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## Contents

### Special Issue: A Half Century of Polysilane Chemistry

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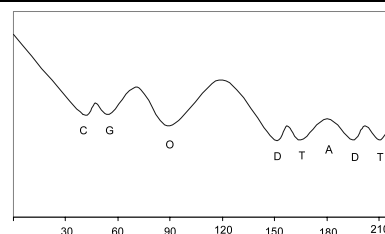
### Papers

#### Robert West

*J. Organomet. Chem.* 685 (2003) 6

A new theory for rotational isomeric states: polysilanes lead the way

Conformational studies of polysilanes have led to a new model for rotational isomerism. The permitted rotational states are *transoid*,  $\pm 165^\circ$ ; *deviant*,  $\pm 150^\circ$ ; *ortho*,  $\pm 90^\circ$ ; *gauche*,  $\pm 55^\circ$ ; and *cisoid*,  $\pm 40^\circ$ . The new model applies to most linear polymers and oligomers other than hydrocarbons, for which the familiar *anti* and *gauche* minima are valid.

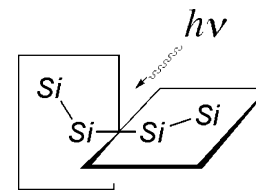


#### Hayato Tsuji, Josef Michl, Kohei Tamao

*J. Organomet. Chem.* 685 (2003) 9

Recent experimental and theoretical aspects of the conformational dependence of UV absorption of short chain peralkylated oligosilanes

A short review of the recent experimental and theoretical studies on conformation dependence of UV absorption of short chain peralkylated oligosilanes such as tetrasilanes and hexasilanes. For tetrasilanes, the strongly avoided crossing between  $\sigma\sigma^*$  and  $\sigma\pi^*$  configurations occurs, and as a result a conformation change does not affect the excitation energies but instead affects the oscillator strengths of the two low-energy transitions into states of B symmetry. For hexasilanes, the  $\sigma\sigma^*$  configuration is the lowest in energy at all angles, and the expected red shift of the  $\sigma\sigma^*$  transition occurs as the dihedral angle grows.



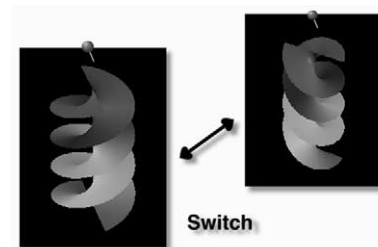
#### Michiya Fujiki

*J. Organomet. Chem.* 685 (2003) 15

Switching handedness in optically active polysilanes

Chain-like optically active polysilanes comprise a helical main chain of Si-Si single bonds and chiral and/or achiral side groups. They exhibit unique absorption, circular dichroism, and fluorescence spectra around 300–400 nm due to the  $\sigma$ -conjugation. This account focuses on screw-sense switchable, optically active poly(dialkylsilane)s, includ-

ing (i) (chir)optical properties, (ii) quantitative chiroptical population analysis of helices, (iii) capability of screw-sense inversion, and (iv) chiroptical switch and memory. Such knowledge and understanding might stimulate a further polysilane research, and also may advance these polymers to the realization of Si-based nanomaterials and Si-based nanodevices in the future.

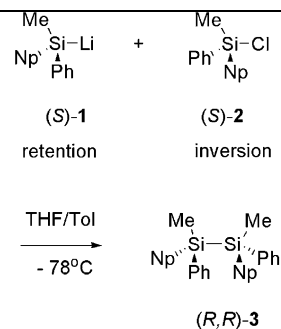


**Hyun-Shik Oh, Ichiro Imae, Yusuke Kawakami, S. Shanmuga Sundara Raj, Takashi Yamane**

*J. Organomet. Chem.* 685 (2003) 35

Synthesis, stereochemistry and chiroptical properties of naphthylphenyl-substituted optically active oligosilanes with  $\alpha,\omega$ -chiral silicon centers

Novel naphthylphenyl-substituted optically active oligosilanes with  $\alpha,\omega$ -chiral silicon centers were synthesized.

