcock eds., ACS Washington DC Chap. 5, 61 (1988)

HYDROSILYLATION OF ALLYL CARBONATES BY POLYMETHYLHYDROSILOXANE  
AND RELATED SIDE-REACTIONS.

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A water soluble polysiloxane was prepared as a model for a controlled drug delivery system by cohydrosilylation of 80% allyl polyethyleneoxide and 20% allyl phenyl carbonate (APC) with polymethylhydrosiloxane (PMHS) in order to study the hydrolysis of the carbonate function under various pH conditions.

However the structure of the polymer did not correspond to the expected one. Thus in order to identify potential side-reactions, a series of model compounds was prepared by hydrosilylation of allyl p-fluorophenyl carbonate (AFPC), allyl butyl carbonate (ABC) and allyl ethyl carbonate (AEC) with PMHS.

A detailed investigation of the structure of these polymers showed that about 50% of the carbonate functions are decomposed during the hydrosilylation reaction. The phenol, p-fluorophenol, butanol and ethanol moieties resulting from the cleavage of the carbonate bond reacted with SiH groups of the polymer leading to Si-O-R side-groups as confirmed by <sup>29</sup>Si NMR.

The behavior of allyl carbonates towards hydrosilylation was also compared with that of allyl carbamates and the mechanism of the reaction will be discussed.

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**THERMOCHROMISM OF DIALKYLSILANES**

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**ABSTRACT:** A number of dialkyl and diaryl polysilanes have been shown to be thermochromic in both solution and the solid state. The origin of this thermochromism, particularly that observed in solution, has been the subject of a number of reports.<sup>1,2</sup> Much of the interest has centered on the question of whether the conformational changes believed to be responsible for the appearance of the long wavelength UV transition observed at low temperature are due to inter or intramolecular effects. It has been proposed that the thermochromism of poly(dihexylsilane) (PDHS) is due to a single molecule coil to rod transition<sup>1</sup> at low temperatures (ca.-35°C). Light scattering data at low temperatures, however, show only large increases in scattering intensity consistent with aggregation at the transition temperatures. Similar results are obtained in variable temperature neutron scattering experiments.

The structure of the side chain substituents can significantly effect the thermochromic behavior. For example, many unsymmetrically substituted dialkyl polysilanes are also thermochromic in solution, however, the rate of polymer precipitation at low temperatures is slower then that observed for PDHS. Low temperature light and neutron scattering results together with recent fluorescence studies and lifetime measurements will be presented in support of a simplified hypothesis which seems to accommodate the data.

#### REFERENCES

1. L. A. Harrah, J. M. Zeigler, *J. Polym. Sci. Polym. Lett.*, Ed. (1985) **23**, 209.
2. P. Trefonas III, J. R. Damewood, R. West, R. D. Miller, *Organometallics*, (1985) **4**, 1318.

CONFORMATIONAL ANALYSIS ON A SERIES OF DI-N-ALKYL  
POLYSILYLENE MODEL COMPOUNDS, William J. Welsh, Samuel  
Tersigni, Peter S. Ritter, and Wangkan Lin, Department of  
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63121.

We are investigating the symmetrically substituted di-n-alkyl polysilylenes  $[-SiRR-]$  with  $R = \text{methyl} \rightarrow \text{hexyl}$ . In this poster we focus on both the conformational dynamics of the di-methyl model compound and on the torsional potentials of the di-ethyl and di-hexyl members of our series. Conformational energies were calculated using the new MM3 molecular mechanics program; the molecular dynamics (MD) trajectories were evaluated using MM3-MD, an MD program developed in-house based on the MM3 force field. Our results indicate that the di-methyl and di-ethyl homologs prefer an off-trans ( $\phi \sim 160-170^\circ$ ) backbone conformation. The di-ethyl sidechains prefer "chair"-like conformations with a  $40^\circ$  tilt in the chair's back. The conformational profiles of the di-ethyl and di-hexyl homologs are similar, although the conformational energy wells associated with the latter are steeper. This research is funded by a grant from the Petroleum Research Fund, administered by the Donors of the American Chemical Society.

