An International Topical Workshop

Advances in Silicon-Based Polymer Science

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The Division of Polymer Chemistry
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ADVANCES IN SILICON-BASED POLYMER SCIENCE WORKSHOP

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ACKNOWLEDGMENT

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ADVANCES IN SILICON-BASED POLYMER SCIENCE WORKSHOP

ORAL PROGRAM

FRIDAY NOVEMBER 20,1987 - ARRIVAL

3:00 - 9:00 P.M.	Registration	
8:00 P.M.	Welcome Gathering	

SATURDAY A.M. NOVEMBER 21, 1987 - FUNDAMENTALS

8:00	Welcome and Announcements	J. Zeigler Sandia National Laboratories
	Session 1 : Chairman - M. Kumada	
8:10	Introduction	J. McGrath Virginia Polytechnic Institute and State Univ.
8:30 OS1-1	Principles of Organosilicon Chemistry	R. West University of Wisconsin
9:30 OS1-2	Principles of Organosilicon Chemistry II Electronic Structures: The Reality of Molecular States	H. Bock Universitat Frankfurt
10:30	Break/poster session 1	
11:00 OS1-3	Overview of Silicon-Containing Polymers	J. Mark University of Cincinnati
12:00 OS1-4	Structure and Morphology of Polysiloxane Homopolymers and Block Copolymers	D. Meier Michigan Molecular Institute
1:00	Lunch	

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

	Session 2: Chairman - R. Lenz	
7:30 OS2-1	Formation of Linear Siloxane Polymers	J. Saam Dow Corning Corporation

8:30	OS2-2	Recent Advances In Organosiloxane Copolymers	J. McGrath Virginia Polytechnic Institute and State Univ.
9:30	OS2-3	Novel Silicone Polyimide Block Copolymers	J. E. Hallgren, F. L. Keohan General Electric Company
10:00	OS2-4	New Metal Silicate Based Route To Alkyl Silicates and Alkyl Silicones	M. E. Kenney, G. B. Goodwin Case Western Reserve Univ.

SUNDAY A.M. NOVEMBER 22, 1987 - FROM 1-D TO 3-D SILOXANES

Session 3: Chairman - D. Meier

8:30	OS3-1	Siloxane and Hybrid Siloxane Sequential Interpenetrating Polymer Networks	B. Arkles, A. Finberg, J. Crosby Dynamit Nobel-Petrarch
9:30	OS3-2	Hybrid Inorganic-Organic Network Materials That Incorporate Silicate and/or Siloxane Structures	G. Wilkes Virginia Polytechnic Institute and State Univ.
10:30		Break/poster session 2	
11:00	OS3-3	Structure and Growth of Silica Condensation Polymers	K. Keefer Sandia National Laboratories
12:00	OS3-4	Organosilicon Polymers for Microlithographic Applications	E. Reichmanis, A. E. Novembre, A. Shugard, R. G. Tarascon, L. F. Thompson AT&T Bell Laboratories
1:00		Lunch	

SUNDAY P.M. - POLYSILANES AND RELATED POLYMERS

Session 4: Chairman - B. Arkles

7:30	OS4-1	Chemistry of Polysilanes - An Overview	H. Sakurai Tohoku University
8:30	OS4-2	Synthesis and Properties of Polysilanes	J. Zeigler Sandia National Laboratories
9:30	OS4-3	Spectroscopy of Polysilylenes	L. Harrah PDA Engineering

MONDAY A.M NOVEMBER 23, 1987 - POLYSILANES AND RELATED POLYMERS

Session 5: Chairman - B. Kanner

8:30	OS5-1	Electronic Structure of Silicon Based Polymers	N. Matsumoto Nippon Telegraph and Telephone Corporation
9:30	OS5-2	The Morphology, Structure, and Phase Transitions of Polysilanes	F. Schilling AT&T Bell Laboratories
10:30		Break/poster session 3	
11:00	OS5-3	Radiation Sensitivity Of Soluble Polysilane Derivatives: Science and Applications	R. Miller IBM Corporation
12:00	OS5-4	Transient Optical Absorption Spectra of Radical Anions and Cations of High Molecular Weight Polysilanes	S. Tagawa University of Tokyo
12:30	OS5-5	Electronic Transport in Polysilylenes	M. Stolka, M. Abkowitz, R. Weagley, K. McGrane Xerox Corporation
1:00		Lunch	

MONDAY P.M. NOVEMBER 23, 1987

7:00		Workshop Banquet "What We Owe"	Eugene G. Rochow

TUESDAY A.M. NOVEMBER 24, 1987 - PRECERAMIC POLYMERS

Session 6: Chairman - H. Sakurai

8:30	OS6-1	An Overview of Polymeric Routes to Silicon Carbide and Silicon Nitride Materials	W. Atwell Dow Corning Corporation
9:30	OS6-2	Advances in the Preparation and Utilization of Organosilicon Preceramic Polymers	D. Seyferth Massachusetts Institute of Technology
10:30		Break	
11:00	OS6-3	New Polymer Precursors for Silicon Nitride	B. Kanner, R. King Union Carbide Corp.

11:30	OS6-4	Oxidation Reaction Of Polycarbosilane	F. Machino Nippon Carbon Company
12:00		Lunch	

TUESDAY P.M. - SILICON CONTAINING POLYMERS

Session 7: Chairman - G. Fearon

1:00	OS7-1	Silicon-Containing Polyacetylenes: Syntheses and Properties	T. Masuda Kyoto University
2:00	OS7-2	Lithographic Applications of Poly(1-trimethylsilyl-1-propyne)	G. Baker, C. Klausner T. Bowmer, A. Gozdz, J. Shelburne III Bell Communications Res.
2:30	OS7-3	Siloxane Surface Activity	M. Owen Dow Corning Corporation
3:00	OS7-4	Surface Effects In Siloxane Grafted (Meth)acrylates: Temporary Surface Siliconization In Elastomeric Systems	M. Mazurek 3M Company
3:30	OS7-5	Synthesis, Properties, and Potential Applications of Silarylene-siloxane Polymers	R. Lenz University of Massachusetts
4:30	OS7-6	Future Directions For Silicon-Based Polymers	D. Weyenberg Dow Corning Corporation
5:00		Closing Remarks	G. Fearon Dow Corning Corporation

Oral sessions will be held in the Makaha Terrace

Poster sessions will take place in the Makua Room

ADVANCES IN SILICON-BASED POLYMER SCIENCE WORKSHOP

POSTER SESSION ONE

SATURDAY, NOVEMBER 21, 1987

PS1-1 Thermal and Rheological Properties of Alkyl Substituted Polysiloxanes
H. A. A. Rasoul, S. M. Hurley, K. M. O'Connor, E. B. Orler, P. B. Rim, and K. M. Scholsky

PS1-2 Syntheses of Various Amine Functional Polysiloxanes
Hiroshi Yoshioka, Shoji Ichinohe, and Yoshitaka Hamada

PS1-3 High Performance, Soluble, Polysiloxane-Polyimide Block Copolymers
J. D. Summers, C. A. Arnold, J. S. Riffle, and J. E. McGrath

PS1-4 Polysiloxanes with Pendant Pyridine 1-Oxide Groups: New Transacylation Catalysts, M. Zeldin, W. K. Fife, C.-x. Tian, and Y. Xin

PS1-5 Thermal and Hydrolytic Stability of Novel Siloxane-Phenolic Condensation Polymers, Arne O. Finberg and James R. Steinmetz

PS1-6 Conformational Analysis and Interpretation of Physical Properties of Substituted Polysiloxanes Polymers, Stelian Grigoras and Thomas H. Lane

PS1-7 Allyl Groups Ended Polysiloxanes
Qingli Zhou, Yongxing Cao, Xiaoxian Xia, and Weishen Yang

PS1-8 Novel Triblock Siloxane Copolymers: Synthesis and Characterization
I. Yilgor, W. P. Steckle, Jr., E. Yilgor, J. S. Riffle, and R. S. Ward

PS1-9 Synthesis and Characterization of New Liquid Crystal Side Chain Polymers, G. de Marignan, D. Teyssie, and S. Boileau

PS1-10 Anionic Ring Opening Polymerization of Sila and Germacyclopent-3-Enes
Xuehai Zhang and William P. Weber

PS1-11 Cure Properties of Ethylidenenorbornyl Group Substituted Organopolysiloxane, Junichiro Watanabe and Yuuichi Funabashi

PS1-12 New Synthetic Route of Hydrogenalkoxysilane
Norio Sato and Michio Zembayashi

PS1-13 Polysiloxane-Based Polymer Electrolyte Complexes
Daryle Fish, Ishrat Kahn, E. Wu, Quangvin Zhou, and Johannes Smid

PS1-14 Hydrolysis and Condensation Kinetics of Dimeric Sol-Gel Species by ^{29}Si NMR, D. H. Doughty, R. Assink, and B. D. Kay

ADVANCES IN SILICON-BASED POLYMER SCIENCE WORKSHOP

POSTER SESSION TWO

SUNDAY, NOVEMBER 22, 1987

PS2-1 Synthesis and Application of Bi-Functional Organopolysiloxane
Tadashi Fujii and Isao Ona

PS2-2 New Fluorinated Polysiloxanes
Rosita Dorigo, Anne-Marie Garnault, Dominique Teyssie and S. Boileau

PS2-3 Synthesis and Properties of Silicon-Branched Organosilicon High Polymers, Yoichiro Nagai, Hamao Watanabe, Hideyuki Matsumoto, Yoshitake Naoi, and Naotake Suto

PS2-4 Soluble Substituted Diaryl Polysilanes: Chemistry and Spectroscopy
R. D. Miller and R. Sooriyakumaran

PS2-5 The Solution Thermochromism of Poly(Di-N-Alkylsilanes)
G. Wallraff, R. D. Miller, P. Cotts, J. Michl, K. Klingensmith, R. West, and J. Maxka

PS2-6 Light Scattering from Dilute Solutions of Aryl Substituted Polysilanes
P. M. Cotts, R. D. Miller and R. Sooriyakumaran

PS2-7 Novel Mono- and Dual-Interpenetrating Network Polymers of Polysiloxane-Polystyrenic Systems, Arne O. Finberg

PS2-8 Novel Mono- and Dual-Interpenetrating Network Polymers of Polysiloxane and Polymethacrylate Esters, Arne O. Finberg

PS2-9 Transition Metal Substituted Polysilanes
Keith Pannell, James Rozell, and Steven Vincenti

PS2-10 Polymers and Copolymers of Disilacyclohexadiene. A Non-Alkali-Metal Route to Polysilanes, Robert A. Rhein

PS2-11 Emission Studies of Solid Poly(Arylmethylsilanes)
Peter I. Djurovich, R. J. Watts, and R. West

PS2-12 Mechanistic Studies of Polysilane Formation
D. J. Worsfold

PS2-13 Physical Properties of Photoactive Polysilane Copolymers
Samuel P. Sawan, Yi-Guan Tsai, and Horng-Yih Huang

PS2-14 Electronic Structure and Conformation Studies of Polysilane Model Systems, J. W. Mintmire and J. V. Ortiz

PS2-15 Modifications of Polysilanes
Krzysztof Matyjaszewski

PS2-16 Exciton-Exciton Annihilation in Polysilanes
R. G. Kepler and J. M. Zeigler

PS2-17 Order-Disorder Transitions and Optical Properties of Polysilanes, Kenneth S. Schweizer

PS2-18 Non-Gaussian Optical Behavior of Bimodal Networks Constituted from Silicon Containing Polymers, Vasilios Galiatsatos

ADVANCES IN SILICON-BASED POLYMER SCIENCE WORKSHOP

POSTER SESSION THREE

MONDAY, NOVEMBER 23, 1987

PS3-1 Glow Discharge Decomposition of Phenylsilanes and Properties of Deposited Films, Takashi Nakamura, Vesselin Sinigersky, Hideomi Koinuma, Kazuo Fueki

PS3-2 A Critical Analysis of Hysteresis, Creep and Elastic Recovery in Novel Interpenetrating Polysiloxane-Addition Polymer Network Systems Arne O. Finberg

PS3-3 Block Interrupt Polysilane Derivatives
R. D. Miller and G. N. Fickes

PS3-4 Soluble Alkyl Substituted Polygermanes: Thermochromic Behavior
R. Sooriyakumaran, R. D. Miller, J. F. Rabolt, and C. Zimba

PS3-5 Silicon Phthalocyanines Useful for the Preparation of Langmuir-Blodgett Films for Sensors, Daniel A. Batzel, C. W. Fu, Scott E. Rickert, W. H. Ko, and Malcolm E. Kenney

PS3-6 Synthesis and Properties of Poly(α,β-Unsaturated Acylsilane)s
Antoni S. Gozdz, Hans J. Reich, and Michael D. Bowe

PS3-7 Structural Factors Influencing the Rate of Migration and Reorganization of Siloxane-Containing, Surface-Modifying Polymeric Additives, R. S. Ward, K. A. White, and I. Yilgor

PS3-8 Stereospecific 1,4-Polymerization of 2-Triethylsilyl-1,3-Butadiene, Yi-Xiang Ding and William P. Weber

PS3-9 Trimethylsilyl Derivative of Layered Polysilicate and Its Thermal Treatment for the Preparation of Microporous Materials
Kazuyuki Kuroda, Tsuneo Yanagisawa, Toshio Shimidzu, and Chuzo Kato

PS3-10 AM1 and MNDO/2 Molecular Orbital Conformational Energy Calculations on Model Compounds of Simple Polysilanes and Polygermanes
William D. Johnson and William J. Welsh

PS3-11 Pyrolysis Behavior of SiC Preceramics
Hal H. Streckert and Fred C. Montgomery

PS3-12 The Application of Hydrolyzed Methyltriethoxysilane for the Preparation of Boron-Doped Silicon Carbide Powder
Kazuyuki Kuroda, Yoshiyuki Sugahara, Yasuharu Takeda, and Chuzo Kato

ORAL SESSIONS

PRINCIPLES OF ORGANOSILICON CHEMISTRY

Robert West

Department of Chemistry, University of Wisconsin,
Madison, WI 53706 U.S.A.