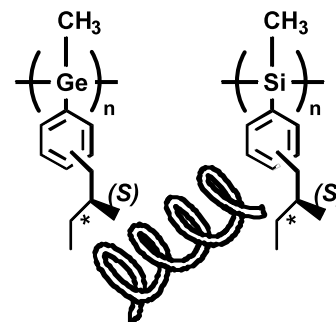


**Masao Motonaga, Hiroshi Nakashima, Sandra Katz, Donald H. Berry, Tatsuya Imase, Susumu Kawauchi, Junji Watanabe, Michiya Fujiki, Julian R. Koe**

*J. Organomet. Chem.* 685 (2003) 44

The first optically active polygermanes: preferential screw sense helicity of enantiopure chiral-substituted aryl polygermanes and comparison with analogous polysilanes

Helicity of the first enantiopure chiral-substituted screw sense-controlled polygermanes is spectroscopically compared with analogous polysilanes using circular dichroism, which indicates that polygermanes are less screw sense selective than their silicon analogues. Origin of this discussed in terms of longer E–E bond for germanes reducing steric interaction between chiral side groups.

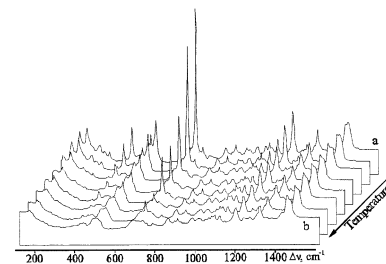


**Sergey S. Bukalov, Larissa A. Leites, Gaidar I. Magdanurov, Robert West**

*J. Organomet. Chem.* 685 (2003) 51

Excitation dependence of Raman spectra of various polydialkylsilane conformations and  $\sigma$ – $\sigma$  conjugation

Excitation dependence of the Raman spectra in a wide region (from blue to infrared) was investigated for hmw polysilanes [ $^n\text{Hex}_2\text{Si}$ ] $_n$  and [ $^n\text{Pent}_2\text{Si}$ ] $_n$  at various temperatures.

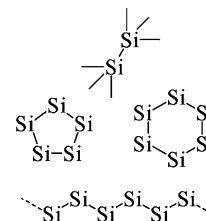


**Daniel Bratton, Simon J. Holder, Richard G. Jones, William K.C. Wong**

*J. Organomet. Chem.* 685 (2003) 60

The role of oligomers in the synthesis of polysilanes by the Wurtz reductive coupling reaction

Size exclusion chromatography and  $^{29}\text{Si}$ -NMR spectroscopy have been used to investigate the evolution of low-molecular weight molecules during the synthesis of poly(methylphenylsilane) by alkali metal-mediated reductive coupling in diethyl ether, tetrahydrofuran and toluene, revealing clear evidence for the important role played by a dimer. In addition, the distinct origins of the stable cyclic oligomers that are ubiquitous side products of these reactions have been established, cyclopentamers being formed through endbiting during chain growth and cyclohexamers by a degradative backbiting reaction.

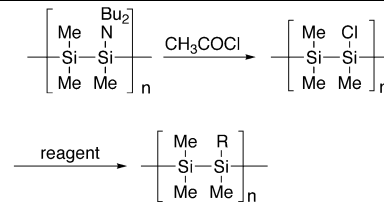


**Takanobu Sanji, Shin Isozaki, Masaru Yoshida, Kenkichi Sakamoto, Hideki Sakurai**

*J. Organomet. Chem.* 685 (2003) 65

Functional transformation of poly(dialkylaminotrimethyldisilene) prepared by anionic polymerization of the masked disilenes. The preparation of a true polysilastyrene

The Si–N bond of the amino-substituted polysilane, poly[1,1,2-trimethyl-2-(dibutylamino)disilene] yields chloro-substituted polysilanes. Substitution with some nucleophiles, such as a Grignard reagent, organolithium reagents, hydrides, and alcohols, yields a new class of polysilanes. This synthetic route provides a true polysilastyrene with a head-to-tail structure.