The Second International Topical Workshop  
*ADVANCES IN SILICON-BASED POLYMER SCIENCE*

# *POSTER SESSION TWO ABSTRACTS*



## **Anaerobic Silicone Adhesives**

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Silicone adhesives and sealants have many unique characteristics — including excellent thermal stability, chemical resistance and electrical properties — and a wide range of applications in both industrial and household fields. The most common mechanisms for curing silicone adhesives are condensation and addition reactions. However, both of these have inherent limitations. With the former for example, deep-section curing is slow and sufficient time is necessary to ensure complete curing. The addition-cure reaction on the other hand necessitates the use of heat to give good adhesion.

We sought to eliminate such drawbacks by formulating and examining a number of new anaerobic-cure silicone compositions. After synthesizing several silicone resins containing methacrylate groups we formulated samples of anaerobic silicone adhesives. These experimental formulations are stable and do not cure when exposed to air. When placed in an airless environment provided by a narrow space between mated metal surfaces, these silicones cure immediately and demonstrate outstanding adhesion. Potential applications for these unique anaerobic silicone adhesives include mechanical assembly systems. We will discuss these new anaerobic silicone formulations, their properties and applications.

## Synthesis and Photooxidation of Hydropolysilanes

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Hydropolysilane copolymers and terpolymers were synthesized by the reaction of methylhydrodichlorosilane and other comonomers (e.g. phenyl-methyldichlorosilane and methyltrichlorosilane) using a sodium dispersion in toluene or light oil, with toluene as the solvent. Synthetic methods evaluated included both the normal and inverse addition modes. Polymers prepared using toluene sodium dispersions were different than those prepared using the light oil sodium dispersions. Additional peaks in the infrared spectra at  $2922\text{ cm}^{-1}$  and  $2853\text{ cm}^{-1}$  indicate that the light oil becomes incorporated into the polysilane during synthesis. The presence of this hydrocarbon fraction was found to significantly alter some properties of these polymers.

The photooxidation of these hydropolysilanes have been investigated by infrared spectroscopy. Polymer films were exposed in air to known amounts of UV light which resulted in significant photooxidation of these polymers. The formation of Si-OH ( $3385\text{ cm}^{-1}$ ),  $\text{-C=O}$  ( $1721\text{ cm}^{-1}$ ), Si-O-Si (very strong bands at  $1130\text{-}1000\text{ cm}^{-1}$ ), and the shift of the  $\text{-CH}_3$  bending in Si- $\text{CH}_3$  group from  $1248\text{ cm}^{-1}$  to  $1260\text{ cm}^{-1}$  were used to follow the oxidation of these materials. Interestingly, the Si-H stretching band shifts from  $2080\text{ cm}^{-1}$  to  $2160\text{ cm}^{-1}$  with increasing exposure energy with a concurrent decrease in the integrated intensity of this band. It was found that the Si-H absorbance frequency can be used as a direct means of evaluating the photosensitivity of hydropolysilanes.

## **Optical Properties and UV Photosensitivity of Hydropolysilanes**

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The optical properties and UV photosensitivity of hydropolysilanes for both linear and branched copolymers and terpolymers have been investigated. The UV photosensitivity of these hydropolysilanes were evaluated by UV/VIS spectroscopy on films that were exposed to varying amounts of UV energy. The results indicate that both Si-H units and the silicon branch sites impart photosensitivity to these polymers. Si-H structural units result in greater photosensitivity to oxidation than do the branch sites in these soluble polymers. In photoluminescence studies with an excitation wavelength 344 nM, the linear hydropolysilanes show a single sharp emission peak at 347 nM while the branched hydropolysilanes show an additional emission peak centered at 445 nM with a half height band width of 90 nM. This broad emission band is shown to originate from the high dimensionality of these hydropolysilane structures.

## THE BONDING OF FUNCTIONALISED SILICONES TO SILICA SURFACES

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Organofunctional silane coupling agents have been used successfully for many years on silica surfaces to improve the performance of polymer composites, and to promote retention of properties in the presence of moisture. The bonding mode of these silanes at the silica-resin interface is complex, but now well understood<sup>1</sup>.

