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Homopolymerization and copolymerization of phenyltrichlorosilane by sonochemical reductive coupling in the presence of sodium

Krzysztof Matyjaszewski and Hwan Kyu Kim

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA

SUMMARY

Soluble polymers have been prepared by the sonochemical reductive coupling of phenyltrichlorosilane in toluene in the presence of sodium. Copolymers of phenyltrichlorosilane with phenylmethyldichlorosilane were synthesized. The obtained products are of relatively low molecular weight ($\bar{M}_n<10{,}000$). Investigations by ^{29}Si NMR, UV and by the kinetic studies of the iodine addition indicate that polymers consist of fused cyclopolysilanes with 40% content of strained rings (probably four-membered). Homopolymerization and copolymerization of n-hexyl-trichlorosilane and methyltrichlorosilane is compared with that of phenyltrichlorosilane. The former monomer yields soluble homopolymer and copolymers of relatively higher molecular weights than phenyltrichlorosilane. Methyltrichlorosilane yields usually insoluble products and only at a concentration below 20%, were soluble copolymers formed.

INTRODUCTION

Polysilanes are novel materials with exciting physical and chemical properties which lead to a number of potential applications (1, 2, 3). Polysilanes are photosensitive in the UV region and can be used as self-developing high-contrast positive photoresists in microlithography (4). Electrons in the main chain of polysilanes are strongly delocalized. This σ-delocalization leads to an excellent photoconductivity (5), and promising nonlinear optical properties (6). The current main commercial application of polysilanes is in the field of ceramic precursors and reinforcement agents for ceramics (7).

Typical synthesis of polysilanes is based on the reductive coupling of disubstituted dichlorosilane with sodium at temperatures exceeding the melting point of sodium. Usually, a significant amount of cyclooligosilanes (cyclopentasilanes and cyclohexasilanes) is formed in addition to a polymer of low molecular weight ($\bar{M}_n<5.10^3$) and of high molecular weight ($\bar{M}_n>10^5$). In some reports some insoluble material has been ascribed to the presence of small amounts of trichlorosilanes which could lead to crosslinking and gelation.

Very recently the preparation of soluble polymers from alkyltrichlorosubstituted silanes has been reported (8). The ^{29}Si NMR revealed that instead of the polyalkylsilyne structure (...-RSi=RSi-...), the rigid but soluble polymer with silicon atoms bound to three neighboring silicon atoms was formed. The structure of the resulting polymer was suggested as sheets or cages of fused five to seven-membered rings.

Below we report on the synthesis of branched polysilanes from phenyltrichlorosilane by homopolymerization and by copolymerization with phenylmethyldichlorosilane. Some results for methyltrichlorosilane and hexyltrichlorosilane are given for comparison. The possible structure of the obtained polymers is discussed.

EXPERIMENTAL

Phenyltrichlorosilane, n-hexyltrichlorosilane, methyltrichlorosilane, and phenylmethyldichlorosilane (Petrarch) were distilled prior to use and dried over CaH_2. Toluene was distilled from CaH_2 and dried over CaH_2. Known amounts of sodium were placed in a flask filled with toluene and purged with dry argon. This flask was sonicated with an immersion-type ultrasonic probe (W-140, Heat Systems-Ultrasonics, Inc.) until a stable dispersion of sodium was formed. A toluene solution of trichlorosilane or a mixture of the trichlorosilane and the dichlorosilane was added to the reaction flask in a controlled manner under inert gas. The reaction was quenched after the required time by using equimolar mixtures of water and ethanol. The organic phase was later added to a large excess of isopropanol leading to the precipitation of the polymer. The polymer was dried and the yield determined gravimetrically. Molecular weights and polydispersities were determined by gpc using polystyrene standards. For some low-molecular weight polymers the measurements of absolute molecular weights were performed by isopiestic method. Dodecamethylcyclohexasilane was used as a reference. The compositions of the polymers were measured by NMR. The filtrate remaining after the evaporation of the isopropanol was analyzed by gc/ms, gpc and hplc.

RESULTS AND DISCUSSION

Characterization of polysilanes requires studies on polymers with relatively narrow molecular weight distribution, since several properties of polysilanes strongly depend on the degree of polymerization (4). We have previously reported on the sonochemical homopolymerization of phenylmethyldichlorosilane by reductive coupling with sodium (9,10):

$$n\ PhMeSiCl_2 + 2n\ Na \rightarrow \ldots\text{-}(PhMeSi)_n\text{-}\ldots + 2n\ NaCl \downarrow$$