Silicon-based polymers, as well as simpler silicon compounds, are strikingly different in their physical, chemical and electronic properties from their more familiar carbon analogs. For example, 1. Silicon compounds are much more susceptible to nucleophilic substitution than carbon compounds; 2. Silicon forms rather strong single σ-bonds but weak π-bonds; 3. Siloxanes show great chain flexibility but no electron delocalization; 4. Polysilanes, both cyclic and linear, exhibit easy delocalization of electrons in the Si-Si single bonds.

These profound differences can be traced back to fundamental differences between silicon and carbon atoms: 1. The radius of the silicon atoms is much larger than that for carbon; 2. Silicon has much lower ionization potentials than carbon; 3. Mixing of s and p orbitals is much less favorable for silicon than for carbon. The consequences of these differences will be considered, as well as their implications for the chemical bonding and properties of several classes of silicon compounds, including organosilyl halides, R_3SiX; silylenes, R_2Si; disilenes, $R_2Si{=}SiR_2$, and other multiply-bonded silicon compounds; polysiloxanes, $(R_2SiO)_n$; and polysilanes, $(R_2Si)_n$.

PRINCIPLES OF ORGANOSILICON CHEMISTRY II

ELECTRONIC STRUCTURES: THE REALITY OF MOLECULAR STATES

Hans Bock

Department of Chemistry, Johann Wolfgang Goethe University,
Niederurseler Hang, D 6000 Frankfurt, West Germany

The properties of molecules depend on their respective energies and will change especially on acquisition or loss of electrons. The individual state of a molecule or its ion, therefore, is characterized by the energy difference to the preceding or to the subsequent one as well as by its charge distribution and by its molecular dynamics. This molecular state approach has been and is used by the chemist for his own benefit in many ways - from comparison of 'chemically related' molecules (cf. Principles I by R. West) to defining e.g. 'substituent perturbations' of 'parent systems'.

As concerns organosilicon compounds, their tremendously wide scope of bonding will be illustrated by two recently discovered novel molecules: for single coordination by phenylsilaisonitrile H_5C_6-N≡Si, and for ten-fold coordination by silicocene, $(H_5C_5)_2Si$; many others, still unknown, seem to be capable of excistence like silico prismane $(RSi)_6$. Among the numerous principles deducible from molecular state comparison, the rather low effective nuclear charge of silicon centers will be pointed out as well as the stabilization of single electron transfer oxidation and reduction products, supported by ion pairing. The importance of molecular dynamics is emphasized by discussing the thermal dehydrogenation of silahexadiene and reactions involving chemical activation. Wherever possible and especially for polysilanes, relations to polymers or to polymer precursors are suggested.

OVERVIEW OF SILICON-CONTAINING POLYMERS

J. E. Mark

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

The major categories of homopolymers and copolymers to be discussed include (i) linear siloxane polymers [-SiRR'O-] (with various R,R' side groups), (ii) siloxane polymers possibly having a ladder structure, (iii) siloxane-silarylene polymers [-$Si(CH_3)_2OSi(CH_3)_2C_6H_4$-] (where the phenylenes are either meta or para), (iv) silalkylene polymers [-$Si(CH_3)_2(CH_2)_m$-], (v) random and block copolymers of the above, (vi) polysilanes and polysilylenes [-SiRR'-], and (vii) polysilazanes [-SiR_2NR'-]. Topics of particular importance are the structure, conformations, configurations, other physical properties, and selected applications of these polymeric materials. Also of interest are the use of silicon-containing materials to prepare model elastomeric networks and novel reinforcing fillers, ceramics by the sol-gel technique, and high-performance fibers by controlled thermolyses.

STRUCTURE AND MORPHOLOGY OF POLYSILOXANE HOMOPOLYMERS AND BLOCK COPOLYMERS

Dale J. Meier

Michigan Molecular Institute
Midland, Michigan 48640

A variety of homopolymers and block copolymers of polydiphenylsiloxane and polydimethylsiloxane have been prepared by anionic polymerization techniques. Such block copolymers are of interest since they contain only polysiloxane units and combine blocks of a rigid chain, high-melting component (polydiphenylsiloxane) with a highly flexible, low Tg component (polydimethylsiloxane). Elastomeric tri- and star-block copolymers can be prepared with strength properties among the highest ever reported for a siloxane elastomer.

Polydiphenylsiloxane homopolymers can be prepared in soluble form by the anionic polymerization of hexaphenylcyclotrisiloxane in diphenyl ether solution at high temperatures. Thermal and X-ray evidence indicate that polydiphenylsiloxane undergoes a crystal - liquid crystal transition at temperatures near 250°C, with a clearing temperature near 500°C. It has been reported that polydiethylsiloxane and polydipropylsiloxane also show liquid crystalline behavior, albeit at much lower temperatures than that oberved with polydiphenylsiloxane.

The preparation, characterization, morphology and properties of various homopolymers and block copolymers of polydialkylsiloxanes will be described.

FORMATION OF LINEAR SILOXANE POLYMERS

John C. Saam

Dow Corning Corporation
Midland, MI 48686

Linear polydialkylsiloxanes are formed by either ring opening or condensation polymerization. Either acid or base catalyzed siloxane ring opening is distinguished from other types of ring opening polymerizations by a high degree of reversibility and the fact that it is almost entirely entropically driven when the monomeric rings consist of four or more siloxy units. The extensive background on the synthetic and mechanistic aspects of siloxane ring opening polymerization has been reviewed by a number of recent authors. Nevertheless, several questions still remain. These are concerned with the exact nature of the active chain ends and the role of the counterion in both the acid and base catalyzed ring opening mechanisms. Other questions concern an unusual order of reactivity seen with changing ring size. A quantitative picture of ring opening copolymerization at equilibrium has only recently begun to emerge. Information on the kinetics of copolymerization of unstrained rings is still, however, only qualitative.

The background on condensation polymerization of silanol-ended linear oligomers is not as extensive as that of siloxane ring opening polymerization. There is however similarity in the nature of the proposed active ends in both types of process when catalysis is by either strong acids or bases. An unusual feature is that, in contrast with organic condensation polymerizations where water is eliminated, silanol condensation polymerization may be conducted in aqueous emulsion even though it is a reversible dehydration process.

"RECENT ADVANCES IN ORGANOSILOXANE COPOLYMERS"

James E. McGrath

Department of Chemistry
Polymer Materials and Interfaces Laboratory
Virginia Polytechnic Institute & State University
Blacksburg, VA 24061-0699

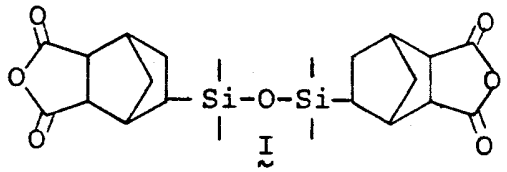
Poly(dimethylsiloxane) and related structures have a number of interesting properties including a low glass transition temperature, high gas permeability, good thermal and light stability and a rather low surface energy. Many of these property characteristics can be maintained if one develops well-defined microphase separated block or graft copolymers. In addition, it is possible to introduce desirable mechanical properties through the second segment. We have investigated the ring-opening polymerization of the cyclic siloxane tetramers in the presence of functional disiloxanes. This method allows for the synthesis of perfectly difunctional oligomers of known number average molecular weight. Some kinetic results obtained during the synthesis of aminopropyl functional oligomers will be discussed. In addition, the various aminopropyl functional siloxane oligomers prepared have been incorporated into both elastomeric and rigid segmented copolymers wherein the second segment may be a urea, arylate, amide and especially, imide. The synthesis and characteristics of these copolymers will be described. In particular, it is possible to obtain the bulk properties of the more rigid component while maintaining the microphase separation of the siloxane. In general, the siloxane dominates the surface structure of these phase separated copolymers as judged by traditional contact angle measurements and photo electron spectroscopy. Ramifications of this phenomena in the space environment will also be mentioned.

NOVEL SILICONE POLYIMIDE BLOCK COPOLYMERS

J. E. Hallgren and F. L. Keohan

General Electric Company
Corporate Research and Development Center
Schenectady, New York 12301

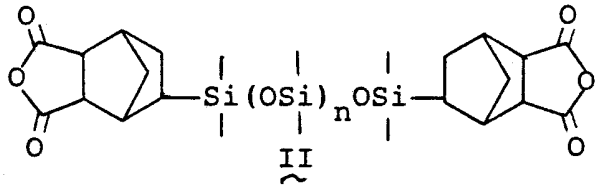
The synthesis of a novel disiloxane bis(dicarboxylic anhydride), I, and of poly(imide-siloxane) copolymers and



I

terpolymers based on I are described. The disiloxane, I, was prepared in high yield by the platinum catalyzed reaction of dimethylchlorosilane and bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride followed by hydrolysis and condensation.

High molecular weight polymers could be isolated from solution utilizing I, the polysiloxane derivative, II,



II

aromatic diamines, and organic dianhydrides. By varying the average siloxane block length ("n" of II) both thermoplastics and elastoplastics could be prepared. The thermal, mechanical and thermal oxidative stability properties were investigated for a variety of copolymer compositions, with siloxane content having the greatest effect on these properties.

NEW METAL SILICATE-BASED ROUTE TO ALKYL SILICATES AND ALKYL SILICONES

George B. Goodwin and Malcolm E. Kenney

Department of Chemistry, Case Western Reserve University
Cleveland, OH 44106

A new route to alkyl silicates and organosiloxanes is reported. The route starts with a metal silicate having a silicate ion with a suitable structure. This metal silicate may be obtained by collection, mining, laboratory synthesis, or commercial synthesis. Three reactions take place in the route. In the first, the silicate is protonated or protonated and esterified to a silicic acid with, in either case, full or substantial framework preservation. In the second, the silicic acid is esterified to an alkyl silicate, again with full or substantial framework preservation. Finally, the alkyl silicate is organodealkoxylated to an organosiloxane with structure preservation. For the case in which the metal silicate is a disilicate the reactions are:

$$O_3SiOSiO_3^{6-} + H^+ + ROH \longrightarrow (HO)_{3-x}(RO)_xSiOSi(OR)_x(OH)_{3-x}\cdot yROH \quad (1)$$

where x = 0-3

$$(HO)_{3-x}(RO)_xSiOSi(OR)_x(OH)_{3-x}\cdot yROH + ROH \longrightarrow (RO)_3SiOSi(OR)_3 \quad (2)$$

$$(RO)_3SiOSi(OR)_3 + R'MgX \longrightarrow R'_3SiOSiR'_3 \quad (3)$$

The route is illustrated with a number of examples using main-group and transition-metal silicates of both natural and synthetic origin.

"SILOXANE AND HYBRID-SILOXANE SEQUENTIAL INTERPENETRATING POLYMER NETWORKS"

Barry Arkles, Arne O. Finberg and Jane Crosby

Petrarch Systems, Inc.
Pearl Buck Road
Bristol, PA 19007

A large number of Sequential Interpenetrating Silicone Polymer Networks have recently been reported. The networks are generated by the hydro-silylation reaction. The area of greatest interest from research and commercial perspectives has been the case in which a silicone network has been generated in the presence of a thermoplastic polymer. This technology leads primarily to products consistent with thermoplastic processing. A new development is the formation of the silicone network prior to polymerization of monomeric components. This technology leads primarily to products consistent with RTV and LTV thermoset silicone processing. These two approaches produce interesting parallels and contrasts in terms of chemistry, morphology, and physical properties.

Hybrid Inorganic-Organic Network Materials That Incorporate Silicate and/or Siloxane Structures

Garth L. Wilkes
Virginia Polytechnic Institute & State University
Department of Chemical Engineering
and
Polymer Materials and Interfaces Laboratory
Blacksburg, VA 24061-6496

Over the last several years, there has been efforts made to develop new hybrid materials by combining metal alkoxides with appropriate functionalized monomers, oligomers and/or polymers thereby leading to new solids obtain via a sol gel process. Many of these materials have been based on utilizing either tetramethylorthosilicate (TMOS) or tetraethylorthosilicate (TEOS) sometimes in conjunction with other metal alkoxides such as titanium isopropoxide. These alkoxides in conjunction with appropriate functionalized organics or inorganic oligomers such as polydimethylsiloxane, have led to some new and interesting materials. This lecture will be directed at reviewing the present status of the development of these hybrid systems and implications will be made concerning their potential for applications. Remarks will also include the future direction of this new research area of material science.