Here we present the effect of surface treating glass with several kinds of siloxanes. With the advent of ESCA surface analysis, the possibilities of elucidating changes in the surface composition of polymers submitted to various treatments were considerably improved. Furthermore, the performance of ESCA in the detection of surface functional groups has been extended using derivatization techniques. This results in specific labels for functional groups on the surface<sup>2</sup>.

A variety of silicones containing epoxy, ester, amino, enamine, hydrido and phosphorus functional groups were synthesized, and applied to glass in dilute solution. The effectiveness of coupling the siloxane to the glass fiber was dependant on molecular weight, the degree of functionality, the solvent used to apply the siloxane to the glass fiber, and the siloxane concentration. ESCA studies were diagnostic of the distribution and the binding of these siloxanes on the glass surface.

It is generally held that covalent bonds can form between a hydrolyzed silane and typical silicate surfaces such as glass<sup>3</sup>. However, other theories suggest a dynamic equilibrium at the silane-glass interface, involving the breaking and reformation of bonds in the presence of water<sup>1</sup>. The aim of this study is to evaluate in some detail the adsorption and binding of various siloxanes on glass fibers.

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### References:

- 1 E.P. Plueddeman, "Silane Coupling Agents", Plenum New York, (1982).
- 2 N.H Turner, B.I. Dunlop and R.J. Colton, Anal. Chem., 56, 373 (1984).
- 3 S. Navroij, S.R. Culler, J.L. Koenig and H. Ishida, J. Colloid Interface Sci., 97, 308 (1984).

## DYNAMICS OF ELECTRON AND HOLE PAIRS IN POLYSILANES

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The present paper describes about the dynamics of electron and hole pairs in solid states and liquid solutions.

The time resolved absorption spectra of radical anions and cations of polysilanes have been observed in irradiated solid polysilanes. In the case of polysilanes, the geminate recombination processes of holes and electrons due to diffusion processes are observed, since hole mobilities are very high. ( Generally recombination processes of hole and electron pairs in irradiated solid polymers are due to long range electron transfer processes. Recombination processes due to diffusion of charged species are hardly observed. ) Electron and hole pairs recombine in geminate recombination processes on shorter time scale and in bulk recombination processes on longer time scale in irradiated solid polysilanes. Reaction rate constants and diffusion constants of electrons and holes are estimated on the basis of the analysis of dynamics of electron and hole pairs.

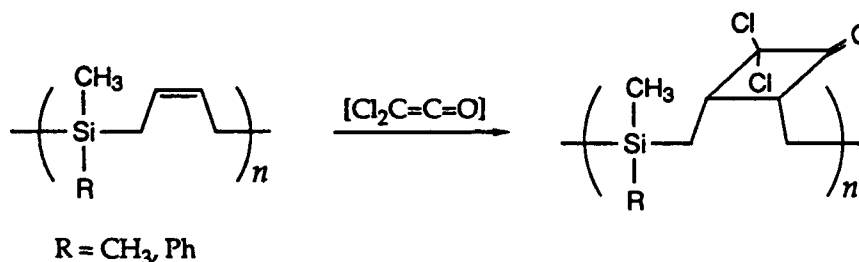
The recombination processes of polysilane radical anions and solvent positive species are protected in irradiated polysilanes in tetrahydrofuran solutions. Similar phenomena are observed in the case of recombination processes of polysilane radical cations and solvent negative species in irradiated polysilanes in chlorinated hydrocarbons such as chloroform and methylene chloride. These phenomena are not observed in the case of recombination of solute ions and solvent ions in irradiated other polymers and low molecular compounds in these solvents.

# ADDITION OF DICHLOROKETENE TO POLY(1-SILA-CIS-PENT-3-ENES)

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Dichloroketene, generated by the ultrasound promoted dechlorination of trichloroacetyl chloride with zinc powder, has been added to the carbon-carbon double bonds of poly(1,1-dimethyl-1-sila-cis-pent-3-ene) and those of poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene). The microstructure of these chemically modified polymers has been determined by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR. Properties of these modified polymers will be presented.