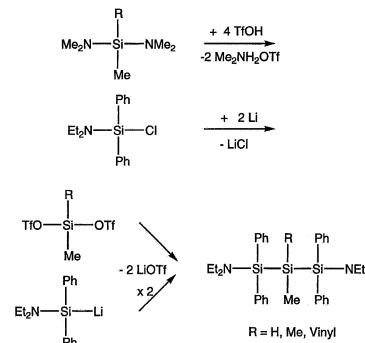


**Wolfram Uhlig**

*J. Organomet. Chem.* 685 (2003) 70

Tailor-made synthesis of functional substituted oligo- and polysilanes from silyl triflates and (aminosilyl)lithium compounds

Diethylamino substituted silyllithium compounds have been prepared in situ from the corresponding phenylchlorosilanes and lithium. These reagents undergo coupling reactions with triflate derivatives of silanes and oligosilanes.

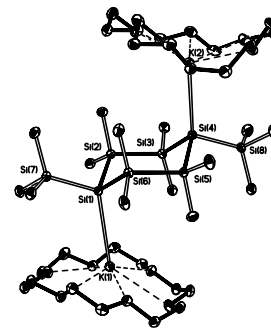


**Roland Fischer, Tina Konopa, Stephan Ully, Judith Baumgartner, Christoph Marschner**

*J. Organomet. Chem.* 685 (2003) 79

Route Si<sub>6</sub> revisited

Starting from 1,4-dipotassiotetrasilane 1,1,4,4-tetrakis(trimethylsilyl)octamethylcyclohexasilane can easily be obtained. This can be used to generate *trans*-1,4-dipotassio-cyclohexasilane. Transmetalation with magnesium leads to a formal inversion of configuration at one of the anionic silicon atoms.

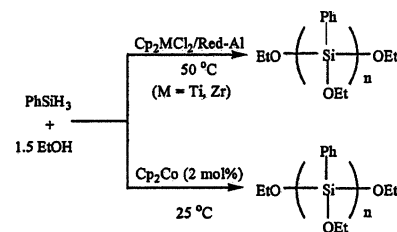


**Bo-Hye Kim, Myong-Shik Cho, Mi-Ae Kim, Hee-Gweon Woo**

*J. Organomet. Chem.* 685 (2003) 93

One-pot synthesis of poly(alkoxysilane)s by Si–Si/Si–O dehydrocoupling of silanes with alcohols using Group IV and VIII metallocene complexes

Si–Si/Si–O dehydrocoupling reactions of silanes with alcohols (1:1.5 mole ratio), catalyzed by Cp<sub>2</sub>MCl<sub>2</sub>/Red-Al (M = Ti, Zr) and Cp<sub>2</sub>M' (M' = Co, Ni), produced poly(alkoxysilane)s in one-pot in high yield. This is a mild and one-pot procedure with considerable synthetic flexibility for the preparation of wide variety of functionalized polysilanes.

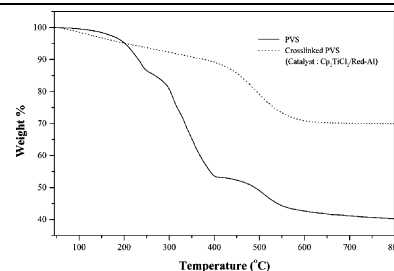


**Myong-Shik Cho, Bo-Hye Kim, Jung-Il Kong, A-Young Sung, Hee-Gweon Woo**

*J. Organomet. Chem.* 685 (2003) 99

Synthesis, catalytic Si–Si dehydrocoupling, and thermolysis of polyvinylsilanes  $[\text{CH}_2\text{CH}(\text{SiH}_2\text{X})]_n$  ( $\text{X}=\text{H}, \text{Ph}$ )

$[\text{CH}_2\text{CH}(\text{SiH}_2\text{X})]_n$  ( $\text{X}=\text{H}, \text{Ph}$ ) were prepared by reaction of  $[\text{CH}_2\text{CHSi}(\text{OEt})_2\text{X}]_n$  ( $\text{X}'=\text{OEt}, \text{Ph}$ ) with  $\text{LiAlH}_4$ . PVSs were modified by Si–Si dehydrocoupling cross-linking with the group 4 metallocene, group 6 metal hexacarbonyl, and group 8 metallocene catalysts to give polyethylene–polysilane hybrids showing improved ceramic yields.