Polymers prepared by this method are monomodal and have relatively low polydispersity ($\bar{M}_n/\bar{M}_w < 1.3$). At ambient temperatures dialkyldichlorosilanes could not be homopolymerized in toluene using sodium and ultrasound. However, copolymerization with phenylmethyldichlorosilane is possible. Most likely the reduction potential of alkylsubstituted monomers is too high, and the reaction is too slow at ambient temperature. Addition of solvents which interact strongly with sodium cations (such as diglyme) decreases the energetic barrier (and probably also shifts the equilibrium) and facilitates the formation of polymers. This can be ascribed either to anionic intermediates involved in propagation or to the stabilization of sodium cations which are produced in the first electron transfer reaction resulting in the formation of radical anions. The electron transfer proceeds very slowly with monomers and much faster with a chloroterminated macromolecular polysilane. This has the origin in the additional stabilization of a radical anion by the polysilane chain. Thus, polymerization has a typical behavior of a chain process with slow initiation and rapid propagation which involves addition of a monomer into reactive propagating chain. Successful copolymerization of dialkyldichlorosilanes with phenylmethyldichlorosilane under conditions in which homopolymerization is not possible suggests ionic rather than radical intermediates in the propagation step (11).

Polymerization of monosubstituted trichlorosilanes proceeds differently. Phenyltrichlorosilane polymerizes quite slowly but yields higher amount of soluble polymer than phenylmethyldichlorosilane (Table 1).

Table 1
Sonochemical Copolymerization of Phenylmethyldichlorosilane (M_1) and Phenyltrichlorosilane (M_2) with Sodium

M_1/M_2	0/1	1/1	5/1	10/1	1/0
yield,%	37.2*	30.6	14.0	11.1	12
m_1/m_2 #	0/1	1.3/1	4/1	6/1	1/0
$\bar{M}_n \cdot 10^{-3}$	3.2	2.0	2.3	2.5	104
$\bar{M}_w/\bar{M}_n$	1.73	1.10	1.18	1.32	1.5
λ_{max}, nm	<266	332	333	336	340
$\varepsilon_{Si\text{-}Si} \cdot 10^{-3}$	-	1.3	4.7	5.5	9.0

$[M]_0$=0.35 mol/L, $[Na]_0/[Si\text{-}Cl]_0$=1.02, 3 hrs, toluene, 40 °C, immersion type probe
*-15 hrs, after 3 hrs no polymer was formed
#-ratio of comonomers in a polymer precipitated from isopropanol

Hexyltrichlorosilane could be polymerized in toluene, contrary to dihexyldichlorosilane. Copolymers of hexyltrichlorosilane have higher molecular weights than other copolymers (Table 2).

Table 2
Sonochemical Copolymerization of Phenylmethyldichlorosilane (M_1) and Hexyltrichlorosilane (M_3) with Sodium

M_1/M_3	0/1	2/1	5/1	10/1	1/0
yield,%	23.8*	7.6	10.5	11.2	12
m_1/m_3 #	0/1	10/1	13/1	15/1	1/0
$\bar{M}_n \cdot 10^{-3}$	3.0	40	69	70	104
$\bar{M}_w/\bar{M}_n$	2.4	1.68	1.69	1.60	1.5
λ_{max}, nm	<266	338	-	340	340
$\varepsilon_{Si\text{-}Si} \cdot 10^{-3}$	-	6.2	-	7.6	9.0

$[M]_0$=0.35 mol/L, $[Na]_0/[Si\text{-}Cl]_0$=1.02, 1 hr, toluene, 40 ^{0}C, immersion type probe, molecular weights based on polystyrene standards
*-67% yield after 15 hours
#-ratio of comonomers in a polymer precipitated from isopropanol

Eventually, methyltrichlorosilane reacts with sodium very slowly resembling dimethyldichlorosilane. On the other hand copolymers are formed readily. Only products with low content of methyltrichlorosilane are soluble (Table 3).

Table 3
Sonochemical Copolymerization of Phenylmethyldichlorosilane (M_1) and Methyltrichlorosilane (M_4) with Sodium

M_1/M_4	0/1	1/1	5/1	10/1	1/0
yield,%	90*+	20.1+	10.8	11.6	12
m_1/m_4 #	0/1	-	4/1	6/1	1/0
$\bar{M}_n \cdot 10^{-3}$	-	-	2.3	2.4	104
$\bar{M}_w/\bar{M}_n$	-	-	1.4	1.4	1.5
λ_{max}, nm	-	-	330	332	340
$\varepsilon_{Si\text{-}Si} \cdot 10^{-3}$	-	-	2.5	3.5	9.0