THEORETICAL AND EXPERIMENTAL INVESTIGATION OF A NON-STATISTICAL DISTRIBUTION OF STEREOISOMERS IN THE SYNTHESIS OF ASYMMETRICALLY-SUBSTITUTED POLYSILANE PRECURSORS. Judith E. Durham, Joyce Y. Corey, and William J. Welsh, Department of Chemistry, University of Missouri-St. Louis, St. Louis, MO 63121.

The synthesis of tetrasilanes from certain trisilanes gives rise to a non-statistical distribution of possible stereoisomers, as indicated by chromatographic and spectroscopic evidence. We are applying MM3 force field calculations to explore a conformational basis for this fascinating effect. Specifically, the steric bulk of the pendant groups (e.g., n-butyl, t-butyl, phenyl) may be dictating preferences for certain stereoisomers over others during the chain-growth process. Understanding the origins of this phenomenon could forecast the long-sought goal of selective synthesis of stereospecific polysilanes. This research is funded by a grant from the Donors of the Petroleum Research Fund, administered by the American Chemical Society.

# Anionic Polymerization of the Masked Disilenes to High Molecular Weight Polysilylenes I. Structural Determination of Monomers and the Mechanism of Polymerization

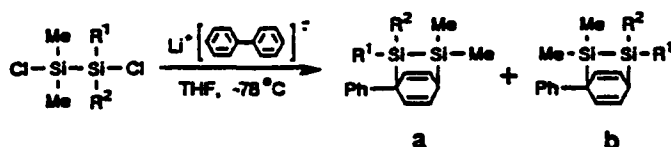
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Very recently we have reported an entirely new method of preparing polysilanes based on anionic polymerization of masked disilenes, 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes. We report here the mechanism of the polymerization together with regioselective synthesis of some masked disilenes.

Masked disilenes prepared from unsymmetrically substituted dichlorodisilanes have two regio isomers, **a** and **b**. Table 1 summarized the results. The predominant isomer is **a** determined by  $^1\text{H}$ -NMR NOE difference spectra.

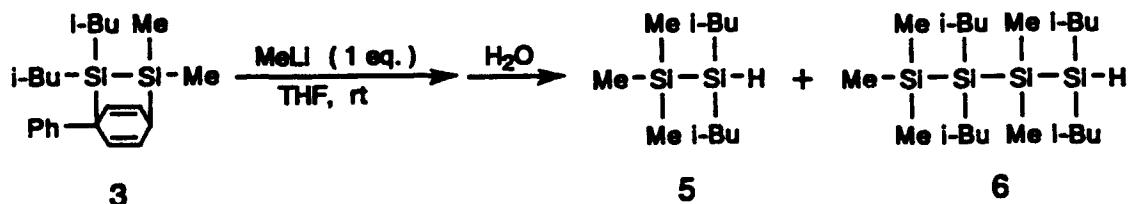
Table I Syntheses of Masked Disilene Monomers



| Monomer | R <sup>1</sup> | R <sup>2</sup> | yield (%) | a : b <sup>1)</sup> |
|---------|----------------|----------------|-----------|---------------------|
| 1       | n-Pr           | n-Pr           | 48        | 85 : 15             |
| 2       | n-Hex          | n-Hex          | 50        | 89 : 11             |
| 3       | i-Bu           | i-Bu           | 24        | 96 : 4              |
| 4       | i-Bu           | Me             | 53        | 89 : 11             |

1) Determined by  $^1\text{H}$  NMR

The reaction of a masked disilene **3** and 1 equivalent of methyllithium followed by quenching with ethanol resulted in the formation of disilane **5** and tetrasilane **6** as low molecular weight products, but no regio isomer of them could be observed. Judging from these results, the polymerization reaction is initiated and propagated by attacking of anionic species such as organolithium and propagating polysilanyllithium at the 8 position of silicon atoms of 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes.





