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<p>Polysilanes are novel materials with exciting electronic, photochemical, and nonlinear optical properties and various potential applications. Some of them require polymers with controlled structure.</p> <p>Three synthetic routes to well defined polysilanes were undertaken and successfully accomplished: sonochemical reductive coupling of disubstituted dichlorosilanes with sodium at ambient temperatures, two-step modification of poly(phenylmethylsilylenes) with trifluoromethanesulfonic acid and various nucleophiles, and ring-opening polymerization.</p> <p>Sonochemistry leads to polymers with high molecular weight ($M_n > 50,000$) and narrow polydispersity ($M_w/M_n < 1.3$). Modification provides polysilanes with side functional groups which are not available by direct synthesis. Ring-opening polymerization allows control of polymer macro and microstructure. The latter is extremely important since most interesting properties of polysilanes are related to delocalization of electrons in the main chain.</p>													
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"Polysilanes by Ring-Opening Polymerization
of Cyclic Monomers"

Krzysztof Matyjaszewski

Carnegie Mellon University

Department of Chemistry

4400 Fifth Avenue
Pittsburgh, PAS 15213

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Final Report

This research project has been devoted to the synthesis of novel polysilanes. Polymers with a Si-Si linkage in the main chain have interesting photochemical, photophysical, optical, and electronic properties. They are usually prepared as ill-defined materials in the reductive coupling of dichlorosilanes with molten sodium. In addition to high polymer, low molecular weight oligomers are usually formed. Preparation of high molecular weight, well defined polysilanes is very important, since chemical and physical properties of polysilanes depend strongly on molecular weight up to $M_n \approx 10,000$. Moreover, reductive coupling in the presence of sodium does not allow other substituents at silicon but only alkyl and aryl groups. To tune electronic properties of polysilane it would be very interesting to incorporate electron donating and withdrawing groups. It is possible to change mechanical, physical, chemical, as well as surface properties of polysilanes by the incorporation of special substituents.

We have concentrated at three new and original routes to polysilanes (cf. Report 2): sonochemical reductive coupling, ring-opening polymerization, and modification of polysilanes which contain aryl substituents. The latter process is based on rapid and quantitative displacement of phenyl groups from silanes by strong acids such as trifluoromethanesulfonic acid. This reaction has been performed for model compounds (Report 1), as well as for high polymers (Report 3). Polysilanes with alkoxy and amino side groups have been prepared and characterized (Report 5). Trimethylsilyl triflate is a 10^9 more powerful silylating reagent than classical trimethylsilyl chloride. Therefore, silyl triflates can react with weak nucleophiles and they can also initiate polymerization of various heterocyclics and alkenes. In some system polymerization proceeds as a "living" process (Report 7). Polymerization occurs readily with cyclic ethers such as tetrahydrofuran via formation of oxonium ions which have been directly observed in model and macromolecular systems by NMR (Report 9). Polymerization of less nucleophilic alkenes such as styrene is initiated by traces of triflic acid which is a product of hydrolysis of silyl triflate. There is no direct reaction between silyl triflate and styrene in the presence of hindered pyridine which serves as a proton trap but which does not interact with silyl triflate (Report 10).

We have observed that reductive coupling carried out at ambient temperatures in the presence of ultrasound leads to monomodal polysilanes (Report 2). We investigated this process for several dichlorosilanes with various alkyl and aryl substituents (Report 4) and

we found that monomers with two alkyl substituents can be polymerized only in the presence of solvents which well solvate alkali metal cations such as diglyme but not in less polar solvents such as pure toluene. However, copolymerization of dialkyl and arylalkyl dichlorosilanes is possible in toluene. This indicates the presence of anionic intermediates in the reductive coupling process. We have prepared several new copolysilanes with special substituents (e.g. perfluoroalkyl groups) as well as first copolymers of polysilanes with polystannanes (Report 6). We investigated the possibility of radical intermediates in the polymerization and we found that reductive coupling proceeds as a two step process with radicals which can be trapped by alkenyl substituents but which have very short life time and which are rapidly converted to more stable anions (Report 11). The anionic mechanism is additionally supported by the formation of soluble polymers and copolymers from trichlorosilanes. The sonochemical reductive coupling leads to soluble high molecular weight products. The resulting "polysilynes" have highly branched structure which involves several fused rings, mostly four-membered rings (Report 8). We plan to continue the studies of reductive coupling in order to optimize reaction conditions which should lead to safe and economical method for preparation of polysilanes with controlled chain dimensions.

