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Electroreductive Synthesis of Some Functionalized Polysilanes and Related Polymers[1]

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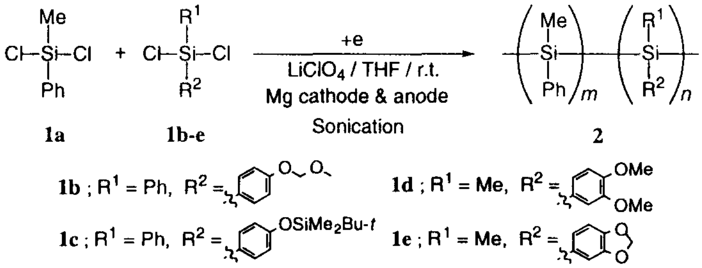
Abstract: Polysilanes having hydroxyl and related functional groups have been synthesized by the electroreduction of appropriate dichlorosilanes with Mg electrode, and a vinyl polymer which has oligosilane unit in the side chain has also been synthesized. © 1997 Elsevier Science Ltd.

Polymers containing silicon in the main chain has attracted considerable attention due to their usefulness as the precursors for thermally stable ceramics[4] or materials for microlithography,[5] and also due to their potentiality in the preparation of new types of material showing conducting, photoconducting, or nonlinear optical property.[6] One of the most important innovation required in this field is the introduction of suitable functional groups into the polymer since the property of silicon containing polymers must remarkably be modified by such functional groups. Applying some synthetic methods of the silicon containing polymers[7-9] to well designed monomers, several successful results have been reported so far in the preparation and application of the functionalized polysilanes.[10-19]

As an alternative the electroreductive method found in our previous studies[20-22] seems highly promising for the synthesis of such fuctionalized silicon containing polymers. The preparation of polysilanes having hydroxyl and related functional groups has been achieved in this study by adopting the electroreductive method. In addition, the synthesis of a vinyl polymer containing oligosilane unit in the side chain has also been preliminary studied in order to create a new tool of modification of the polysilanes.

The mildness of the reaction conditions of the electroreductive method is remarkably favorable for the synthesis of the polysilanes having a variety of hydroxyl-related functional groups. As illustrated in Scheme 1, the electroreduction of a mixture of **1a** and a dichlorosilane having a protected hydroxyphenyl group (**1b-e**) with Mg electrode afforded the corresponding copolymer **2** (**2b**-**e**),[24] and the deprotection of the resulting copolymer gave polysilane having a hydroxyl group.



Scheme 1

As the typical results are shown in Table 1, the reactivity of **1** (**1b**, **1c**, **1d**, and **1e**) highly depends on the type of protecting group. Homopolymerzation of **1b**, for example, gave **2b** (run 3), whereas that of **1c** or **1d** did not afford **2c** (run 5) or **2d** (run 8). The bulkiness of *tert*-butyldimetyl silyl protecting group of **1c** may be the main reason why its homopolymerization was inhibited. In the case of **1d**, however, the reason is not always clear, though the steric bulkiness of the substituents also seem one of the major factors.

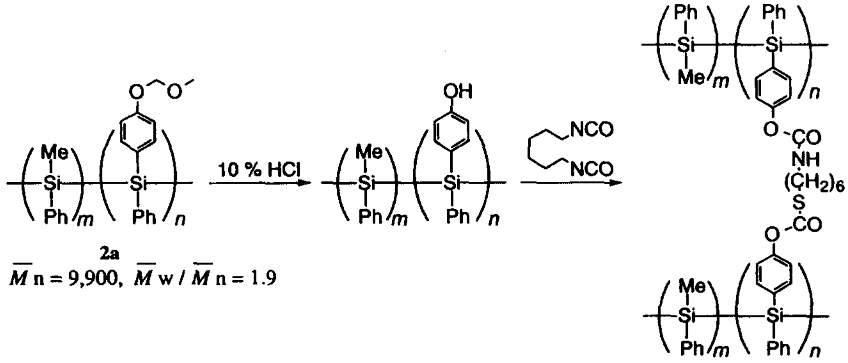
Electroreductive polymerization was carried out as follows: Into the electrolysis cell (30-mL three-necked flask equipped with a pair of Mg electrodes and a three-way stopcock jointed to a balloon of nitrogen), was placed 1 g of $LiClO_4$, and the cell was dried at 50°C *in vacuo* for 3 hr. The substrate **3** and THF (30 mL) were added into the reaction cell under an atmosphere of nitrogen. The electroreduction was carried out under a constant current condition (50 mA), and anode and cathode were alternated with the interval of 15 sec by using a comutator. During the electrolysis, ultrasound (47 kHz) was applied to the reaction mixture with cooling by water. After 4F/mol of electricity was passed through the cell, the reaction was quenched by addition of EtOH (10 mL). The mixture was then poured into an ice cold 1N HCl (100 mL) and the aqueous solution was extracted with ether (50 mL x 3). The combined organic layer was washed twice with 50 mL of brine, dried over $MgSO_4$, and concentrated. The resulting crude polymer was dissolved in 4 mL of benzene and reprecipitated from EtOH (100 mL). The molecular weight of the polymer was determined by GPC with THF as the eluent.