STRUCTURE AND GROWTH OF SILICA CONDENSATION POLYMERS*

Keith D. Keefer, Ceramics Development Division 1845
Sandia National Laboratories, Albuquerque, New Mexico 87185

The condensation polymerization of silica to form inorganic polymers is the basis for several new methods of chemical processing of ceramic materials. In these processes, reactive silanol groups are generated by the hydrolysis of silicon compounds such as alkoxides. The silanols subsequently condense and to form siloxane linkages. The relative rates of the hydrolysis and condensation reactions may be varied by changing the pH, water concentration or hydrolyzible group. A variety of different structures can be generated depending on the number and distribution of active silanols among the monomers. Small angle x-ray scattering measurements show that the structures can range from highly ramified, fractal structures to homogeneous particles with fractally rough surfaces to non-fractal colloidal particles. Computer simulations of simplified random growth processes whose rules are based on this chemistry generate fractal structures which are consistent with the x-ray scattering measurements.

*This work performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract number DE-AC04-76DP00789.

ORGANOSILICON POLYMERS FOR MICROLITHOGRAPHIC APPLICATIONS

E. Reichmanis
A. E. Novembre
A. Shugard
R. G. Tarascon
L. F. Thompson

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

The incorporation of silicon into resist systems has been shown to effectively instill oxygen etching resistance while maintaining lithographic utility. Such materials may be used as the imaging layer for two-level resist processes involving RIE pattern transfer through a planarizing layer of organic polymer. Treatment of the silylated polymer with an oxygen discharge results in formation of a thin barrier layer of silicon oxide that retards further erosion of the underlying material. Numerous polymers containing either backbone or side-chain silicon have been described that have potential utility in bilevel resist applications. Prominent examples include the polysiloxanes and polysilanes, and materials such as the silylated novolacs, methacrylates, sulfones and styrenes that contain side-chain silicon.

This paper will discuss the materials properties that are required for the development of effective, oxygen RIE resistant lithographic materials and how the nature of the silicon moiety affects those properties. Included in the discussion will be the effect of RIE processing conditions on the differential etching rates of two-level resist systems and the feasibility of developing practical, production worthy, RIE developed, bilevel resist processes.

CHEMISTRY OF POLYSILANES -- AN OVERVIEW

Hideki Sakurai

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Polysilanes were prepared and reported for the first time by F. S. Kipping in 1924. In 1949, C. A. Burkhard described the preparation of permethylpolysilanes. However, the chemistry of high molecular weight polysilanes has been almost ignored because of the untractable nature until S. Yajima and J. Hayashi had discovered that permethylpolysilane could be converted to silicon carbide in 1975. Since then the chemistry of polysilanes attracts interests quite rapidly.

In this paper, the author will try to review critically the progress of the chemistry. The author will lay emphasis on the reaction of polysilanes. Reactions of lower homologs of polysilanes such as hexamethyldisilane and octamethyltrisilane will be included also as the matter relevant to the subject.

Finally new possibilities in the method of preparing polysilanes as well as in new ways of applications will be discussed briefly.

SYNTHESIS AND PROPERTIES OF POLYSILANES*

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Delocalization of the backbone sigma electrons endows polysilanes (polysilylenes) with molecular weight dependent properties reminiscent of those of polyenes. Recent rapid growth in the technological importance of polysilanes has underscored the necessity for well-understood and flexible synthetic procedures which allow control of the polysilane molecular weight distribution and provide a wide range of functional as well as hydrocarbon substituted materials. This presentation will summarize the currently known methods for the synthesis of polysilanes and provide an introduction to their physical and morphological properties.

Recent work has demonstrated several promising routes to oligosilanes including catalytic homogeneous oxidation of monosilanes, rearrangement of disilanes, and reductive coupling of monochlorosilanes (R_2SiHCl). Similarly, methods have been developed for modifying the structures of some polysilanes which show promise for the synthesis of functional copolymers. However, the only known route to high molecular weight polysilanes remains a highly heterogeneous, until recently, poorly understood Wurtz-type coupling of dichlorosilanes with molten alkali metals, primarily sodium. This coupling reaction produces highly non-statistical, often multimodal molecular weight distributions which are exquisitely sensitive to slight changes in solvent composition. We have shown that the heterogeneity of the coupling reaction, which has hindered mechanistic understanding, is the key to its success in producing high molecular weight polysilanes. The predominate pathway to high polymer involves radical intermediates, a surprising result in light of the finding of silylene intermediates in high temperature gas phase couplings by Voronkov, et al. The solvent sensitivity is not due to chain transfer, by and large, but is, rather, a bulk solvent effect. A simple model is proposed in which the solvent composition sensitivity of the molecular weight distribution is seen to result from polymer-solvent compatibility induced changes in the degree of coverage of the metal surface by the growing polymer chains and corresponding modifications in their conformations which affect the concentration of monomer in the relevant near-surface regime.

*This work performed at Sandia National Laboratories supported by the U. S. Department of Energy under contract number DE-AC04-76DP00789.

PHOTOPHYSICS AND ELECTRONIC STRUCTURES OF POLYSILYLENES

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High molecular weight polysilylenes are receiving considerable attention as photoresists [1] and photoconductors [2]. Because of this interest in their photochemistry and photophysics, many recent studies of electronic spectra have been reported [3]. These spectral studies have revealed a wealth of extremely interesting physical and photophysical phenomena which are intimately connected to the electronic structure of these interesting polymers. I will review the absorption, fluorescence, and phosphorescence behavior of the alkyl and aryl substituted polysilylenes solution thermochromism in these materials, and discuss the nature of the photochemical precursor. Of particular interest is the solution thermochromism of these polymers and its implications to the nature and behavior of the electronic states. This problem has been treated theoretically [4] and the experimental observations will be compared with this treatment. The relationships between electronic structure and substitution on the silicon chain will be discussed and related to possible structures which may either increase or decrease the photochemical reactivity.

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Electronic Structures of Silicon-Based Polymers

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Crystal Si and amorphous Si are currently investigated in the field of *solid state physics,* while polysilanes and related macromolecules are treated in the field of *organosilicon chemistry*. Therefore, they are still thought of as nonrelated materials.

A new idea is proposed that these materials are related and can be understood in terms of the dimensional hierarchy of silicon backbone materials.

The electronic structures of one-dimensional polymer (polysilanes) are further discussed. The effects of side groups and conformations are calculated theoretically and discussed in light of such experimental data as UV absorption, photoluminescence and thermochromism.

Finally, the future of silicon-based polymer science is discussed on the basis of some challenging efforts to extend silicon-based polymers, which includes the synthesis of high dimensional polymers, one-dimensional superlattices and the theoretical consideration for metallic polymers with alternative double bonds.

THE MORPHOLOGY, STRUCTURE, AND PHASE TRANSITIONS OF POLYSILANES.

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The synthesis of soluble polysilane homopolymers was first reported in 1980. The most striking characteristic of the polysilanes is their intense UV absorption at 300-380 nm, both in solution and in the solid state. Furthermore, certain polysilanes are observed to exhibit abrupt transitions in the UV spectrum at low temperatures in solution and at phase transitions in the solid state. In order to understand the properties of silane polymers a significant amount of work during the past several years has been directed toward the characterization of the morphology and solid state structures for these materials. Recent reports have included solid state analyses by X-ray and electron diffraction, UV, IR, Raman, NMR, and DSC. The results of these studies, together with solution analyses, provide a detailed description of the polymer conformation and microstructure, crystal structure, polymer morphology, and solid state phase transitions. Many of the interesting properties of the polysilanes can be related to the nature of the solid state structures. Variable temperature studies have been especially useful in this regard. This talk will present an overview of the work described above, using specific examples to illustrate what is known concerning the nature of polysilanes in the solid state. Areas where additional research is desirable will also be discussed.

"RADIATION SENSITIVITY OF SOLUBLE POLYSILANE DERIVATIVES: SCIENCE AND APPLICATIONS"

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High molecular weight substituted silane polymers represent a new class of radiation sensitive polymers which are attracting considerable attention. Although the backbone is comprised only of sigma bonded silicon units, all of the polysilanes absorb strongly in the UV-visible region. In this regard, both the λmax and the ϵ/SiSi depend on molecular weight, increasing rapidly at first with increasing molecular weight and finally approaching limiting values around a degree of polymerization of 40-50. The absorption spectra also depend strongly on the backbone conformation. Irradiation of polysilane derivatives invariably results in the bleaching of the initial absorption. In degassed solution, this spectral bleaching is accompanied by a progressive reduction in the molecular weight. Although bleaching of films irradiated in air is complicated by the formation of siloxane oxidation products, in vacuum the spectral bleaching results in lower molecular weight fragments. The polysilanes are quite photosensitive and in solution the quantum yields for scission (Φs) range from 0.5 - 1.0. Exhaustive irradiation in solution results in the formation of both silylenes and silyl radicals as determined by trapping experiments. The decomposition of polysilane derivatives in the solid state, particularly under photoablative conditions appears to be more complex.

The radiation sensitivity of the polysilanes have resulted in a number of microlithographic applications. In this regard, they have been employed as passive oxygen etch resistant barriers, as materials for both wet and dry bilayer imaging, as short wavelength contrast enhancing layers and as positive, bilayer e-beam resists.

Transient Optical Absorption Spectra of Radical Anions and Cations of High Molecular Weight Polysilanes

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Recently a number of papers both on photo- and radiation (EB) chemical reactions and on optical and electric properties of high molecular weight polysilanes have been reported. However, properties of radical anions and cations of high molecular weight polysilanes have not been published, although a number of papers on properties of ground states and excited states of high molecular weight polysilanes have been reported. Very recently transient optical absorption, formation, lifetimes, and reactivities of radical anions[1,2] and cations[3] have been measured directly at room temperature by using pulse radiolysis techniques. Very strong absorption of radical anions and cations of high molecular weight polysilanes exists in ultraviolet region. As example, transient absorption spectrum and time profile of radical anion of polymethylpropylsilane (PMPrS) observed in pulse radiolysis of PMPrS solutions in THF are shown in figures. Wavelengths at absorption peaks and absorption intensities of radical anions of polysilane oligomers become longer and stronger with increasing in monomer units. Electronic states of radical anions of high molecular weight polysilanes are considered to be delocalized as well as ground states and lowest excited singlet states. Absorption spectra of radical anions and cations of high molecular weight polysilanes are similar to each other. The reactivities of the radical anions will be also reported in the Symposium.

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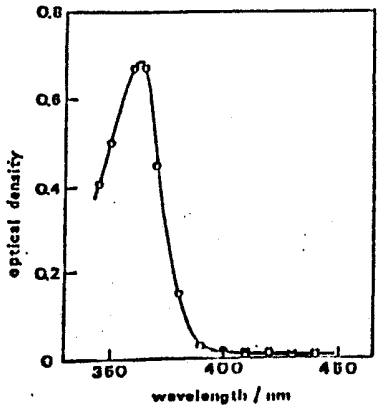
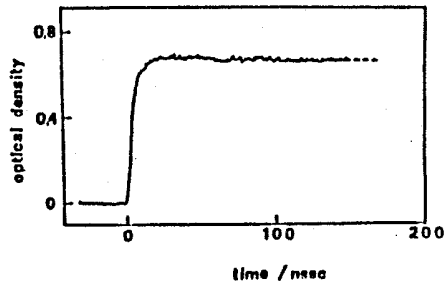


Transient UV absorption spectra of PMPrS in THF solutions at 40nsec after an electron pulse.



Optical density change of 93mM PMPrS solution in THF after the pulse, which was monitored at 365nm.

ELECTRONIC TRANSPORT IN POLYSILYLENES

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The ability to efficiently transport charges photoinjected from adjacent photoconductors makes polysilylenes suitable candidates for exploration as materials for charge transport layers (TL) in xerographic photoreceptors. As most known organic charge-transporting polymers, polysilylenes transport only holes. Electron transport is not typically observed. The TL must transit charges in a time dictated by machine cycle requirements with no loss to deep traps. Hole mobilities in several polysilylenes is $\sim 10^{-4}$ $cm^2/V.s.$, greater than needed for practical applications. Furthermore, transport in poly(methylphenylsilylene) PMPS, a model polysilylene, is nondispersive over a wide range of temperatures and fields. Qualitative characteristics of transport in PMPS are remarkably similar to the previously studied materials such as poly(N-vinylcarbazole) and so-called molecularly doped polymers where charges are known to migrate by hopping among discrete molecules or polymer side groups. In polysilylenes, however, transport is insensitive to the nature of side groups and therefore must involve states associated with the sp^3 silicon backbone. In certain aspects, polysilylenes also resemble a-Si:H. Properly prepared PMPS samples are essentially trap-free. Charge traps of varying depth can, however, be introduced into the polymer. Some aromatic polysilylenes appear sufficiently stable, both chemically and photolytically, for typical xerographic application. These polymers are exploratory at present. The understanding of their electronic behavior and other general properties may however lead to discoveries of novel high performance materials and processes for electrophotography and other forms of imaging.

AN OVERVIEW OF POLYMERIC ROUTES TO SILICON CARBIDE AND SILICON NITRIDE MATERIALS

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The use of "chemical approaches" to improve the processing, properties and performance of advanced ceramic materials is a rapidly growing area of research and development. One such chemical approach involves the preparation of organometallic polymer precursors and their controlled pyrolysis to ceramic materials. This paper will review some of the key preparation and application publications dealing with silicon, carbon and nitrogen containing polymer systems.

Improvements in this field will be dependent on the ability to advance present day understanding and capabilities in the areas of materials synthesis, processing and characterization. A discussion of each of these areas will be presented.