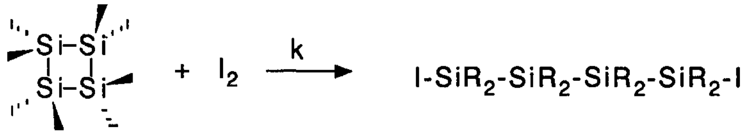
$[M]_0$=0.35 mol/L, $[Na]_0/[Si\text{-}Cl]_0$=1.02, 1 hr, toluene, 40 ^{0}C, immersion type probe, molecular weights based on polystyrene standards
*-yield after 15 hours, no polymer formed after 1 hr
+ -insoluble polymer
#-ratio of comonomers in a polymer precipitated from isopropanol

Homopolymers of monosubstituted silanes usually have low molecular weights and moderately narrow molecular weight distributions. Molecular weights based on polystyrene standards are in the range of $\bar{M}_n \approx 3{,}000$. Measurements of molecular weight of the 1:4 copolymer of phenyltrichlorosilane with phenylmethyldichlorosilane by isopiestic method (12) showed molecular weight $\bar{M}_n = 6{,}460$ which is more than two times higher than the value obtained from gpc using polystyrene standards ($\bar{M}_n = 2{,}300$). This value can be explained by the smaller hydrodynamic volume of the highly branched copolymer in comparison with a linear polystyrene standard. The observed molecular weights suggest the formation of oligomers with 30 to 60 silicon atoms. The ^{29}Si NMR chemical shift of phenyltrichlorosilane homopolymer is -52 ppm. This indicates that all silicon atoms have three neighboring silicon atoms, since disilenes ($R_3Si{=}SiR_3$) absorb at a much lower field (approximately +60 ppm).

$$\begin{array}{l} n\ PhSiCl_3 + 3n\ Na \rightarrow \ \ldots\text{-}(PhSi)_n\text{-}\ldots\ +3n\ NaCl\downarrow \\ \qquad \not\updownarrow \\ \ldots\text{-}(SiPh{=}SiPh)_{n/2}\text{-}\ldots \end{array}$$

On the other hand the chemical shift of a homopolymer is 22 ppm downfield in comparison with the simplest model compound, phenyltris(trimethylsilyl)silane. The downfield shift may be due to the presence of small rings. It has been observed that octamethylcyclotetrasilane absorbs 14 ppm downfield in comparison with decamethylcyclopentasilane and dodecamethylcyclohexasilane (3). A similar phenomenon is observed for n-hexyltris(trimethylsilyl)silane (-74.8 ppm) and a homopolymer derived from hexyltrichlorosilane (-58 ppm). Broad NMR signals indicate that there is probably a large variety of structures and the polymer is not an idealized ladder-like macromolecule with silicon atoms connected exclusively by four-membered rings. However, it is well known that bulky substituents on silicon favor the formation of small strained cycles. For example, diphenyldichlorosilane yields above 20% of cyclic tetramer. Dimesityl or di(trimethylsilyl) substituted dichlorosilane could form either cyclotrisilane or disilene. Bicyclic systems are formed from 1,2-diisopropyltetrachlorodisilane(13). Octasilacyclocubane was formed in a surprisingly high yield (55%) from 1,1,1-tribromo-2-t-butyl-2,2-dimethyldisilane and sodium in toluene. The dimer (1,1,2,2-tetrahalodisilane) which is formed first subsequently cyclizes to four-membered rings because of the presence of bulky substituents on silicon atoms (14).

We have tried to determine the proportion of "strained" four-membered rings by the kinetic measurements of the cleavage of rings with iodine. It has been reported that the rate constants of the iodine cleavage of cyclopolysilanes depend strongly on the ring size (15).



We observed two-step kinetics for the iodine reaction with a polymer formed by the homopolymerization of phenyltrichlorosilane. The first fast step (k=0.036 L/mol/s) can be related to the cleavage of strained rings and the second slow step (k=0.004 L/mol/s) can be related to the cleavage of nonstrained Si-Si bonds (16). The latter rate constant is very similar to the reaction of iodine with poly(phenylmethylsilylene) and the corresponding cyclopentasilane (k=0.003 L/mol/s). In the cleavage of cyclopentasilane, an initial fast step accounting for 5% of total silicon atoms is due to a small proportion of four-membered rings, which were also detected by ^{29}Si NMR. The kinetic plots are shown on Figure 1. In the cleavage of the polymers based on the phenyltrichlorosilane, the first step involves approximately 10% of silicon-silicon bonds, which can be translated to 40% content of the four-membered rings in the polymer.