Table 1. Electroreductive Synthesis of Functionalized Polysilanes[a]

run	charged mol% of **1b-d**[b]	yield of **2**, %[c, d]	$\overline{M}$n	$\overline{M}$w/$\overline{M}$n	run	charged mol% of **1b-d**[b]	yield of **2**, %[c, d]	$\overline{M}$n	$\overline{M}$w/$\overline{M}$n
1	7 (**1b**)	79 (7)	9900	1.9	6	10 (**1d**)	50 (6)	4500	1.3
2	10 (**1b**)	57 (12)	6900	1.7	7	50 (**1d**)	22 (46)	4600	1.3
3	100 (**1b**)	28 (100)	1100	1.2	8	100 (**1d**)	—[e] (100)	1700	1.3
4	10 (**1c**)	36 (11)	6100	1.5	9	10 (**1e**)	56 (17)	4600	1.3
5	100 (**1c**)	—[e] (100)	1100	1.2	10	100 (**1e**)	57 (100)	4000	1.1

a) The electroreduction was carried out by using Mg electrodes under sonication (47 kHz) ,and anode and cathode were alternated with the interval of 15 sec. Total momomer concentration, 0.67 mol/L;Supplied electricity, 4 F/mol. b) **1b-e** /(**1b-e**+**1a**) x 100. c) Purified by reprecipitation from benzene-EtOH. d) The values in parentheses indicate the mol% of **1b-d** units in the resulting copolymers determined by ^{1}H NMR. e) Polymer was not obtained by reprecipitation.

As it is predicted, the modification of the property of polysilane must be achieved by using the hydroxyl group located on the polymer **2b** as a key functional group. As seen in the Scheme 2, for example, the deprotection[25] of the methoxymethyl group of **2b** (Table 1, run 1) with 10% HCl aqueous solution followed by the reaction with hexamethylene diisocyanate resulted in a remarkable increase in the molecular weight of polymer with indicating the linkage of polymer chain.



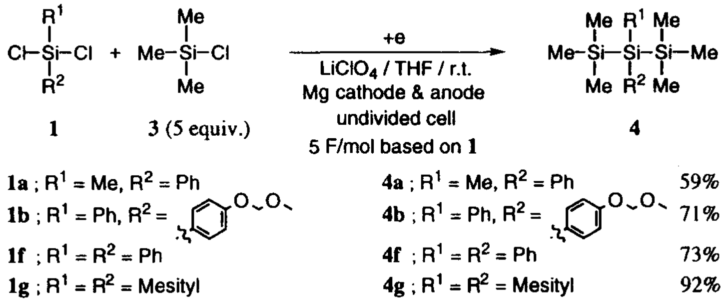
2a

$\overline{M}$n = 9,900, $\overline{M}$w / $\overline{M}$n = 1.9

Scheme 2

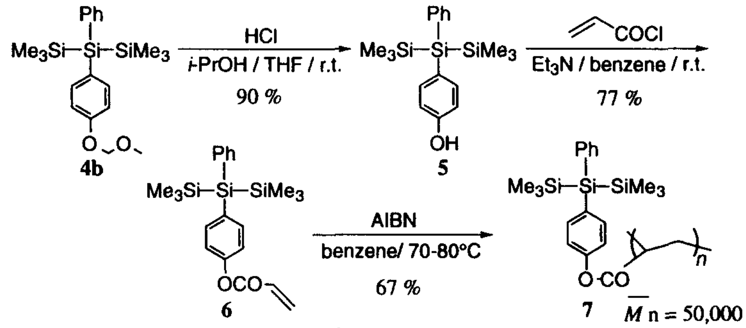
$\overline{M}$n = 16,300, $\overline{M}$w / $\overline{M}$n = 1.8