ADVANCES IN THE PREPARATION AND UTILIZATION OF ORGANOSILICON PRECERAMIC POLYMERS

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Following general comments about the "why" and "how" of the preceramic polymer approach to the preparation of ceramic materials we describe the results of research at M.I.T. on the preparation of polysilazane precursors for silicon nitride, silicon carbonitride and silicon oxynitride in which methyldichlorosilane was used as the starting material.

NEW POLYMER PRECURSORS FOR SILICON NITRIDE

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Silicon nitride, Si_3N_4, is currently a material of great potential and interest for the production of fibers, powders and composites. Its ceramic properties include high temperature stability, chemical inertness and extreme hardness. In the past, silicon nitride has been prepared by a wide variety of methods frequently involving the reactions of chlorosilanes as intermediates.

Polysilazanes have now been prepared free of chloride impurities via the catalyzed transamination and condensation of $HSi(NMe_2)_3$ and its derivatives, with ammonia, primary amines, hydrazines or diamines. This approach avoids the cumbersome separation technics generally used to remove amine hydrochloride salts. Aminosilanes containing silicon-bonded hydrogen, such as $HSi(NMe_2)_3$, are readily transaminated or condensed in the presence of a variety of catalysts, including carbon dioxide, ammonium carbamates, carbamatosilanes, organic acids or inorganic acids. In addition to broad mixtures of polysilazane polymers, discrete silazanes have been isolated and identified.

Those aminosilanes that do not contain an Si-H linkage are more effectively transaminated or condensed when catalyzed by strong organic or inorganic acids. Both classes of polysilazanes are useful as precursors for silicon nitride or silicon nitride containing ceramic compositions upon thermolysis at temperatures up to 1550 C. High purity α-Si_3N_4 (alpha phase crystalline form of silicon nitride) has been efficiently prepared by this process.

Oxidation Reaction of Polycarbosilane

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Polycarbosilane(PCS) is organic polymer which consists of the skeleton of Si-C bond. SiC fiber is produced from PCS by the steps of spinning, curing and heat treatment. Curing process of SiC fiber is generally oxidation reaction of PCS by heat treatment in air. Structures and characteristics of SiC fiber is affected by oxidizing conditions of PCS. However, details and mechanism of PCS-oxidation has not yet been clarified. Therefore, the change of PCS after oxidation treatment in air was studied by measurement of weighting, oxygen analysis, mp, GPC, solubility in THF and infrared spectrum. The oxidation of PCS gave the following reaction; 1) oxidation reaction of two SiH bonds to give Si-O-Si bond through condensation, 2) hydrated reaction of SiH bond to give SiOH bond, 3) oxidation reaction of $SiCH_3$ bond to give SiOH bond and formaldehyde, 4) Dehydrated condensation of two SiOH bonds to give Si-O-Si bond, (reaction equation(1)-(4)). PCS became to be infusible by crosslinkage of Si-O-Si bonds. However infusible PCS consisted of more than 7 wt% of oxygen because it had more SiOH bonds than Si-O-Si bonds.

Condensation reaction of SiOH bonds has also given Si-O-Si bond by heat treatment in nitrogen. By applying this fact, we got the infusible PCS which consisted of 3 - 6 wt% of oxygen.

$$\equiv SiH + HSi \equiv + O_2 \longrightarrow \equiv Si-O-Si \equiv + H_2O \qquad (1)$$

$$\equiv SiOH + HOSi \equiv \longrightarrow \equiv Si-O-Si \equiv + H_2O \qquad (2)$$

$$\equiv SiH + H_2O \longrightarrow \equiv SiOH + H_2 \qquad (3)$$

$$\equiv SiCH_3 + O_2 \longrightarrow \left[\equiv SiCH_2OOH \longrightarrow \equiv Si\cdot + \cdot OH + CH_2O\right]$$

$$\longrightarrow \equiv SiOH + CH_2O \xrightarrow{O_2} \equiv SiOH + CO_2 + H_2O \qquad (4)$$

$$\xrightarrow{\frac{1}{2}O_2} \equiv SiOH + HCOOH$$

SILICON-CONTAINING POLYACETYLENES: SYNTHESES AND PROPERTIES

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Previously we exploited groups 5 and 6 transition metal (Nb, Ta, Mo, and W) catalysts, and obtained by using these catalysts high-molecular-weight polymers ($\bar{M}_w$ 1×10^6) from various substituted acetylenes such as HC≡C-*t*-Bu, MeC≡C-*n*-C_5H_{11}, MeC≡CPh, ClC≡C-*n*-C_6H_{13}, and ClC≡CPh.[1] The substituted polyacetylenes formed had alternating double bonds along the main chain and various substituents in the side chain. Unlike polyacetylene, these polymers were usually colorless, soluble, air-stable, and electrically insulating.

The present paper surveys the synthesis, structure, properties and functions of Si-containing polyacetylenes, mainly on the basis of our recent work.

Polymerizations of (trimethylsilyl)acetylene (HC≡CSiMe_3; 1), 3-(trimethylsilil)-1-octyne[2] [HC≡CCH(SiMe_3)-*n*-C_5H_{11}; 2], *o*-(trimethylsilyl)phenylacetylene (HC≡CC_6H_4-*o*-SiMe_3; 3), and 1-(trimethylsilyl)-1-propyne[3] (MeC≡CSiMe_3; 4) have been examined. 1 provides only a partly insoluble polymer in the presense of W catalysts. 2 and 3 polymerize with Mo and W catalysts to give high-molecular-weight polymers ($\bar{M}_w$ 1×10^5-1×10^6). In the case of 4, not Mo or W catalysts but Nb and Ta catalysts work effectively, and the polymer molecular weight reaches 1×10^6 or above.

Spectroscopic data of the polymers support the alternating double-bond structure. Poly(2), poly(3), and poly(4) are yellow, purple, and colorless solids, respectively. They are thermally fairly stable in air, are soluble in solvents like toluene, and can be cast into free-standing filmes. Salient features of poly(4) include the extremely high oxygen permeability and the ethanol permselectivity in the ethanol-water pervaporation.[4] Thus, these Si-containing polyacetylenes might be new promissing materials which show unique functions.

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LITHOGRAPHIC APPLICATIONS OF POLY(1-TRIMETHYLSILYL-1-PROPYNE).

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Poly(1-trimethylsilyl-1-propyne), PTMSP, has nearly all of the properties desired for the imaging layer in a bilayer lithographic process: excellent plasma etch resistance, high Tg, excellent film forming properties, and thermal stability. Although the sensitivity of PTMSP to deep UV radiation (<300nm) was found to be too low for a practical resist material, bromination of PTMSP with N-bromosuccinimide in CCl_4 greatly increased its sensitivity. Bromination slightly decreased the thermal stability of the polymer, but the excellent etch resistance and film forming properties of PTMSP were retained. Infrared, ^{13}C and ^{29}Si NMR spectroscopy confirmed that bromination occurred exclusively at allylic sites in the polymer. The increased lithographic sensitivity resulted from efficient photooxidation of the brominated polymer, allowing the formation of fine line positive images.

SILOXANE SURFACE ACTIVITY

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Polyorganosiloxanes, particularly polydimethylsiloxane, have many, varied surface applications. The structure, property and use considerations pertaining to the surface activity of polydimethylsiloxane are surveyed emphasizing fundamental causes such as low intermolecular forces between methyl groups, the unique flexibility of the siloxane backbone, and the high bond energy and partially ionic nature of the siloxane bond. These basic attributes are used to understand the general interaction of polydimethylsiloxane with high and low energy substrates. Specific siloxane/substrate interactions are discussed to highlight structural or applicational aspects of key surface properties. Emphasis is on liquid and solid surface tension with Langmuir trough studies and water contact angle data also included.

The surface activity of variations of the pendent organic group and the backbone is reviewed and examples given of current research and applications in these areas. Longer alkyl and more polar pendent groups are considered but the chief focus is on aliphatic fluorosilicones as this class contains the lowest surface energy polyorganosilicon polymers. Some comparison is made with nonsilicon fluoropolymers. There is little information about organosilicon polymers with backbones other than siloxane. The limited data on polysilazanes, polysilalkylenes and polysilanes is reviewed. Some thoughts on future surface directions of organosilicon polymers are included.

SURFACE EFFECTS IN SILOXANE-GRAFTED (METH)ACRYLATES: -TEMPORARY SURFACE SILICONIZATION IN ELASTOMERIC SYSTEMS

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There has been strong interest in siloxane-grafted copolymers ever since Yamashita et al. demonstrated the feasibility of the synthesis of well-characterized copolymers by free-radical copolymerization of siloxane macromers with vinyl monomers. The unique surface characteristics of siloxanes can be imparted in this way to various polymeric coatings, as siloxane grafts tend to dominate the polymer-air interface. For vinyl copolymers with high T_g backbones a permanent surface modification can be achieved even with a very small concentration of siloxane grafts.

We have studied surface effects in e l a s t o m e r s composed of low T_g acrylic polymers grafted with siloxanes, many of them showing pressure sensitive adhesive (PSA) properties. In such siloxane-grafted systems, changes in the interface can be observed at room temperature depending on the character of the surface in contact with the copolymer coating. The polymer-air interface of the coating is always completely siliconized, as observed by ESCA measurements, even at a concentration of siloxane grafts as low as 5 wt. %. Also functional tests, such as peel adhesion measurements, are indicative of surface modification by siloxane grafts. Siliconization of the surface of pressure sensitive adhesive coatings leads to a dramatic decrease of peel adhesion values on immediate application of the adhesive coating to a high energy surface by preventing the acrylic component of the coating from building an adhesive bond. This "low adhesion frontsize" formed by siloxane grafts also prevents normally tacky adhesive coatings from adhering to themselves. The phenomenon is time-dependent, as adhesion builds with time, presumably accompanied by some kind of segmental rearrangement in a newly-formed interface.

Although direct studies of the interfacial changes are not readily available, the phenomenon can be conveniently studied by indirect methods, such as PSA tests. It has been found that the time required for the interface to rearrange on contact with high energy surfaces is a function of the molecular weight and the concentration of siloxane grafts, as well as the physical characteristics of the elastomeric backbone.

SYNTHESIS, PROPERTIES AND POTENTIAL APPLICATIONS OF SILARYLENE-SILOXANE POLYMERS

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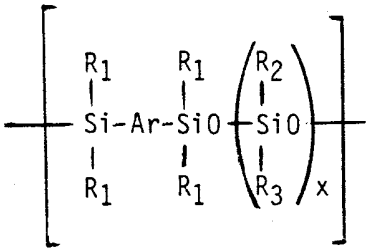
Silarylene-siloxane polymers were studied initially in this laboratory as candidates for high temperature elastomers because they can be designed to have acceptably low glass transitions in combination with excellent thermal stability. As a class they may be represented by the following general structure:



but for high temperature applications, the most promising are the exactly alternating polymers with x=1. In our studies Ar is p-phenylene, m-phenylene and p,p'-diphenyl ether; R_1 is methyl; and R_2 and R_3 are a wide variety of silane substituent groups. Very high molecular weight polymers can be prepared by the low temperature, step-growth polymerization of arylenedisilanol monomers with a bis-ureido silanes in solution. Copolymerization with vinyl silane monomers provides a reactive unit for vulcanization, and the polymers with a very high content of vinyl silane units form an unusually high amount of residue at high temperatures. Potential applications for this family of polymers include ablative elastomers, membranes for gas separation, electron resist substrates, stationary phases for gas chromatography, and precursors for silicon carbide.

FUTURE DIRECTIONS FOR SILICON-BASED POLYMERS

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Polymers based on silicon chemistry extend into the domains of three major classes of materials -- metals, ceramics, and plastics -- and thus provide an ever expanding array of potential new materials which uniquely match the emerging commercial needs for new structural and optoelectronic materials. These commercial demands along with the integration of materials synthesis with systems design will provide a strong driving force for continued development of this field of polymer science. They will also require that we deal with these novel polymers as the complex materials concepts that they represent, requiring an understanding of structure, synthesis, and behavior at several different hierarchical levels of complexity -- from monomeric through segmental, network, and domain to final system. The role of molecular modeling in bridging this gulf between polymer backbone design and physical behavior will be emphasized.

The commercial development and continued expansion of silicones will illustrate the dynamics of this cyclic process of science, invention, and innovation and will provide insight for the continued development of this field.

POSTER SESSION ONE

THERMAL AND RHEOLOGICAL PROPERTIES OF ALKYL SUBSTITUTED POLYSILOXANES

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E. B. ORLER, P. B. RIM & K. M. SCHOLSKY

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Two series of polysiloxanes containing paraffinic side chains namely poly(methylalkylsiloxane)s and methylalkyl-dimethyl-siloxane copolymer of varying alkyl length were synthesized. Their thermal and rheological properties were investigated. Calorimetric results show that the alkyl side chains are crystallizable. The side chain melting temperature and heats of fusion, normalized for side-chain weight fraction were observed to increase with increasing side chain length. For a given main-chain molecular weight, both the intrinsic and the melt viscosity of the poly(methylalkylsiloxane)s were observed to increase with increasing side-chain molecular weight. Solution and melt viscosity data were analyzed with classical relations given by Flory and Rouse, respectively. Comparison of the thermal and the rheological behavior of the two series will be discussed.