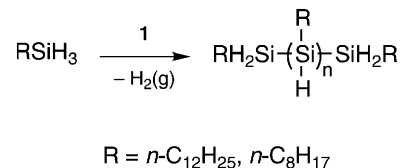


**Lisa Rosenberg, Danielle N. Kobus**

*J. Organomet. Chem.* 685 (2003) 107

Dehydrogenative coupling of primary alkyl silanes using Wilkinson's catalyst

Primary alkyl silanes ( $\text{RSiH}_3$ , where  $\text{R} = n\text{-C}_{12}\text{H}_{25}$  or  $n\text{-C}_8\text{H}_{17}$ ) undergo dehydrogenative coupling in the presence of  $(\text{Ph}_3\text{P})_3\text{RhCl}$  (**1**) to give oligomeric products.  $^{29}\text{Si}\{^1\text{H}\}$ -NMR and gel permeation chromatography suggest that chains of up to 5–6 silicons are forming in these reactions.

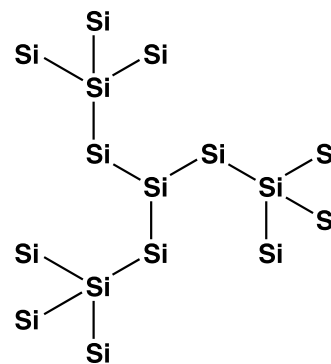


**Joseph B. Lambert, Jodi L. Pflug, Hongwei Wu, Xiaoyang Liu**

*J. Organomet. Chem.* 685 (2003) 113

Dendritic polysilanes

Dendritic polysilanes consist of silicon chains that emanate from a silicon core and branch one or more times. First- and second-generation dendrimers have been prepared that possess longest chains up to 13 silicon atoms.

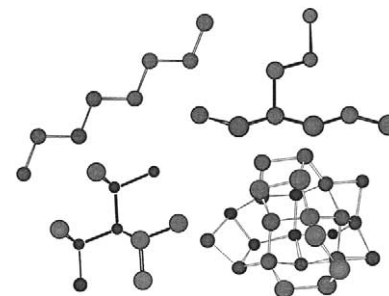


**Akira Watanabe**

*J. Organomet. Chem.* 685 (2003) 122

Optical properties of polysilanes with various silicon skeletons

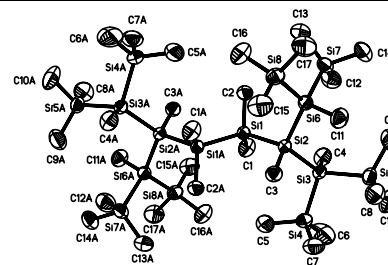
In this account, I present a brief overview of the optical properties of polysilanes with various silicon skeletons reviewing previous studies and supplying new experimental results.



**Helmut Reinke, Clemens Krempner***J. Organomet. Chem.* 685 (2003) 134

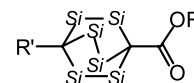
Structure and UV spectroscopic properties of a novel dendritic oligosilane

The synthesis, structure and unusual UV spectroscopic properties of a novel double-cored dendritic oligosilane with a longest chain of eight silicon atoms are reported. The compound exhibit an absorption maximum at 285 nm ( $\epsilon = 5.6 \times 10^4$ ), a value that is the longest observed for structurally well-defined oligosilane dendrimers so far. The conformational analysis on the available X-ray data reveal mainly all-*trans* conformers in the longest silicon chains causing a noticeably lower excitation energy of the first intense peak in the near UV.

**Masaki Shimizu, Susumu Sugimoto, Hirofumi Mizukoshi, Tamejiro Hiyama***J. Organomet. Chem.* 685 (2003) 138

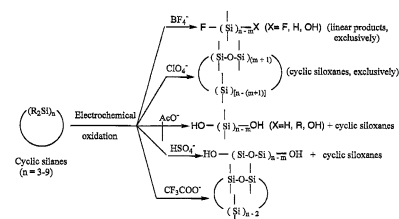
2,3,5,6,7,8-Hexasilabicyclo[2.2.2]octane-1-carboxylic acids and esters: preparation and structure

A single crystal of polysilacage acid  $\text{HC}(\text{SiMe}_2\text{SiMe}_2)_3\text{CCO}_2\text{H}$ , prepared by treatment of  $\text{HC}(\text{SiMe}_2\text{SiMe}_2)_3\text{CH}$  with  $\text{BuLi}/t\text{-BuOK}$  and then  $\text{CO}_2$ , formed a hydrogen-bonded enantiomerically homodimers to construct layers similar to smectic phase. Esterification of the polysilacage acid with various kinds of alcohols proceeded in good yields via the Mitsunobu reaction using diisopropyl azodicarboxylate.