**Synthesis of Linear and Cyclic Copolymers  
of Silylthiophenes**

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**The synthesis and structural characterization of a new class of materials of linear and cyclic copolymers of silylthiophenes will be presented. Our ultimate goal is the understanding of the correlation and coupling of the  $\pi$ -electron systems with  $\sigma$ -electron ones and their effect on the conjugation length.**

The Second International Topical Workshop  
*ADVANCES IN SILICON-BASED POLYMER SCIENCE*

# *POSTER SESSION THREE ABSTRACTS*

POLYGERMYNES: SYNTHESIS AND PROPERTIES OF  
GERMANIUM-GERMANIUM BONDED NETWORK POLYMERS

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The synthesis of the first soluble germanium-germanium bonded network polymers, the polygermynes  $[\text{RGe}]_n$ , has been accomplished using high-intensity ultrasound to effect the reductive condensation of alkyl and aryltrichlorogermanes with liquid sodium-potassium alloy. The resulting yellow to dark brown polymers remain hydrocarbon-soluble and may be cast into transparent films. Spectroscopic data suggest a network backbone analogous to that of the polyalkylsilynes, their silicon-backbone analogues. Reduction of  $\text{RGeCl}_3$  in the presence of varying amounts of  $\text{RSiCl}_3$  results in the formation of apparent silyne/germyne copolymers whose properties are intermediate between those of the parent homopolymers. The synthesis, properties, and pyrolysis behavior of these new materials will be discussed.

**FLUORESCENCE QUENCHING AND PHOTODEGRADATION IN SOLID POLYSILANES**

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**ABSTRACT:** The quantum yield for photoscission in solid polysilanes is nearly two orders of magnitude lower than it is in solution, while the quantum yield of fluorescence is higher. The low rates of photoscission translate into low sensitivity when these materials are employed as high resolution photoresists for deep UV lithography. In an effort to circumvent this problem, we have investigated the effect of a variety of additives on the rate of photodegradation of solution cast films of dialkyl and diaryl polysilanes. We have observed efficient fluorescence quenching both in solution and in the solid state for a number of additives with relatively low reduction potentials ( $< -2.1$  V vs SCE). The Stern-Volmer constants for quenching in the films are generally much higher than those observed in solution. The lifetimes of the polysilanes studied are very short, typically several hundred picoseconds. It is observed that, while some quenchers significantly accelerate the photodegradation, others act as equally effective stabilizers toward photodegradation. Similar behavior is observed in solution, but the effect is much less dramatic. The results of these experiments along with data from fluorescence lifetime experiments will be presented.

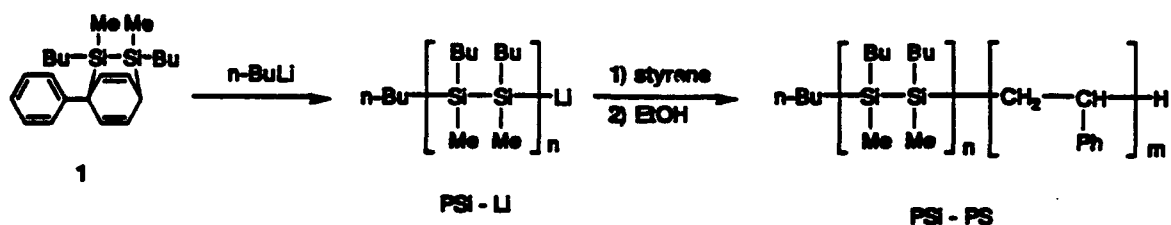
# Anionic Polymerization of the Masked Disilenes to High Molecular Weight Polysilylenes II. Block Copolymerizations

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We have found a novel method of preparing polysilanes based on anionic polymerization of masked disilanes. The polysilane end, prepared in this way, is a living anion enough to initiate the second polymerization with a conventional vinyl monomer. It is possible to prepare block copolymers containing polysilanes, which can not be prepared by the Wurtz-type coupling reactions of dichlorodialkylsilanes. We report here results of block copolymerization of 1-phenyl-7,8-dibutyl-7,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene(1) as masked disilenes with styrene and methyl methacrylate together with the properties of these block copolymers.

Anionic polymerization of the monomer (1) was carried out in THF using *n*-butyllithium as an initiator. The reaction mixture became orange-red when an initiator was added to the THF solution of monomer (1) at  $-100^{\circ}\text{C}$ . After the mixture was stirred at room temperature for 20 minutes, styrene was added to the mixture at  $0^{\circ}\text{C}$ . Then a reddish solution of polysilanyl anion changed to purple-red. The reaction was terminated by addition of a small amount of ethanol. GPC analysis of the polymer indicates the presence of a single polymer. The elution profiles of PSi-PS, detected by both UV (300 nm) and RI, show the same molecular weight distribution curves which should be taken as a strong support for the formation of a block copolymer.