SYNTHESES OF VARIOUS AMINE FUNCTIONAL POLYSILOXANES

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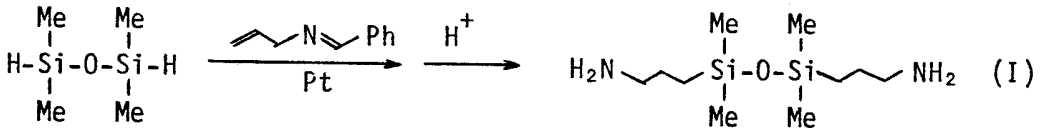
So many attempts have been made over the years to modify various organic polymers by incorporating with polysiloxane chain. Heretofore, a series of reports have disclosed preparations of polyamides, polyimides and polyureas in utilizing typically α,ω-bis-aminoalkyl or -aminoaryl polysiloxanes. Among these amino-modified polysiloxanes, 1,1,3,3-tetramethyl-1,3-bis-γ-aminopropyldisiloxane(I) is one of the most important compounds.

New synthetic method for preparing (I) has been developed and will be reported. The method commercially affords high purity compound by blocking amino group with benzaldehyde.



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Other types of syn-bisaminoalkyldisiloxanes and amino-terminated polysiloxanes which were introduced from the dimers will be also reported.

HIGH PERFORMANCE, SOLUBLE, POLYSILOXANE-POLYIMIDE BLOCK COPOLYMERS

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High performance aromatic polyimides have traditionally been synthesized via bulk thermal cyclization of solution cast poly(amic acid) resins. In order to obtain quantitative imidization in the solid state, it has been necessary to use "curing" temperatures higher than the glass transitions of the products. Recently, several solvent-azeotroping agent systems have been described which can be used to imidize certain polyimides and imide-containing copolymers in solution. This method alleviates the necessity of using high temperatures by solvating the polymers throughout the synthetic process. Our work has centered on the development of a solution imidization step for polysiloxane-polyimide copolymers based on benzophenone tetracarboxylic dianhydride, 3,3'-diamino-diphenyl sulfone, and preformed, primary amine functional polydimethyl siloxane oligomers. The resulting block copolymers have been found to possess much higher solubilities in polar aprotic solvents than the analogous polymers prepared via the traditional high temperature route. We are now in the process of extending this work to include both a variety of aromatic monomers and also to other polysiloxane structures in order to investigate the solubility, thermal, and rheological properties of these systems.

POLYSILOXANES WITH PENDANT PYRIDINE 1-OXIDE GROUPS: NEW TRANSACYLATION CATALYSTS

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A new family of polysiloxanes that carry the pyridine 1-oxide group has been synthesized by the hydrolysis of the appropriate silane monomer. These materials exhibit unusual thermal properties and effectiveness as transacylation catalysts for carboxylic and phosphoric acid derivatives; e.g. conversion of benzoyl chloride to benzoic anhydride with yields exceeding 80% in well-stirred suspensions of CH_2Cl_2/HCO_3^-(aq), synthesis of mixed anhydrides, and rapid ($t_{1/2}$ 10 min. 25° C) hydrolysis of $(PhO)_2POCl$ in HCO_3^-(aq). The results are compared to those with other catalysts: i.e. pyridine 1-oxide (PNO), poly(4-vinyl pyridine 1-oxide) (PVPNO), 3-(trimethylsilyl)pyridine 1-oxide (TMSPNO), 4-(dimethyl-amino)pyridine (DMAPNO), and related substances. The enhanced reactivity of the water insoluble polysilaxanes in aqueous media has been interpreted as evidence for the importance of lipophilic binding in catalysis.

Thermal and Hydrolytic Stability of Novel Siloxane-Phenolic Condensation Polymers

by Arne O. Finberg and James R. Steinmetz
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Synthesis and characterization of novel condensation polymers based on dimethyl or diphenyl siloxane and diphenols will be presented. Emphasis will be made on the thermal, oxidative and hydrolytic properties of these polymers. A brief evaluation of physical and mechanical properties and potential applications will be dicsussed.

CONFORMATIONAL ANALYSIS AND INTERPRETATION OF PHYSICAL PROPERTIES OF SUBSTITUTED POLYSILOXANES POLYMERS

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The conformation of polysiloxanes has been explained by analyzing the balance between electrostatic and van der Waals nonbonding interactions. The importance of the electrostatic contributions becomes apparent when the system is analyzed using only van der Waals forces. In this case the siloxane assumes the conformation of a normal hydrocarbon, trans-trans. When the electrostatic contribution is added, cis-trans sequences are shown to be the most stable for the siloxanes.

The polysiloxane backbone is formed by alternating positive and negative electrostatic charges located at Si and O atoms respectively. The attractive force is maximized and the repulsive is minimized when cis-trans conformation occurs. The cis-gauche and trans-gauche are also favored, but their energy is higher than cis-trans.

The electronic charge localized at the lone pairs on oxygen is transferred to the covalent bonding region between Si and O. Therefore, the character of the lone pairs is diminished and the sp3 hybridization geometry is altered. This is the reason why the Si-O-Si bond angle is very large. The wider the Si-O-Si angle the lower the barrier between the isomeric states (from cis-trans to trans-gauche or cis-gauche).

Study of large polydimethylsiloxanes chains had shown that their conformation is not highly oriented. There are planar segments of cis-trans sequences which are interrupted randomly by gauche bonds. When bulky substituents replace one of the methyl groups at Si, the energy of gauche isomers is greatly increased when compared to cis-trans conformation. These features account for the chain flexibility and differences in physical properties.

Allyl Groups Ended Polysiloxanes

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The People's Republic of China

A new kind of addition cure silicone rubber based on allyl groups ended polydimethylsilane has been prepared and studied. To our surprise, the silicone rubber based on triallylsilyl or methyldiallylsilyl ended polysiloxane shows an excellent adhesive property to metals, plastics and ceramics. Its adhesive shear strength to pure copper and stainless steel is about 3.5 MP with cohesive failure, and the strength is retained after immersion of the samples in water for more than twenty days. Furthermore, the allyl-based polysiloxane-Pt curing system is not sensitive to some foreign substances, which, when added to vinyl-based addition cure silicone rubber, would retard the curing. In our experiment, The allyl ended polysiloxanes were easily prepared by the reaction of hydroxyl ended polysiloxane with triallyl silane or methyldiallyl silane, and the latter two silanes were synthesized in high yield by modified Grignard reaction. The above results show that these polymers may be considered as a potential industrial product and used as adhesives, coatings and potting agents.

The curing behavior of allyl groups ended polysiloxane-Pt system is also discussed in the paper.

NOVEL TRIBLOCK SILOXANE COPOLYMERS: SYNTHESIS AND CHARACTERIZATION

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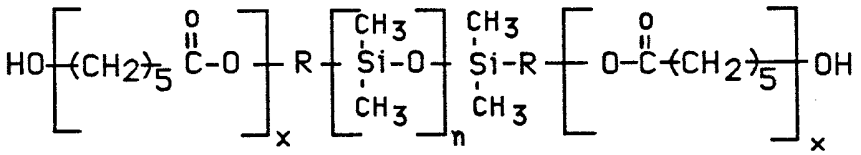
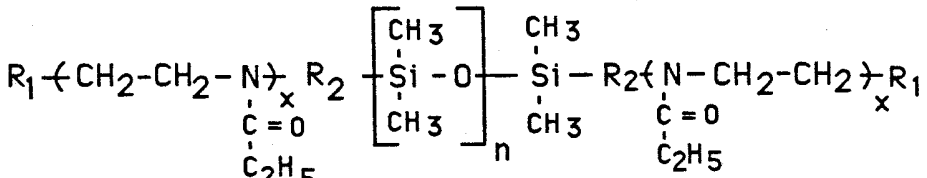
Siloxane containing multiphase copolymers display unique combination of surface/bulk properties which are not possessed by any other copolymeric system. It is possible to obtain siloxane copolymers with desired properties through proper design of the backbone structures and controlled copolymerization reactions. During our presentation we will discuss the synthesis and characterization of novel polycaprolactone-b-polydimethylsiloxane (PDMS) (1) and poly(2-ethyl-2-oxazoline)-b-PDMS (2) triblock copolymers. These materials are obtained via the ring opening polymerization of ϵ-caprolactone or 2-ethyl-2-oxazoline monomers by using organofunctionally terminated PDMS oligomers as initiators and comonomers. Segment molecular weights in these copolymers were varied between 500 and 15,000 g/mole. DSC and TMA studies showed the formation of two phase morphologies with siloxane (Tg ≈ -120°C) and polycaprolactone (Tm ≈ 50-60°C) or poly(2-ethyl-2-oxazoline) (Tg ≈ 40-60°C) transitions respectively. Resultant copolymers are used as reactive oligomers having improved solubilities in polar solvents or as surface modifying additives in polymer blends.



(1)



(2)

SYNTHESIS AND CHARACTERIZATION OF NEW LIQUID CRYSTAL SIDE CHAIN POLYMERS.

G. de MARIGNAN, D. TEYSSIE and S. BOILEAU

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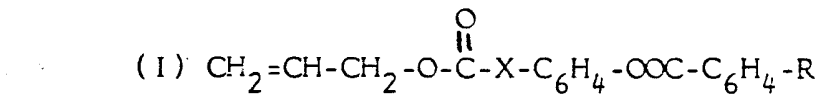
75231 Paris Cédex 05, France.

A series of new unsaturated carbonate and thiocarbonate compounds was prepared by reaction of allylchloroformate with different para-substituted phenylbenzoate esters under phase transfer catalysis conditions according to the general formula below.



(I) $CH_2=CH-CH_2-O-\overset{\overset{O}{\|}}{C}-X-C_6H_4-OOC-C_6H_4-R$

with X = S or O

R = $-OCH_3$, $-OC_2H_5$, $-OC_6H_{13}$, $-CN$

All these low molecular weight nematic compounds were subsequently hydrosilylated with polymethylhydrosiloxanes and (methylhydro)(dimethyl)siloxane copolymers. Several side reactions were identified by ^1H NMR, in the hydrosilylation step, and after studying the influence of the solvent, the catalyst (H_2PtCl_6 or tetramethyldivinyl Pt) and the temperature the most favorable conditions for yielding a pure polymer were determined. Although the hydrosilylation of compounds (I) proceeded readily, attempts to hydrosilylate the corresponding vinyl derivatives, which are also nematic, failed under the experimental conditions investigated.

All the polymers modified with compounds I were purified and characterized by ^1H NMR, GPC, and by observation on the hot stage of a polarizing microscope. All the polymers exhibited mesomorphic properties which were analysed in terms of the nature of the spacer, of the length and the nature of the tail group.

ANIONIC RING OPENING POLYMERIZATION OF SILA- AND GERMACYCLOPENT-3-ENES

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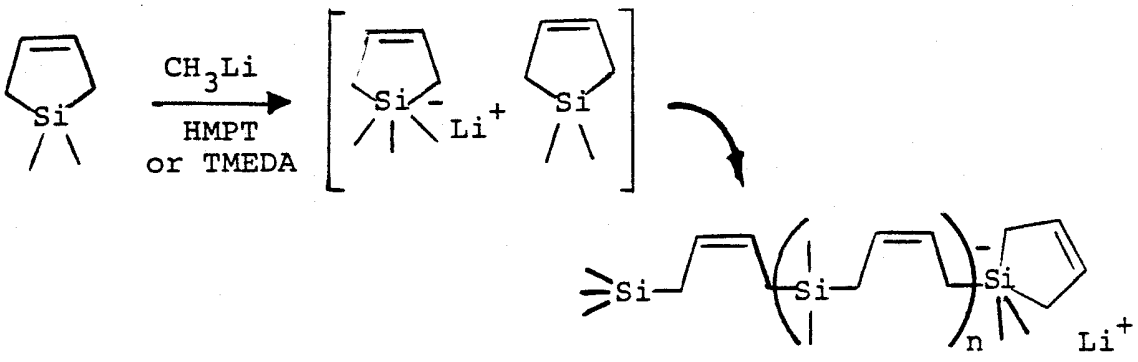
1,1-Dimethyl-1-silacyclopent-3-ene, 1-methyl-1-phenyl-1-silacyclopent-3-ene, 1,1-diphenyl-1-silacyclopent-3-ene, 1,1,3-trimethyl-1-silacyclopent-3-ene and 1,1-dimethyl-1-germacyclopentene undergo ring opening polymerization catalyzed by alkyl lithium reagents and hexamethylphosphorous triamide or N,N,N',N'-tetramethyl ethylenediamine to yield respectively poly(1,1-dimethyl-1-sila-cis-pent-3-ene), poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene), poly(1,1-diphenyl-1-sila-cis-pent-3-ene), poly(1,1,3-trimethyl-1-sila-cis-pent-3-ene) and poly(1,1-dimethyl-1-germa-cis-pent-3-ene). These polymers have been characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. Their molecular weight distributions have been determined by gel permeation chromatography. Their thermal stability has been measured by thermogravimetric analysis. The mechanism of this novel ring opening polymerization is discussed.



Cure properties of Ethylidenenorbornyl group substituted organopolysiloxane

Junichiro Watanabe and Yuuichi Funabashi

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Nishishin-machi 133, Ohta-Shi, Gunma 373, JAPAN

To improve physical properties of organic rubber by co-valcanization with silicone rubber, Ethylidene-norbornyl group was introduced to dimethylpolysiloxane polymer(ENB silicone). We studied the reactivity and compared with conventional Vinylsiloxane polymer(Vi silicone).

As a organic rubber, IIR was chosen. The results were summarized in Fig. 1.