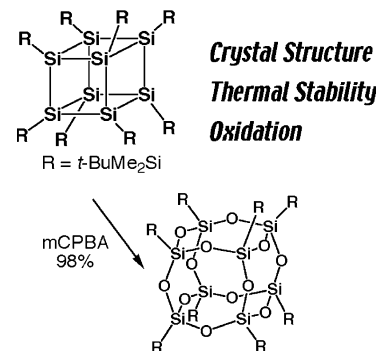
Si =  $\text{SiMe}_2$ **James Y. Becker***J. Organomet. Chem.* 685 (2003) 145

Electrochemical oxidation of cyclic polysilanes

During the past decade, the electrochemical properties of cyclic polysilane derivatives, namely  $[\text{Mes}_2\text{Si}]_3$  (**I**),  $[t\text{-Bu}(\text{Me})\text{Si}]_4$  (**IIa**),  $[\text{Et}_2\text{Si}]_4$  (**IIb**),  $[(n\text{-Pr})_2\text{Si}]_5$  (**IIIa**),  $[\text{Et}_2\text{Si}]_5$  (**IIIb**),  $[\text{Me}_2\text{Si}]_6$  (**IVa**),  $[\text{Et}_2\text{Si}]_6$  (**IVb**),  $[\text{Et}_2\text{Si}]_7$  (**V**),  $[\text{Me}_2\text{Si}]_8$  (**VI**), and  $[\text{Me}_2\text{Si}]_9$  (**VII**), have been explored in our laboratory. Various parameters have been investigated, such as anodic peak potentials, the effect of anode material, nature of supporting electrolyte, atmosphere under which electrolyses were conducted, extent of electricity consumption, solvent, ring size, applied potential, and more.

**Masafumi Unno, Takayoshi Matsumoto, Kikuo Mochizuki, Koichi Higuchi, Midori Goto, Hideyuki Matsumoto***J. Organomet. Chem.* 685 (2003) 156Structure and oxidation of octakis(*tert*-butyldimethylsilyl)octasilacubane

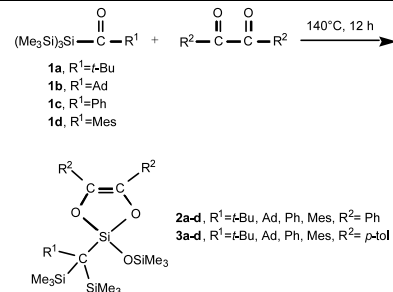
The molecular structure of octasilacubane  $[(t\text{-BuMe}_2\text{Si})\text{Si}]_8$  (**1**) was determined by X-ray crystallography, and the structural parameters were compared with those of the alkyl- and aryl-substituted octasilacubanes. A thermogravimetric analysis revealed that **1** was more thermally stable than  $(\text{ThexSi})_8$  (Thex = 1,1,2-trimethylpropyl). Oxidation of **1** with *m*CPBA gave octasilsesquioxane in 98% yield.



**Akinobu Naka, Mitsuo Ishikawa***J. Organomet. Chem.* 685 (2003) 162

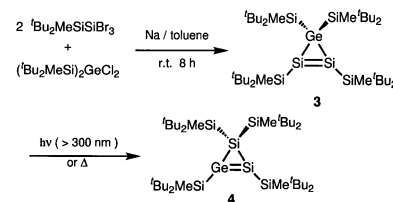
Silicon-carbon unsaturated compounds. 68. Reactions of silenes produced thermally and photochemically from acylpolysilanes with diketones

The reactions of the silenes produced thermally from  $(\text{Me}_3\text{Si})_3\text{SiCOR}$  (**1a–1d**;  $\text{R} = t\text{-Bu}$ ,  $\text{Ad}$ ,  $\text{Ph}$ , and  $\text{Mes}$ ) with benzil and 4,4'-dimethylbenzil in a sealed glass tube at  $140^\circ\text{C}$  gave the respective five-membered cyclic compounds, 2,5-dioxa-1-silacyclopent-3-enes (**2a–2d**, **3a–3d**) in high yields.