### The Nature of the Silicon Germanium Bond

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There is some considerable interest in the nature of the interactions between Si and Ge, in part because of the role of these elements in semi-conductor technology. However, only recently were the first structural investigations concerning the Si-Ge bond reported [1]. In these studies it appeared that by interchanging the groups attached to the two elements, i.e.  $\text{Me}_3\text{SiGePh}_3$  and  $\text{Ph}_3\text{GeSiMe}_3$ , it was possible to predict the effect upon the Si-Ge bond length. Electron-withdrawing groups on Ge and electron-releasing groups on Si would cause better overlap between the elements, hence a shorter bond length. We have pursued this idea with a fresh pair of isomers,  $\text{Et}_3\text{SiGePh}_3$  and  $\text{Ph}_3\text{SiGeEt}_3$ , however this pair does not exhibit the predicted result. In order to obtain more information we have resorted to *ab initio* calculations on simple molecules  $\text{H}_3\text{EE}'\text{F}_3$ ,  $\text{E} = \text{C, Si, Ge}$ ;  $\text{E}' = \text{C, Si, F}$ . For the systems with Si-C and Ge-C bonds the prediction noted above holds, i.e. electron-withdrawing on the higher energy valence orbital element, electron-donating group on the lower energy element gives rise to shorter bond distances, but for the Si-Ge system it does not.

1. *J. Organometallic Chemistry*, 1990, 384, 41.

## Differential Photocalorimetric Studies of Hydropolysilanes

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Hydropolysilane terpolymers containing silicon branch sites have been investigated by differential photocalorimetry. Hydropolysilane films with thicknesses between 0.2 and 0.4  $\mu\text{M}$  were irradiated under air with UV light intensities of approximately 1  $\text{mW}/\text{cm}^2$ . A highly exothermic reaction immediately takes place due to photooxidative crosslinking in these polymers. Higher temperatures during the photoirradiation leads to greater amounts of concurrent thermooxidation in these systems. The enthalpy of the reaction was proportional to the content of both Si-H and silicon branch sites, with higher percentages of either group leading to greater enthalpies of reaction. The photooxidative reaction was significantly enhanced when experiments were conducted under oxygen as compared to air.

## **Hydropolysilanes as Negative Tone Photoresists**

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Hydropolysilanes have been studied as potential negative tone photoresists for lithographic applications. Exposure of the hydropolysilanes to deep UV radiation in air results in the rapid crosslinking of the polymer. Increasing amounts of hydrosilane units result in increased sensitivity of the resist. Additionally, incorporation of branch sites into the polymeric material results in superior resist sensitivity. Contrast ratios ( $\gamma$ ) from 3 to 10 have been obtained with these materials using different wet developers.



ION-BEAM INDUCED CHANGES OF MOLECULAR STRUCTURES AND  
SOLUBILITIES OF POLYSILANES

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Reactivities of polysilane radical anions and cations have been studied extensively. Reactions of polysilane radical anions and cations with aromatic hydrocarbons such as pyrene and naphthalene (generally both electron and cation scavengers), halogenated hydrocarbons (generally electron scavengers), and aromatic and aliphatic amines (generally cation scavengers) have been studied by using pulse radiolysis techniques. Polysilane radical ions are very stabilized and do not react with some of electron and cation scavengers. Especially polysilane radical cations are very stable and less reactive. Rate constants for reactions of polysilane radical ions with electron and cation scavengers are discussed related to ionization potential and electron affinity. Polymer effects, especially effects of delocalized ionic states of polymer chains are discussed.