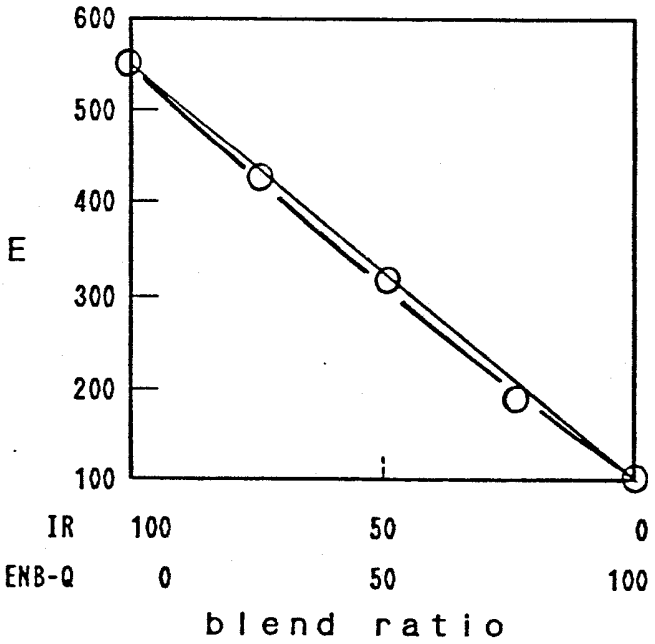

Fig.1

Fortunately ENB silicone itself could be valucanized in hot air by alkyl peroxide. Further details will be discussed.

New Synthetic Route of Hydrogenalkoxysilane

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Hydrogenalkoxysilane is commonly synthsized from hydrogenchlorosilane by alkoxylation, however, in many cases, the alkoxylation was accompanied with decomposition of Si-H bond. We found that hydrogenakloxysilane is easily synthesized by the reaction of alkoxysilane and hydrogenorganosiloxane catalyzed by Ti compound.

$$\text{Si-OR}' + -\left(\begin{array}{c}\text{Me}\\ \text{OSi}\\ \text{H}\end{array}\right)_n- \xrightarrow{\text{Ti}} \text{MeHSi(OR}')_2 \qquad (1)$$

$$\text{Si-OR}' + (\text{Me}_2\text{HSi})_2\text{O} \xrightarrow{\text{Ti}} \text{Me}_2\text{HSi(OR}') \qquad (2)$$

Details will be discussed.

Polysiloxane-Based Polymer Electrolyte Complexes

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Syracuse, New York 13210

Polysiloxanes with oligo-oxyethylene side chains of the type $-O(CH_2CH_2O)_7CH_3$ or $-(CH_2)_3O(CH_2CH_2O)_nCH_3$ (n = 7, 11), and those with a $-(CH_2)_3OCH_2CH(OH)CH_2SO_3^-$ side chain were synthesized from poly (hydrogenmethysiloxane) or by ring opening polymerization of the corresponding substituted cyclic tetramethyl siloxane. The polymers were characterized by ^1H NMR, ^{29}Si NMR, IR and GPC. Polymer electrolyte complexes of the neutral polysiloxane comb polymers with $LiClO_4$ were made by solvent casting from THF, and conductivities measured as a function of temperature and salt concentration. Maximum conductivities close to $10^{-4}Ohm^{-1}cm^{-1}$ were achieved at room temperature and at Li^+ to ethylene oxide unit ratios of about 25. Cross-linking or blending with high molecular weight poly(oxyethylene) lowers the conductivity somewhat but considerably improves the mechanical properties of these solvent-free polymer electrolytes. Blends with PEO can be cast into flexible, tough films with good conducting properties. The sodium salt of the single ion conductor with a polymer-bound-SO_3^- ion has a conductivity at 70°C of only $10^{-6}Ohm^{-1}cm^{-1}$, but this is increased by an order of magnitude by incorporating tetraethylene glycol into the polymer film.

HYDROLYSIS AND CONDENSATION KINETICS OF DIMERIC SOL-GEL SPECIES BY ^{29}Si NMR*

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Sandia National Laboratories, Albuquerque, NM 87185

The chemical and physical structure of silicate sol-gel polymers is determined, in part, by the reaction kinetics during the early stages of polymerization. Using high resolution ^{29}Si NMR, the reaction kinetics of monomeric and dimeric species have been studied. Peak assignments were determined by comparing acid catalyzed reacting solutions prepared with limited amounts of water to the synthetically prepared dimer and linear trimer. In the tetramethoxysilane sol-gel system, peak positions of Q1 species follow predictable trends; conversion of $-OCH_3$ to -OH on the neighboring silicon results in a downfield shift of 0.05 ppm while conversion of $-OCH_3$ to -OSi on the neighboring silicon results in an upfield shift of 0.19 ppm. Thus, all 10 possible dimers are distinguishable and can be monitored by ^{29}Si NMR.

The temporal evolution of hydrolysis and condensation products has been compared to a kinetic model** developed in our laboratory and rate constants have been determined. These results indicate that the water producing condensation of dimeric species (Q1 silicon) is approximately 5X slower than the water producing condensation of monomeric species. The alcohol producing condensation of dimeric species is comparable to that of monomeric species.

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*This work performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract number DE-AC04-76DP00789.

**B. D. Kay and R. A. Assink, Mat. Res. Soc. Proc. 73, 157 (1986).

POSTER SESSION TWO

SYNTHESIS AND APPLICATION OF BI-FUNCTIONAL ORGANOPOLYSILOXANE

TADASHI FUJII, ISAO ONA
TORAY SILICONE

We have been investigating several kinds of α, ω-organo-functional silicone polymers, and developing their applications.

The α, ω-organofunctional silicone polymer is synthesized by two methods. One is "dimer-method", dimethyl cyclics is polymerized in the presence of α, ω-Biorganofunctional disiloxane. The other is "Si-H base polymer-method", organofunctional group is introduced to the silicone polymer containing terminal Si-H carboxy, acryl et al. The functional group is placed in γ-carbon or α-carbon. Typical applications being investigated now are modification of plastics such as epoxy, urethane and acrylics. The α, ω-organofunctional silicone polymer is copolymerized into the organic polymer chain and the characteristics of siloxane are imparted to host organic polymer. Oxygen or water vapor permeability is given to contact lens, oxygen enrich membrane or wall coating paint. Improved toughness is given to the thermosetting resin.

NEW FLUORINATED POLYSILOXANES

Rosita Dorigo, Anne-Marie Garnault, Dominique Teyssié and Sylvie Boileau.

Laboratoire de Chimie Macromoléculaire, Collège de France, 11 place Marcelin Berthelot, 75231 Paris Cédex 05, France.

Fluorinated silicones represent a very active field of research mainly because of their applications in high performance coatings and in sealants resistant to heat and chemicals. These polymers can be prepared by several methods like polycondensation of fluorinated dichlorosilanes obtained by hydrosilylation of fluorinated olefins, by ring-opening polymerization of fluorinated cyclosiloxanes as well as by chemical modification of polysiloxanes. Some of these methods have been successfully applied to the preparation of new polysiloxanes containing fluorinated side groups linked to the backbone through an ether or thioether function like $C_6F_{13}(CH_2)_2O(CH_2)_3-$ and $C_6F_{13}(CH_2)_2S(CH_2)_2-$. The synthesis and the physical properties of these new polymers will be discussed.

SYNTHESIS AND PROPERTIES OF SILICON-BRANCHED ORGANOSILICON HIGH POLYMERS

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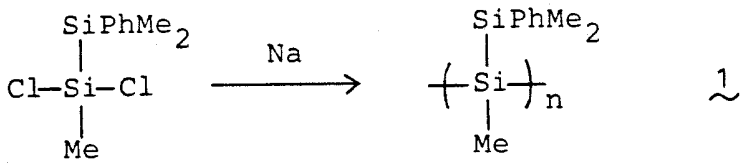
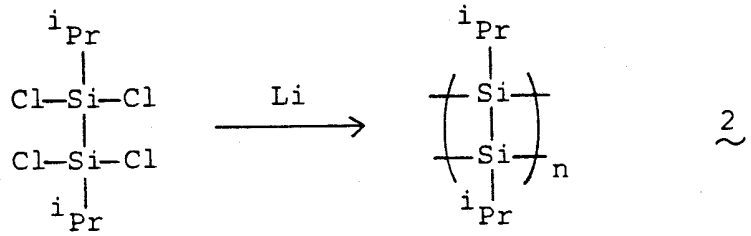
Recently, much interest has been directed to study the radiation sensitivity of soluble alkyl and aryl substituted linear polysilanes and to access their lithographic potential.

Since it is known that silicon-branching in the silicon frameworks results in electronic stabilization effect to some extent, silicon-branched organosilicon high polymers are expected to exhibit unique properties different from those of existing organosilicon high polymers.

Along this line, we have prepared the following two soluble silicon-branched organosilicon high polymers according to the equations shown below.



1



2

Irradiation of polymer 1 (white powder) produces smaller fragments first, while prolonged irradiation gives a yellow material with much higher molecular weights. Ladder polymer 2 appears as white powder and absorbs in the region from 330-350 nm. These and other experimental details will be presented.

SOLUBLE SUBSTITUTED DIARYL POLYSILANES: CHEMISTRY AND SPECTROSCOPY

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and R. Sooriyakumaran

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Substituted silane polymers have attracted considerable attention recently because of their curious spectral properties and the development of a host of new applications. Even though the backbone is composed entirely of a sigma bonded silicon framework these materials absorb strongly in the ultraviolet. Simple atatic alkyl substituted derivatives absorb around 300-325nm. The λmax depends strongly on the backbone conformation and is red shifted by over 60nm when the backbone is locked into a planar zigzag conformation. Aryl substituents directly bonded to the backbone in atatic systems cause red shifts of 25-30nm.

We have prepared the first, soluble high molecular weight substitute of poly(diarylsilane) derivatives. Most of these materials absorb strongly at extraordinarily long wavelengths (~400nm) making them the most red shifted of all the polysilanes. The spectral shifts are much greater than the predicted electronic substituent effects and the difference is believed to be conformational in origin. Surprisingly, the bis-p-alkoxyphenyl polymers, unlike their alkyl substituted counterparts, have an absorption maximum around 330nm at room temperature. These materials are, however, strongly thermochromic and the absorption maxima shifts to ~400nm upon heating. This thermochromism is reversible and is again believed to be conformational in origin. The synthesis, spectroscopy, and radiation sensitivity of a variety of substituted diaryl polysilanes will be described.

THE SOLUTION THERMOCHROMISM OF POLY(DI-N-ALKYLSILANES)

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J. Michl, K. Klingensmith,
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R. West
J. Maxka
University of Wisconsin, Madison, Wisconsin 53706

A number of polysilane derivatives are thermochromic in solution at low temperatures. In this regard, the behavior of poly(di-n-hexylsilane) (PDHS) is particularly dramatic. Upon cooling solutions of PDHS to ~-30°C a very sharp, intense band appears ~35-40nm red shifted from the original absorption. The origin of this dramatic spectral change has been the source of considerable speculation[1,2].

We will discuss some aspects of our studies on the solution thermochromic behavior of diakyl polysilanes. The effect of concentration, solvent, thermal history, and rate of cooling on the transition of PDHS at low temperatures will be described. Although the earlier work has suggested that the nature of this transition is conformational in origin, recent low temperature light scattering studies have shown that aggregation occurs in solutions of PDHS around the transition temperature[3]. We will discuss the results of experiments designed to probe the temporal relationship between the onset of the low angle scattering (i.e. increase in molecular weight) and the emission from the low temperature form of PDHS as a function of solvent, concentration, cooling rate etc.

References

1. Trefonas, P., III; Damewood, J.R., Jr.; West, R; Miller, R.D. Organometallics 1985, 4, 1318.
2. Harrah, L.A.; Zeigler, J.M. J. Polym. Sci. Polym. Lett. Ed., 1985, 23, 209.
3. Cotts, P.M.; Maxka, J.; Miller, R.D.; West, R. Polym Preprints 1987, 28, 450.

Light Scattering from Dilute Solutions of Aryl Substituted Polysilanes

P. M. Cotts, R. D. Miller and R. Sooriyakumaran

IBM Almaden Research Center, San Jose, California

The electronic absorption maximum of aryl substituted polysilanes occurs at an unusually long wavelength[1], suggesting that an extended conformation may exist even in dilute solution. Static and dynamic light scattering measurements have been employed to determine the thermodynamic and hydrodynamic dimensions of one of these polymers in dilute solution. Preliminary results on a moderate molecular weight sample ($M_w = 42000 \pm 5000$) show an unusually large difference between the thermodynamic root mean square radius of gyration ($R_g = 300\text{Å} \pm 30\text{Å}$) , and the hydrodynamic radius ($R_h = 50\text{Å} \pm 2\text{Å}$) . In addition, the concentration dependence of both the integrated scattered intensity (c/R_θ) and the mutual diffusion coefficient ($D_{m,c}$) were nearly negligible. These results were consistent among the three solvents used: cyclohexane, tetrahydrofuran, and toluene. This suggests an asymmetric particle which is rather compact. Further investigation of higher molecular weight samples and polydispersity effects will permit a more definitive conclusion.