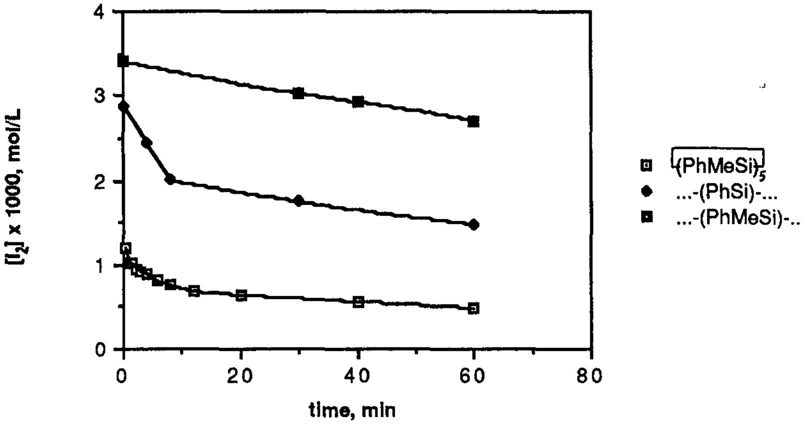


Figure 1. Change of the concentration of iodine, followed by UV, in CH_2Cl_2 at 25 °C, in the reaction with polysilanes. Initial concentrations of silicon atoms: $[(PhMeSi)_5]_o$=0.0536 mol/L, $[(PhSi)_n]_o$=0.0206 mol/L, $[(PhMeSi)_n]_o$= 0.0203 mol/L.

As shown in Tables 1-3, the UV spectra of branched polysilanes show a maximum at the range typical for linear polysilanes (330 to 340 nm) and a broad absorption typical for fused silicon rings extending nearly to the visible region (some of these polymers are slighly yellow).

All studied trichlorosilanes simultaneously copolymerize with phenylmethyldichlorosilane. The proportion of trichlorosilanes in polymers is higher than in the monomer feed, in contrast to the copolymerization of dichlorosilanes. Dimethyldichlorosilane and dihexyldichlorosilane have much lower reactivity ratios than phenylmethyldichlorosilane in copolymerization. Probably the same is true for trichlorosilanes, but the latters are preferentially found in polymer rather than in cyclic oligomers. This indicates that a presence of a branch would lead to a species with higher molecular weight and would shift distribution of silicon atoms substituted with three other silicon atoms from low molecular cyclics to a polymer. Solubility of polymers formed during simultaneous copolymerization also indicates that the condensation of macromolecules does not play an important role in the chain growth. Otherwise, an insoluble gel would be formed. However, addition of trichlorosilane after homopolymerization of phenylmethyldichlorosilane leads to the formation of insoluble polymer. In this case, anions at the chain ends react with trichlorosilanes. Thus, the simultaneous copolymerization kinetically resembles polycondensation in the system RA_3 /A-B, which is capable of branching but unable to form a gel. The ultrasound could degrade the highly branched structure easier than linear polymers, which were not degraded below $\overline{M}_n \approx 50{,}000$ (9).

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REFERENCES

1. J. M. Ziegler, Synth. Metals, 28, 581 (1989)
2. R. West, J. Organomet. Chem., 300, 327 (1986)
3. R. West, in "Comprehensive Organometallic Chemistry", ed. by G. A. Wilkinson, F. G. A. Stone, E. W. Abel, Pergamon Press, Oxford, Vol. 9, 365 (1983)
4. P. Trefonas III, R. West, R.D. Miller, D. Hofer, J. Polym. Sci., Letters, 21, 283 (1983)
5. M. Stolka, H. J. Yuh, K. McGrane, D. M. Pai, J. Polym. Sci., Chem. Ed., 25, 823 (1987)
6. F. Kajzar, J. Messier, Polymer J., 19, 275(1987)
7. S. Yajima, Y. Hasegawa, J. Hayashi, M. Ijmura, J. Mater. Sci., 13, 2569 (1978)
8. P. A. Bianconi, F. C. Schilling, T. W. Weidman, Macromolecules , 22, 1697 (1989)
9. K. Matyjaszewski, H. K. Kim, J. Amer. Chem. Soc., 110, 3321 (1988)
10. K. Matyjaszewski, Y. L. Chen, H. K. Kim, ACS Symposium Series, 360, 78 (1988)
11. K. Matyjaszewski, H. K. Kim, ACS Polymer Preprints, 29(1), 168 (1988)
12. E. P. Clark, Ind. Eng. Chem., Anal. Ed., 13, 820 (1941)
13. H. Matsumoto, H. Miyamoto, N. Kojima, Y. Nagai, J. Chem. Soc., Chem. Comm., 1987, 1316
14. H. Matsumoto, K. Higuchi, Y. Hoshino, H. Koike, Y. Naoi, Y. Nagai, J. Chem. Soc., Chem. Comm., 1988, 1083
15. H. Watanabe, H. Shimoyama, T. Muraoka, Y. Kougo, M. Kato, Y. Nagai, Bull. Chem. Soc. Jpn., 60, 769 (1987)
16. All rate constants are based on the cleavage of Si-Si bonds; therefore the rate constants of the cleavage of the four membered rings are four times higher.

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