The modification of **2b** is also thought to be possible by coverting **2b** an acrylic ester at the hydroxyl group. As a preliminary investigation, the synthesis of functionalized trisilanes has been achieved by the electroreductive cross-coupling of a variety of dichlorosilanes (**1**) and chlorotrimethylsilane (**3**), and it was found that the electroreduction of a solution of **1** and **3** (5 equiv. based on **1**) with Mg cathode and anode gave the corresponding trisilane **4** (Scheme 3) in a reasonable yield.[26] The hydroxyl group located on **4b** must be effective as the key function for the modification of **4b**.



Scheme 3

In fact, the deprotection of **4b** gave trisilane bearing *p*-hydroxyphenyl group (**5**, Scheme 4), which gave an acrylic ester **6** upon treatment with acryloyl chloride. The radical initiated polymerization of **6** gave the vinyl polymer **7** containing trisilane unit on the side chain.



Scheme 4

References and Notes

This study is dedicated to Professor Hans J. Schäfer, University of Münster in order to celebrate his 60 th birthday.

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22) The same type of electroreductive Si-Si bond formation with aluminum, silver, or copper sacrificial electrodes has been reported.[21]

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24) The Si-Si linkage structures of the resulting polymers (**2b-e**) were confirmed by their spectroscopic data. For example, **2b** (Table 1, run 1): IR (film) 3050, 2950, 1565, 1425, 1250, 1020, 695 cm^{-1}; ^{29}Si CP/MAS NMR (79.48 MHz) -35.0 ppm; ^{1}H NMR (200 MHz, $CDCl_3$) δ -0.90-0.40 (br, SiCH_3), 3.42 (br, OCH_3), 5.10 (br, OCH_2OCH_3), 6.20-7.70 (br, *aromatic*). The monomer units ratio of the copolymer was calculated by ^{1}H NMR.

25) The integral ratio between methyl and phenyl protons in ^{1}H NMR spectrum of the deprotected polymer was found to remain unchanged. This result indicates that the cleavage of the Si-C bond did not proceed in this reaction condition

26) All products (**4a-d**) gave following satisfactory spectroscopic values for the assigned structures.[27]

27) **4a**: IR (neat) 3050, 2940, 2890, 1425, 1245, 1095, 830, 775, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 18H), 0.37 (s, 3H), 7.25-7.34 (m, 3H), 7.36-7.42 (s, 2H); MS *m/e* (relative intensity) 266 (23, M^+), 193 (100, M^+ - $SiMe_3$), 135 (75), 116 (43), 73 (61). **4b**: IR (KBr) 2950, 2900, 1590, 1500, 1240, 1150, 1100, 1080, 1000, 840, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 18H), 3.51 (s, 3H), 5.21 (s, 2H), 6.95-7.05 (m, 2H), 7.25-7.50 (m, 7H). **4c**: IR (neat) 2950, 2875, 1430, 1250, 1100, 835, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 18H), 7.26-7.37 (m, 6H), 7.40-7.50 (m, 4H); MS *m/e* (relative intensity) 328 (28, M^+), 255 (67, M^+ - $SiMe_3$), 178 (100, M^+ - $SiMe_3$ - Ph), 163 (55), 135 (48); HRMS calcd for $C_{18}H_{28}Si_3$ 328.1499, found 328.1493. **4d**: IR (KBr) 2950, 1600, 1440, 1240 1100, 830 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.25 (s, 18H), 2.12 (s, 6H), 2.29 (broad s, 12H), 6.75 (s, 4H); MS *m/e* (relative intensity) 412 (10, M^+), 397 (4, M^+ - Me), 339 (100, M^+ - $SiMe_3$), 220 (39), 205 (38), 177 (22); HRMS calcd for $C_{24}H_{40}Si_3$ 412.24377, found 412.24542.

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