1. R. D. Miller and R. Sooriyakumaran, *J. Pol. Sci., Pol. Lett. Ed.* **25**, 321 (1987).

Novel Mono- and Dual-Interpenetrating Network Polymers of Polysiloxane-Polystyrenic Systems

by Arne O. Finberg
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2731 Bartram Road, Bristol PA 19007

Sequential polymerization of polysiloxane networks via hydrosilylation reactions, followed by controlled free radical polymerization of styrenics in bulk are presented. The parameter controlling the separate networks and influences of these on final overall properties will be discussed. The effects of the styrenic structures on morphology present in polysiloxane polystyrenic interpenetrating network systems will also be discussed.

Novel Mono- and Dual-Interpenetrating Network Polymers of Polysiloxane and Polymethacrylate Esters

by Arne O. Finberg
Dynamit Nobel Chemicals
2731 Bartram Road, Bristol PA 19007

Synthesis of sequential interpenetrating polymeric networks of polysiloxane and polymethacrylate esters in bulk and solution will be discussed. The critical properties of silicone elastomers and how these are significantly improved via the parameters controlling the separate networks will be presented. Results on potential applications of these networks will be presented based on processing and properties of the polysiloxane-polymethacrylate interpenetrating network systems.

TRANSITION METAL SUBSTITUTED POLYSILANES

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Examples of a new class of high molecular weight polysilanes containing transition metal substituents have been synthesised and characterized using the Wurtz coupling reaction 1.

$$x\ LMSiMeSiCL_2 + y\ R_2SiCl_2 \rightarrow [(LMSiMe)_x(SiR_2)_y]_n \quad 1$$

LM = ferrocenyl, $(\eta^5\text{-}C_5H_5)Fe(CO)_2$

In the case of LM = ferrocenyl such reactions result in polymers with molecular weights up to 400,000, while thus far experiments with LM = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ produce much lower molecular weight materials. Our results indicate that the copolymers produced result from statistical incorporation of the metal silanes into the polymer backbone.

While all the various examples of the metal substituted copolymers exhibit photodepolymerization upon ultraviolet irradiation, the rates of depolymerization vary considerably as a function of the type of LM substituent and the ratio x/y.

This research has been supported by a Texas Advanced Technology Research Award and the Robert A. Welch Foundation.

POLYMERS AND COPOLYMERS OF DISILACYCLOHEXADIENE. A NON-ALKALI-METAL ROUTE TO POLYSILANES

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China Lake, California 93555-6001

1,1,2,2-Tetrachlorodimethyldisilane was prepared by a potentially inexpensive route from the process residue of chloromethylsilane manufacture. From the disilane was prepared 1,1,2,2-tetramethoxydimethyldisilane. This was reacted with acetylene in a tube reactor heated to 400 - 425 C to form a mixture liquid at ambient temperature. Careful vacuum distillation of this liquid mixture yielded by-product, methyltrimethoxysilane, and crude 1,4-dimethyl 1,4-dimethoxy-1,4-disila-2,5-hexadiene, identified by infrared spectroscopy and proton NMR. The crude product was reacted with KOH; recrystallization in isopropanol yielded the pure dipotassium salt. Acidification of the dipotassium salt yielded the homopolymer oxy-1,4-dimethyl-1,4-disilacyclohexadiene, and reaction of the dipotassium salt with phenylmethyldichlorosilane yielded oxy-1,4-dimethyl-1,4-disilacyclohexadiene-phenylmethylsiloxane polymer. These polymers were found to be thermally stable by TGA.

Vigorous distillation of the crude reaction mixture yielded the methyltrimethoxysilane by-product and a glassy, transparent reaction product. Infrared spectroscopy and proton NMR suggested the product to be poly(methylmethoxysilane). The reaction of acetylene and 1,1,2,2-tetrachlorodisilane in a heated tube at 500C produced a product liquid at ambient temperature that upon vigorous distillation produced a glassy transparent solid; IR, proton NMR, and UV spectra suggest the product to be poly(methylchlorosilane).

EMISSION STUDIES OF SOLID POLY(ARYLMETHYLSILANES)

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Aryl substituted polysilane polymers emit visible light when irradiated in the solid state. The visible emission is enhanced after melting the polymers and cooling them to room temperature. Variation of the emission energy upon methyl substitution of the aryl ring suggests that rotation about the Si-aryl bond influences the transition energy. Spectroscopic data will be presented on conformationally fixed derivatives of these polymers.

MECHANISTIC STUDIES OF POLYSILANE FORMATION

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The pyrolysis of polysilanes to SiC often gives low yields unless measures are taken to crosslink the polymer before heating. The incorporation of upto 10% vinylmethylsilylene units into the backbone enables yields of above 70% SiC to be obtained without prior crosslinking. The presence of vinylmethyldichlorosilane in the preparation of polysilanes by the reductive coupling of organodichlorosilanes by sodium in refluxing toluene, often reduces the yield of the very high MW product. The major initial product is fairly low in MW and contains some of the very low MW cyclic materials. Continued reaction with sodium does cause an increase in the MW, but with the parallel formation of insoluble polymer.

Some reaction rate studies have been made on these systems of copolymers and terpolymers. These results tend to confirm that the rate determining step is not the reaction of the dichloride with the sodium surface.

PHYSICAL PROPERTIES OF PHOTOACTIVE POLYSILANE COPOLYMERS

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High molecular weight soluble polysilane copolymers have been prepared using five different silane monomers that include; cyclohexyl methyl, dimethyl, i-propyl methyl, n-propyl methyl and phenyl methyl silane repeat units. Copolymers were prepared containing 25, 50 and 75 mole percent of the respective monomers. All polymers were prepared via the standard Wurtz condensation method and were subsequently fractionated. The original polymers and the various fractions have been characterized by a number of techniques including: gel permeation chromatography, ultraviolet and infrared spectrophotometry, thermal gravimetric analysis and differential scanning calorimetry and proton, carbon-13 and silicon-29 nuclear magnetic resonance (NMR) spectroscopy. The ultraviolet light induced degradation rates in solution have also been studied for all copolymers. The relationship between molecular weight and the properties of the polymers will be discussed.

ELECTRONIC STRUCTURE AND CONFORMATION STUDIES OF POLYSILANE MODEL SYSTEMS

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We have recently begun a study of the structure and electronic properties of polysilane model systems. This study has followed a two-pronged approach: *ab initio* calculations on small silane oligomers of the series Si_nH_{2n+2} and LCAO local-density functional polymer band structure calculations on single chains (with one-dimensional periodicity) of both unsubstituted and substituted polysilane chains.

Full geometry optimizations were performed using *ab initio* techniques for *n*-tetrasilane (Si_4H_{10}) and *n*-pentasilane (Si_5H_{12}) to study the relative total energies of the all-*anti* (or planar zig-zag) conformations versus helical conformations of the polysilane backbone. Our results for the optimized geometries show no significant differences in total energy between the rotamers of either the tetrasilane or pentasilane systems. Ionization energies were calculated for the five highest one-electron states using electron-propagator methods. These results were in close agreement with experimental photoelectron spectroscopy results and support earlier speculation that the photoelectron spectra originate from a nearly equal mix of rotamers.

LCAO local-density functional one-dimensional band structure calculations were performed for a series of polymer chain conformations: unsubstituted polysilane $[(SiH_2)_x]$ in the all-*anti* conformation and in a 1*4/1 helical conformation, and dimethyl-substituted polysilane $[(Si(CH_3)_2)_x]$ in the all-*anti* conformation. Absorption spectra, with cross-sections calculated using the Ehrenreich-Cohen perturbative scheme and our one-electron levels and wavefunctions, predict a transition from a highly anisotropic absorption for the *anti* conformation of polysilane with absorption present in the vicinity of the absorption threshold only for polarizations parallel to the chain axis, to nearly isotropic absorption for the helical conformation. Results for the dimethyl-substituted polysilane suggest that the states immediately about the Fermi level retain their silicon-backbone σ character upon alkyl-group substitution, although the band gap decreases roughly 1 eV because of mixing of the frontier states with alkyl substituent states both below the valence band and above the conduction band.

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MODIFICATIONS OF POLYSILANES

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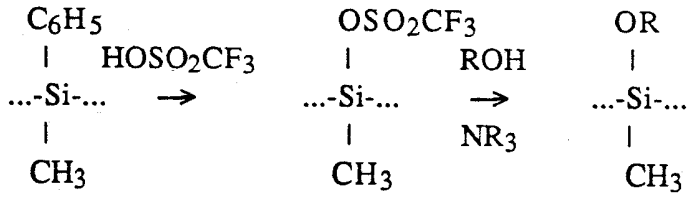
Polysilanes are usually prepared from dichlorodisubstituted silanes by the reductive coupling with molten sodium. The severe reactions conditions of this precess allow the presence of only alkyl and aryl substituents at the silicon atom. Aryl groups in different silanes, disilanes, and polysilanes have been rapidly and quantitatively displaced by strong protonic acids. The obtained silyl esters or halides react with different nucleophiles such as alcohols, secondary amines, and thiols. Thus, the poly(phenylmethylsilylene) was transformed to the triflate derivative (by the action of triflic acid) and later to the poly(methylmethoxysilylene) using methanol and triethylamine:



In this way polymers with different content of methoxy, trifluoroethoxy, allyloxy, phenoxy, tertbutoxy, diethylamino, etc. groups were prepared. This type of modification enables introduction of different functional groups.

Another application of the reactive "triflated" polysilanes is the formation of block and graft copolymers. The properties of these copolymers can be controlled by the lenghts of the side chains. High molecular weight ($\bar{M}_w > 10^6$) graft copolymers of polytetrahydrofuran and polysilane were prepared from low molecular weight ($\bar{M}_n = 4.10^3$) poly(phenylmethylsilylene).

EXCITON-EXCITON ANNIHILATION IN POLYSILANES*

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We have studied exciton-exciton annihilation in poly(n-propyl methyl silane) and have found that it is an important process. The rate of loss of excitons by exciton-exciton annihilation equals the rate of loss by other radiative and non-radiative processes at the very low concentration of about 10^{16} exciton/cm^3. Two types of experiments have been conducted. One in which the excitons are produced uniformly throughout a relatively thick ($\approx$50 μm) film and another in which the excitons are produced near the surface of the film by strongly absorbed light. In both experiments the intensity of fluorescence is measured as a function of the intensity of the incident light. We are presently examining the possibility that a small difference in the rate constant for exciton-exciton annihilation, determined by the two experiments, can be explained by exciton diffusion.

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*This work performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract number DE-AC04-76DP00789.

ORDER-DISORDER TRANSITIONS AND OPTICAL PROPERTIES OF POLYSILANES*

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A microscopic statistical mechanical theory of the coupled electronic-conformational transitions of alkyl-substituted polysilanes in dilute solution is described. Dispersion interactions between the delocalized sigma electrons of the polymer backbone and the surrounding polarizable medium can induce a relatively abrupt rod-to-coil transition. The qualitative phase behavior is predicted to be controlled by the magnitude of the conformation-dependent polarization interaction relative to the degree chain flexibility. The theory is consistent with the dilute solution experiments of Harrah and Zeigler as a function of solvent, molecular weight, and substituent structure. A unified theoretical model for both the electronic absorption and emission spectra in solution has also been developed. Static conformational disorder controls the major temperature-dependent absorption features. The flourescence, however, is very different due to rapid intramolecular singlet excitation transfer. A theoretical model which includes conformational disorder and adiabatic electron-phonon modulation of the silicon bond lengths and angles has been developed. The latter feature is found to be the dominant mechanism for emission line broadening. Excellent agreement between the theory and experiments has been demonstrated for poly(n-propyl methyl silane).

*This work performed at Sandia National Laboratories supported by the U. S. Department of Energy under contract number DE-AC04-76DP00789.

OPTICAL PROPERTIES OF BIMODAL SILICON-CONTAINING NETWORKS

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The present investigation is devoted to the study of the photoelastic properties of (non-Gaussian) bimodal networks consisting of Poly(dimethylsiloxane) chains. Results were obtained from a series of strain-birefringence experiments at 25°C. Calculation of the stress-optical coefficients C of the networks employed shows a marked deviation from linearity and in addition suggests that the residual interchain correlations in the bimodal networks depend strongly on the molar concentrations of the short chains. Finally, comparison of the observed non-Gaussian optical properties to the mechanical ones show a striking similarity.

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POSTER SESSION THREE

GLOW DISCHARGE DECOMPOSITION OF PHENYLSILANES AND PROPERTIES OF DEPOSITED FILMS

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VESSELIN SINIGERSKY, HIDEOMI KOINUMA, KAZUO FUEKI
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We have been carrying out the glow discharge decompositions of phenylsilane and methylphenylsilane to investigate the effects of aromatic substitutions on the reactivity of the source materials and properties of the deposited films. In a capasitively-coupled plasma CVD apparatus (13.56MHz), phenylsilanes were decomposed.

Structures and properties of the deposited films were found to be primarily influenced by the rf power. The structures of the films were analyzed by FT-IR and laser Raman spectroscopy. The phenyl and i-H groups were observed in the films deposited at low (<10W) rf powers, whereas they were scarcely visible in the spectra in the films deposited high ($\geq$ 10W) rf powers. The optical band gaps of the films are increasing (1.5 - 3.0eV) with decreasing the rf power. Judging from these results, it is suggested that the former films have polysilane-like chains with pendant phenyl groups and the latter films are a-Sic containing graphite-like carbon clusters. Although all the as-deposited films were nearly insulators ($\sigma = 10^{-10}$-10^{-12} S cm^{-1}), the conductivitie were improved up to 10^{-6}-10^{-9} S cm^{-1} by both substitutional doping with B_2H_6 and chemical doping with I_2 or $SbCl_5$.