**Vladimir Ya. Lee, Masaaki Ichinohe, Akira Sekiguchi***J. Organomet. Chem.* 685 (2003) 168

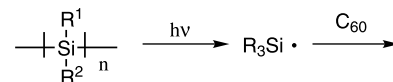
Disilagermirenes: heavy cyclopropenes of Si and Ge atoms

Tetrakis[di-*tert*-butyl(methyl)silyl]-1-disilagermirene (**3**) was prepared by the Würtz-type coupling reaction of 2,2,2-tribromo-1,1-di(*tert*-butyl)-1-methyldisilane and dichlorobis[di-*tert*-butyl(methyl)silyl]germane with sodium in toluene. The molecular structure of **3** was established by X-ray crystallography, which showed a *trans*-bent configuration around the Si=Si double bond with a bond length of 2.146(1) Å. Thermal and photochemical isomerization of **3** to tetrakis[di-*tert*-butyl(methyl)silyl]-2-disilagermirene (**4**) is also reported, as well as the reactions of **3** with MeI,  $\text{PhCH}_2\text{OH}$ , and  $\text{PhCOCH}_3$ .

**Takatsugu Wakahara, Yutaka Maeda, Masahiro Kako, Takeshi Akasaka, Kaoru Kobayashi, Shigeru Nagase***J. Organomet. Chem.* 685 (2003) 177

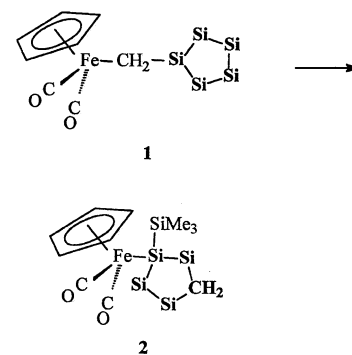
Silylation of fullerenes with active species in photolysis of polysilane

Organosilicon compounds represent a unique feature of materials such as disilane and polysilane.

**Keith H. Pannell, Toshiaki Kobayashi, Francisco Cervantes-Lee***J. Organomet. Chem.* 685 (2003) 189

Photochemical transformation of a cyclic polysilane to a cyclic carbosilane via  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{-}$ ,  $\text{FpCH}_2\text{-}$ , substitution

The complex  $\text{FpCH}_2\text{-c-Si}_5\text{Me}_9$  (**1**),  $\text{Fp} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ , quantitatively transforms to  $[\text{Fp}](\text{SiMe}_3)(\text{c-SiMe}_2\text{CH}_2(\text{SiMe}_2)_2)$  (**2**) upon photochemical irradiation.

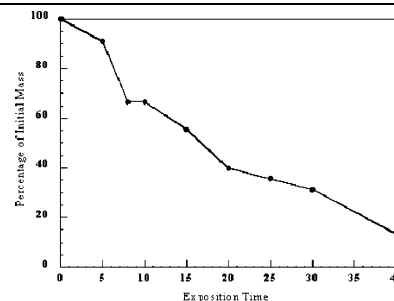


**Antonio Villegas, Roberto Olayo, Jorge Cervantes, Keith H. Pannell**

*J. Organomet. Chem.* 685 (2003) 196

Photoreaction of poly(ferrocenylmethylsilane-co-phenylmethylsilane) in solution

The photoreaction of  $[(\text{FcMeSi})(\text{PhMe-Si})_n]_m$  in solution, Fc = ferrocenyl =  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$ , is reported using a coupled gel permeation chromatography/light scattering system.

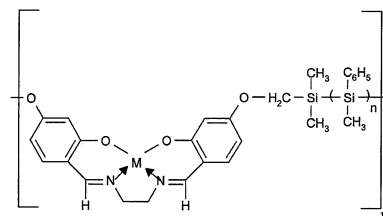


**Gabriela Sacarescu, Rodinel Ardeleanu, Liviu Sacarescu, Mihaela Simionescu**

*J. Organomet. Chem.* 685 (2003) 202

Synthesis of polysilane-bis(salicyliden)ethylenediamine Ni(II) complex

This paper describes the synthesis of a new coordination polymer prepared through the polycondensation reaction of  $\alpha,\omega$ -bis(chloromethyl)-polymethylphenylsilane with the Ni(II) complex of bis(salicylidene)ethylenediamine (salen). For this purpose, a new preparation method of the chloromethylated polysilane was presented along with the synthesis and characterisation of the polymer-metal complex.