Neither reductive coupling nor modification can lead to the control of chain microstructure and potential optical activity in polysilanes. This is, however, possible via ring opening polymerization. We described kinetic and thermodynamic basis of ring opening polymerization of strained cyclopolysilanes in Report 2. Bulky substituents such as two phenyl groups at each silicon atom prevent polymerization even for the potentially strained octaphenylcyclotetrasilane. Moreover, low solubility of the latter cycle (<2 w%) does not allow to reach monomer equilibrium concentration. The introduction of a few methyl substituents instead of phenyl groups leads to the increase of solubility of monomers and also increases their polymerizability. We dearylated up to four phenyl groups from octaphenylcyclotetrasilane with triflic acid and replaced triflate groups with methyl lithium. Anionic polymerization initiated by silyl anions leads to polymerization and subsequent macrocyclization. The termination at the intermediate stage allows isolation of high molecular weight polymer. The most important result from the ring-opening polymerization is formation of polymers with controlled tacticity. Namely, the all trans 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane, which is formed predominantly in the double substitution route, yields polymers which have at least

consecutive three silicon atoms of the controlled chirality. This is clearly seen in the NMR spectra which are very different from polymers prepared by the reductive coupling. This is extremely important for some applications such as nonlinear optical materials in which polysilanes have high potential applicability.

Technical reports submitted to ONR:

1. K. Matyjaszewski and Y.L. Chen, "Synthesis and Reactions of Silanes with Two Triflate Groups", *Journal of Organometallic Chemistry*, 340, 7 (1988)
2. K. Matyjaszewski, Y.L. Chen, and H. K. Kim, "New Synthetic Routes to Polysilanes", in "Inorganic and Organometallic Polymers" M. Zeldin, K. J. Wynne, and H. Allcock Eds., ACS Symposium Series, 360, 78 (1988)
3. K. Matyjaszewski, Y. L. Chen, F. Yenca, "Modification of Polysilanes", *ACS Polymer Preprints*, 28(2), 222 (1987)
4. K. Matyjaszewski and H. K. Kim, "Preparation of Polysilanes in the presence of Ultrasound", *Journal of the American Chemical Society*, 110, 3321 (1988)
5. K. Matyjaszewski, "Modifications of Well Defined Polysilanes"
6. K. Matyjaszewski and H. K. Kim, "Sonochemical Synthesis of Polysilanes", "ACS Polymer Preprints", 29(1), 168 (1988)
7. J. Hrkach, K. Ruehl, and K. Matyjaszewski, "Grafting of Living Polymers from Activated Polysilanes", "ACS Polymer Preprints", 29(2), xxx, (1988)
8. K. Matyjaszewski and H. K. Kim, "Synthesis of Branched Polysilanes by Copolymerization of Phenylmethyldichlorosilane with Trichlorosilanes", "ACS Polymer Preprints", 30(1), 168 (1989)
9. K. Matyjaszewski "Mechanism of the Initiation of the Cationic Polymerization of Styrenes by Silanes and Activated Covalent Esters"

10. J. S. Hrkach, K. Matyjaszewski, "Trimethylsilyl Triflate as Initiator for the Cationic Polymerization of Heterocyclics and Alkenes. Model Reactions for the Cationic Grafting from Polysilanes"
11. H. K. Kim, K. Matyjaszewski, "Homopolymerization and Copolymerization of Alkenyldichlorosilanes by Reductive Coupling", "ACS Polymer Preprints", 30(2), xxx (1989)

B. Papers emanating from the grant:

1. K. Matyjaszewski and Y.L. Chen, "Synthesis and Reactions of Silanes with Two Triflate Groups", Journal of Organometallic Chemistry, 340, 7 (1988)
2. K. Matyjaszewski, Y. L. Chen, F. Yenca, "Modification of Polysilanes", ACS Polymer Preprints, 28(2), 222 (1987)
3. K. Matyjaszewski and H.K. Kim, "Preparation of Polysilanes in the presence of Ultrasound", Journal of the American Chemical Society, 110, 3321 (1988)
4. K. Matyjaszewski, Y.L. Chen, and H. K. Kim, "New Synthetic Routes to Polysilanes", in "Inorganic and Organometallic Polymers" M. Zeldin, K. J. Wynne, and H. Allcock Eds., ACS Symposium Series, 360, 78 (1988)
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C. Papers submitted for publications:

- H. K. Kim, K. Matyjaszewski, "Homopolymerization and Copolymerization of Alkenyldichlorosilanes by Reductive Coupling", "ACS Polymer Preprints", 30(2), xxx (1989)

K. Matyjaszewski, J. Hrkach, H. K. Kim, K. Ruehl, "Modifications of Well Defined Polysilanes", American Chemical Society, "Advances in Chemistry" Series

Personnel who participated in research:

K. Matyjaszewski
Y. L. Chen
Y. N. Gupta
J. Hrkach
K. Ruehl
H. K. Kim
F. Yenca