A Critical Analysis of Hysteresis, Creep and Elastic Recovery in Novel Interpenetrating Polysiloxane-Addition Polymer Network Systems

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The state of the polysiloxane networks present in addition polymer networks will be analyzed. The nature of the second network in view of affine deformation, mechanical strength, modulus, elasticity, tear and elastic recovery will be evaluated. Theoretical models for predicting the mechanical properties of homogeneous interpenetrating network systems of polysiloxane and addition polymers will be presented.

(18:22)

BLOCK INTERRUPT POLYSILANE DERIVATIVES

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Polysilane derivatives comprise a new class of radiation sensitive polymers which are attracting considerable interest because of their curious spectral properties and the evolution of a host of new applications. With regard to the latter, the use of polysilane derivatives for a variety of microlithographic applications has received considerable attention.

In microlithography, the need for higher resolution has led to the development of a variety of deep UV (λ220-280nm) exposure tools. In order to match the spectral output of these sources, we have developed a class of polysilane derivatives containing short and well defined polysilane blocks isolated from one another by nonconjugating backbone atoms and groups. Materials of this type have been prepared by the condensation of a variety of α,ω-disubstituted polysilane derivatives with a number of bis silanols in the presence of tertiary amine catalysts. Using this procedure, we have prepared high molecular weight (Mw 20-150K) block interrupt polysilanes containing discrete silicon blocks which vary from two to six units in length. These materials absorb from 220-290nm depending on the length of the silicon blocks and are radiation sensitive. All of these polymers bleach readily upon exposure in the manner previously demonstrated for other polysilane derivatives. The synthesis and characterization of these silicon block interrupt polymers will be described and their radiation sensitivity will be discussed.

"SOLUBLE ALKYL SUBSTITUTED POLYGERMANES: THERMOCHROMIC BEHAVIOR"

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R. D. Miller,
J.F. Rabolt,
C. Zimba

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Soluble polysilane derivatives which contain only silicon in the backbone represent a new class of radiation sensitive polymers for which a number of new applications have been reported. Much of the scientific interest in catenated silicon polymers has centered around their very unusual electronic spectra. Recently, we have shown that the spectral properties depend not only on the nature of the substituents, but also on the conformation of the backbone. We have demonstrated that poly(di-n-hexylsilane) and certain higher homologs prefer a planar zig zag backbone conformation which is enforced by side chain crystallization. This causes a significant red shift in the absorption spectrum below the side chain melting transition. We have now observed similar thermochromic effects for the related polygermane derivatives.

Soluble, high molecular weight poly(di-n-alkyl) germanes can be prepared by the modified Wurtz coupling of the respective dichlorogermanes as shown below. Films of these materials absorb around 335-340 nm and the absorption changes little upon heating to 100°C. In this regard, the spectra of the germanium polymers are 20-25 nm red shifted from related amorphous poly(di-n-alkylsilane) derivatives.

DSC analysis of poly(di-n-hexlgermane)(PDHG) showed a strong and reversible endotherm around 12°C. This transition is also associated with a thermochromic change in the absorption spectrum which results in the production of a long wavelength transition around 370-375 nm. The thermochromism is completely reversible upon repeating the thermal cycle. By analogy with the related polysilanes we attribute this spectral shift to side chain crystallization which results in a planar zig zag conformation for the germanium backbone. It is interesting that theoretical studies have predicted a convergence of the electronic absorption for long chain silicon and germanium catenates and our studies seem to confirm these predictions.

We will discuss the synthesis and spectral characterization of soluble polygermane homo and copolymers and will compare and contrast their spectral properties with the comparable polysilane derivatives.

SILICON PHTHALOCYANINES USEFUL FOR THE PREPARATION OF LANGMUIR-BLODGETT FILMS FOR SENSORS

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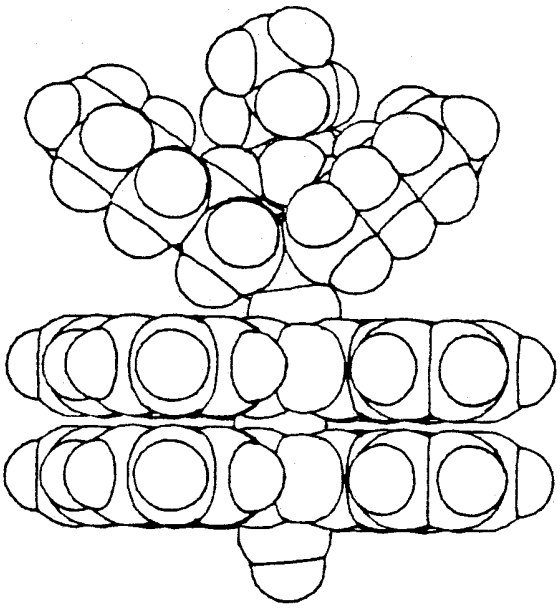
Phthalocyanines which can be formed into monolayers by the Langmuir-Blodgett technique and which are of use for gas sensors are described. These phthalocyanines have unsymmetrical axial groups. The groups are chosen so as to lead to orientation of the rings so that their planes are parallel to the deposition surface. Typically they have an organosiloxy group in one axial position and a hydroxyl group in the other axial position. An example is $(n\text{-}C_6H_{13})_3SiOSiPcOGePcOH$,



This phthalocyanine gives a high collapse pressure and a co-area of the size anticipated. The preparation and properties of these phthalocyanines will be discussed.

SYNTHESIS AND PROPERTIES OF POLY(α,β-UNSATURATED ACYLSILANE)S

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ABSTRACT

1-Trimethylsilyl-2-propen-1-one (vinyl trimethylsilyl ketone, VTMSK) was polymerized in the presence of a free-radical initiator to give a high-molecular-weight linear polymer, poly(1-trimethylsilyl-2-propen-1-one) (PVTMSK). The colorless polymer is soluble in many organic solvents including hexane, has a low glass transition temperature (*ca.* 64 °C), and exhibits moderate absorption at *ca.* 370 nm ($\epsilon \approx 80$). PVTMSK undergoes thermal and photo-initiated decomposition both in the solid state and in solution. The thermal decomposition in air begins at 150–200 °C and results in a rapid weight loss above 300 °C. PVTMSK is rapidly degraded by light in a chloroform solution. The use of PVTMSK as a mid-UV-sensitive, oxygen plasma-resistant resist was hindered by a competing cross-linking reaction during the exposure and by the high solubility of the polymer in almost all organic solvents. Homopolymerization of a homologous α,β-unsaturated acylsilane, 1-methyl-1-trimethylsilyl-2-propen-1-one (isopropenyl trimethylsilyl ketone, IPTMSK) was unsuccessful both under free-radical and anionic initiation conditions, although copolymers with styrene and methyl methacrylate have been obtained.

STRUCTURAL FACTORS INFLUENCING THE RATE OF MIGRATION AND REORGANIZATION OF SILOXANE-CONTAINING, SURFACE-MODIFYING POLYMERIC ADDITIVES

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Siloxane-containing, surface-active ABA block copolymers (B = siloxane) were melt blended with a variety of base polymers to assess the effects of structural features on the rate of surface migration and reorganization of the (fully-developed) surface layer. The rate of surface migration in compression-molded films was monitored using water/methylene iodide contact angles to calculate solid surface tensions, which were used, in turn, to calculate diffusion coefficients for the surface modifying additives (SMA) polymers. As expected, the diffusion rates increase significantly at annealing temperatures greater than the Tg of the base polymer. The degree of surface coverage by siloxane (PSX) in air-annealed blends increased with increasing siloxane block length. In addition, the rate of copolymer diffusion/surface development increased with increasing PSX block length, even when overall SMA molecular weight was increased by the higher molecular weight PSX. Underwater annealing of air-equilibrated blends significantly increased hydrophilicity, apparently through replacement of nonpolar PSX blocks by more polar A blocks (e.g. polycaprolactone). This surface reorientation was reversible through several cycles.

STEREOSPECIFIC 1,4-POLYMERIZATION OF 2-TRIETHYLSILYL-1,3-BUTADIENE

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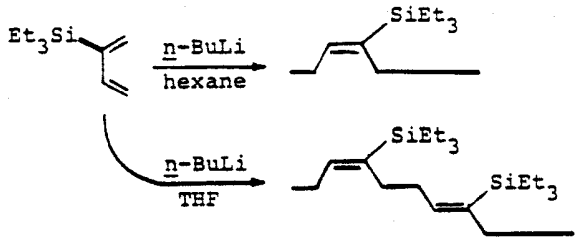
Polymerization of 2-triethylsilyl-1,3-butadiene (I) in hexane catalyzed by n-butyllithium yields cis-1,4-poly-2-triethylsilyl-1,3-butadiene. Cis-1,4-poly-2-trimethylsilyl-1,3-butadiene has been prepared by metathesis ring opening polymerization of trimethylsilylcyclobutene. On the other hand, polymerization of I in THF or THF/hexane catalyzed by n-butyllithium yields a mixture of cis and trans 1,4-poly-2-triethylsily-1,3-butadiene. These polymers have been characterized by ^{1}H, ^{13}C and ^{29}Si, NMR as well as IR spectroscopy, and elemental analysis. Their molecular weight distributions have been determined by GPC and their thermal stability by TGA. Electrophilic desilation substitution reactions on these unsaturated polymers will be discussed.



Trimethylsilyl Derivative of Layered Polysilicate and Its Thermal Treatment for the Preparation of Microporous Materials

Kazuyuki Kuroda, Tsuneo Yanagisawa, Toshio Shimidzu, and Chuzo Kato

Department of Applied Chemistry, Waseda University, Shinjuku-ku, Tokyo 160, JAPAN

Abstract: Two-dimensional silicate layers were trimethylsilylated to form planar organosiloxane like materials. Single layered sodium polysilicate, kanemite, was used in this study. The intercalation of organoammonium ions in the interlayer space of kanemite was necessary in order to enable trimethylsilylation. The formation of the organic derivative was confirmed by ^{29}Si-MASNMR, IR, XRD and elemental analysis. The heat treatment of the organic derivative yielded a microporous material.

AM1 AND MNDO/2 MOLECULAR ORBITAL CONFORMATIONAL ENERGY CALCULATIONS ON MODEL COMPOUNDS OF SIMPLE POLYSILANES AND POLYGERMANES

William D. Johnson and William J. Welsh

Department of Chemistry, University of Missouri-St. Louis

St. Louis, Missouri 63121, U.S.A.

MNDO/2 and AM1 molecular orbital calculations have been carried out on a series of structurally related polysilane and polygermane model compounds. Conformational energies have been computed as a function of rotation ϕ about a bond along the chain backbone. For each conformation, geometry optimized values of the bond angles and bond lengths were obtained. For polysilane [$-SiH_2$] the results indicate nearly equal preferences for both trans and gauche states and a high degree of rotational flexibility. For poly(permethylsilane) [$-Si(CH_3)_2$] the results show a broad minimum surrounding trans with slightly shallower and steeper minima at the gauche states. Overall this chain is less flexible and exhibits greater preferences for specific conformational states (i.e., trans and gauche). For poly(permethylgermane) [$-Ge(CH_3)_2$] the results indicate a broad minimum located at trans with steeper and slightly shallower minima near the gauche states. Compared with poly(permethylsilane), poly(permethylgermane) exhibits qualitatively a very similar profile except that the barriers are substantially lower. The authors wish to acknowledge the financial support provided by the Plastics Institute of America and the Air Force Office of Scientific Research (AFOSR).

PYROLYSIS BEHAVIOR OF SiC PRECERAMICS

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Preparation of ceramics by pyrolysis of polymer percursors has become an active research area. The processing of some ceramic materials by employing similar pyrolysis techniques used for various carbon products and carbon-carbon composites seems possible. A number of effective precursors for SiC and Si_3N_4 formation have been developed recently. Polymerization of organometallics into a uniform gel is one route to advanced ceramics.

In this work the behavior of such gels during pyrolysis is described as determined by the analysis of gaseous by-products. Silicon carbide formation is evident above 1300°C accompanied by loss of CO. The nature of the pyrolysis products is dependent on the stoichiometry of the starting gel. Silicon carbide with up to ~99% purity is obtained for certain gels. Kinetic studies performed under isothermal conditions reveal an apparent activation energy of ~90 kcal/mol between 1300 and 1400°C. Mechanistic aspects of the reaction are discussed in terms of existing solid-state reaction models.

The Application of Hydrolyzed Methyltriethoxysilane for the Preparation of Boron-Doped Silicon Carbide Powder

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Abstract:

Methyltriethoxysilane ($(CH_3)Si(OC_2H_5)_3$, MTES) was hydrolyzed and the resultant polymerized species were used for the preparation of silicon carbide by carbothermal reduction.

^{29}Si-NMR and other data indicated that the Si species in the hydrolyzed solution(MTES:H_2O:HCl=1:1:0.01, 1h, sealed system) were mainly oligomeric. Boron triethoxide was added into the hydrolyzed solution so as to dope boron homogeneously. Polyacrylonitrile dissolved in DMSO was mixed with the solution to form a homogeneous solution. After the evaporation of the solvents and the subsequent heat treatment at 220^{o}C, a brown precursor powder was obtained. Heat treatment at 1600^{o}c in Ar yielded boron-doped SiC powder.

ADVANCES IN SILICON-BASED POLYMER SCIENCE WORKSHOP

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