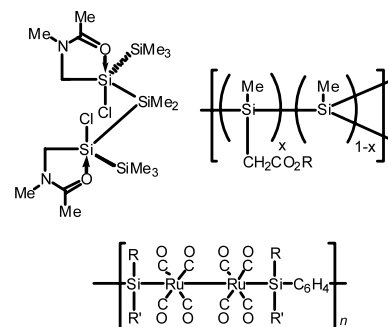


**Yasuo Hatanaka**

*J. Organomet. Chem.* 685 (2003) 207

Unusual behavior of silicon oligomers and polymers having functional groups

Pentacoordinate silicon moieties in oligosilanes effectively reduce  $\sigma_{\text{SiSi}} \rightarrow \sigma^*_{\text{SiSi}}$  excitation energies and rock the conformation of the silicon backbones. Introduction of polar side groups such as  $\text{CH}_2\text{CO}_2\text{R}$  into polysilanes is also effective in reducing the excitation energies. Organometallic polymers containing silicon and ruthenium moieties exhibit remarkable solvent-dependent change of the UV-vis spectra and effectively reduce the excitation energies.

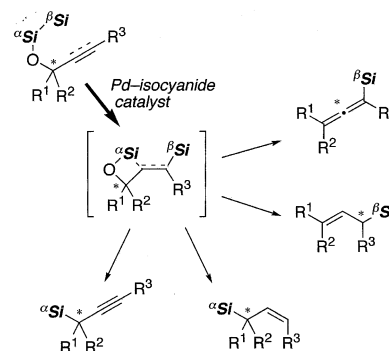


**Michinori Suginome, Yoshihiko Ito**

*J. Organomet. Chem.* 685 (2003) 218

Stereoselective accesses to enantioenriched allyl-, allenyl-, and propargyl-silanes via Si-Si bond activation by palladium-isocyanide catalysts

Palladium-catalyzed intramolecular bis-silylation of optically active allylic and propargylic alcohols followed by Peterson-type elimination or acid-catalyzed 1,2-silyl migration has been established as stereoselective accesses to highly enantioenriched allyl-, allenyl-, and propargyl-silanes.

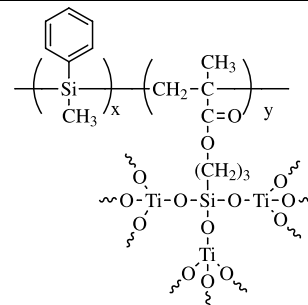


**Yukihito Matsuura, Satoshi Miura,  
Hiroyoshi Naito, Hiroshi Inoue, Kimihiro  
Matsukawa**

*J. Organomet. Chem.* 685 (2003) 230

Nanostructured polysilane–titania hybrids  
and their application to porous titania thin  
films

We have prepared polysilane–titania hybrid thin films using titanium alkoxides with poly(methylphenylsilane)/3-methacryloxypropyltriethoxysilane block copolymer (P(MPS-*co*-MPTES)) via sol–gel reaction. The polysilane block copolymer bonded to titania component through Si–O–Ti derived from hydrolysis/condensation of P(MPS-*co*-MPTES) and  $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4$ .

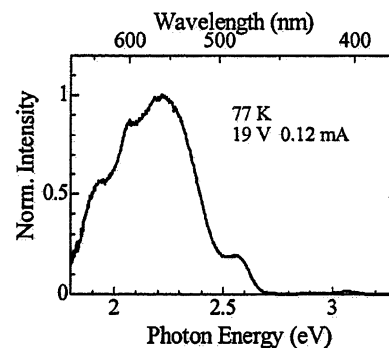


**Norihiko Kamata, Daiyo Terunuma, Reiji  
Ishii, Hiroki Satoh, Satoshi Aihara,  
Yoshiyuki Yaoita, Shinji Tonsyo**

*J. Organomet. Chem.* 685 (2003) 235

Efficient energy transfer from polysilane  
molecules and its application to electrolumi-  
nescence

The resonant energy transfer from conduc-  
tive poly(*m*-hexoxyphenyl)-phenylsilane was  
utilized for electroluminescence (EL) of per-  
ylene (blue), coumarin 6 (green), 4-(dicya-  
nomethylene)-2-methyl-6-(*p*-dimethylami-  
nostyryl)-4H-pyran and Zinc tetra-phenyl-  
porphyrin (red). A white EL was also ob-  
served by mixing four dye molecules before  
spin-coating process.