## KINETIC AND MECHANISTIC STUDIES OF PLATINUM CATALYZED HYDROSILYLATION

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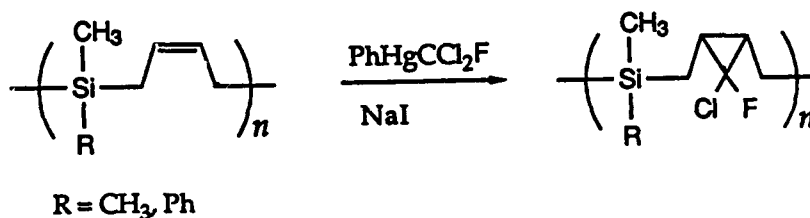
### ABSTRACT

Hydrosilylation is an important industrial reaction although its mechanism is not completely understood. In this paper are presented the results of competitive and relative rate studies of various silicon hydride and silicon olefin compounds. For example, the competitive reaction of bis(trimethylsiloxy)methylsilane with vinylpentamethyldisiloxane (1) and divinyltetramethyldisiloxane (2) show that (2) reacts preferentially; however, the relative rate of reaction is greater for (1) than (2). Mechanistic aspects of hydrosilylation will also be discussed.

## ADDITION OF CHLOROFLUOROCARBENE TO POLY(1-SILA-CIS-PENT-3-ENES)

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Chlorofluorocarbene, generated by the sodium iodide catalyzed thermal degradation of dichlorofluoromethyl phenyl mercury, has been added to the carbon-carbon double bonds of both poly-(1-1-dimethyl-1-sila-cis-pent-3-ene) and poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene). The microstructure of these chemical modified polymers has been determined by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{29}\text{Si}$  NMR spectroscopy. Comparisons will be made between the properties of the parent unmodified polymer: poly(1-sila-cis-pent-3-enes) and dichlorocarbene, difluorocarbene, chlorofluorocarbene and methylene modified polymers.



CHAIN TRANSFER PROCESSES IN DICHLOROSILANE REDUCTIVE POLYMERIZATION  
AND THEIR CONTROL: A SIMPLIFIED ROUTE TO HIGH MOLECULAR WEIGHT POLYSILYLENES

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Because the electronic, as well as physical properties of polysilylenes are sensitive to molecular weight distribution and those properties, in turn, determine suitability for applications, understanding the factors which influence the molecular weight distribution is especially important. Polysilylenes are synthesized by a reductive coupling of diorganodichlorosilanes with molten sodium dispersions in an inert solvent, typically neat toluene or toluene mixed with a cosolvent such as diglyme or heptane. The crude product from this reaction is commonly a complex mixture of low molecular weight linear oligosilanes of varying termination, mixed cyclosilanes, and polydisperse low and high polymer. The surface nature of this reaction leads to broad and poorly reproducible molecular weight distributions in the absence of rigid control over reaction parameters. In this work, we have examined the termination processes in the Na-mediated reductive coupling of dichlorosilanes by comparing rigorously controlled reactions carried out in toluene, a solvent normally thought to be non-chain transferring in these reactions, to those carried out in benzene, which is thermodynamically incapable of undergoing hydrogen abstraction by a terminal polysilyl radical. In the course of these studies, we have identified a back-biting hydrogen abstraction process of low yield unequivocally for the first time. This chain transfer to the polysilylene side chain C-H bonds generates an Si-H terminated polysilylene chain and a reactive site alpha to the silicon. The data also suggest the presence of a second back-biting reaction on the polysilylene backbone itself which produces cyclosilane by-products. An outgrowth of the work is a new modification of the Wurtz coupling process which routinely provides very high molecular weight polysilylenes by the commercially more acceptable "normal" addition procedure.

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## Properties Of Poly(dimethylsiloxane) Elastomers Prepared From Aqueous Emulsion

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The purpose of this research is to investigate the properties of poly(dimethylsiloxane) elastomers prepared from aqueous emulsion. Of primary importance will be the elucidation of the mechanism responsible for the crosslinking of these aqueous-based latices. The effect of various crosslinking agents and their concentrations has been examined in order to demonstrate and typify the curing process. The change in the physical properties of the PDMS elastomers as a function of the crosslinking reaction conditions is determined by mechanical testing of the elastomers under uniaxial extension conditions. Additionally, swelling measurements in toluene have been conducted in order to determine the soluble polymer fraction of the gels, as well as the volume fraction of polymer at equilibrium swelling.

The Second International Topical Workshop  
*ADVANCES IN SILICON-BASED POLYMER SCIENCE*

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