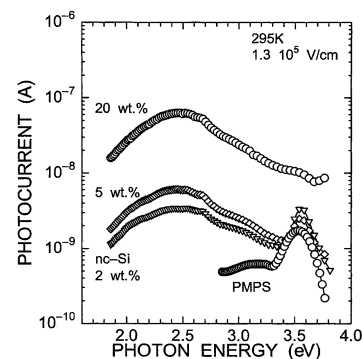


**Masaru Ando, Yoshikazu Ohsawa,  
Hiroyoshi Naito, Yoshihiko Kanemitsu**

*J. Organomet. Chem.* 685 (2003) 243

Photoconduction of (silicon nanocrystals)–  
(organic polysilane) composites

Addition of nc-Si whose average diameter is  
27 nm to poly(methylphenylsilane) PMPS  
induces photoconductive response in a visi-  
ble spectral range from 1.9 to 3.35 eV,  
where no photoconductive response is ob-  
served in pristine PMPS. The roles on nc-Si  
and PMPS in nc-Si/PMPS composites are  
photocurrent generation site and photocar-  
rier transport path, respectively.

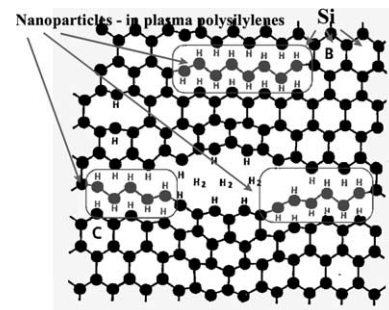


**F. Schauer, P. Horváth**

*J. Organomet. Chem.* 685 (2003) 249

Plasma synthesized polysilanes — organic  
nanostructural materials

Polysilylanes, exemplified on poly(methyl-  
phenyl silylene), prepared by plasma poly-  
merization in radio-frequency and micro-  
wave discharges proved to be nanostructur-  
al organosilicon material suitable for  
(electro)luminescence applications for their  
increased stability to both ultraviolet radi-  
ation and injection of charge-carriers from  
the contacts. The set of conditions were es-  
tablished for the optimum plasma polymeri-  
zation, structure and microphysical prop-  
erties of the films.



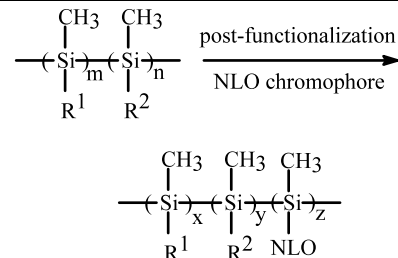


**Jun Li, Zhen Li, Hongding Tang, Huiyi Zeng, Jingui Qin**

*J. Organomet. Chem.* 685 (2003) 258

Polysilanes with NLO chromophores as pendant groups by utilizing different synthetic strategies

Functionalized polysilanes (FPSs) containing nonlinear optic (NLO) chromophores in the side chain have been synthesized successfully through utilizing different synthetic strategies. The second-order optical nonlinear properties of FPSs were determined by in situ second harmonic generation (SHG) experiments.

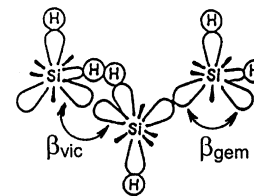


**Stanislav Nespurek, Julinz Sworakowski, Andrey Kadashchuk, Petr Toman**

*J. Organomet. Chem.* 685 (2003) 269

Polysilylenes: charge carrier transport and photogeneration

Charge carrier transport and photogeneration in polysilylenes, specifically in poly[methyl(phenyl)silylene], are discussed. Electronic properties are influenced by electron delocalization along the silicon backbone.



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