

Electroreductive Synthesis of Polysilanes, Polygermanes, and Related Polymers with Magnesium Electrodes¹

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The electroreduction of alkylaryldichlorosilane carried out with Mg cathode and anode in a single compartment cell gave high molecular weight poly(alkylarylsilane) ($M_n = 5200\text{--}31000$, $M_w/M_n = 1.4\text{--}1.8$) in 5–79% yield. The effects of electrode material, monomer concentration, amount of supplied electricity, and ultrasound were investigated. This electroreductive method was also successfully applied to the synthesis of polygermanes, silane–germane copolymers, and also poly- $[\mu\text{-(disilanylene)phenylenes}]$.

Introduction

Polysilanes have recently attracted considerable attention due to their usefulness as precursors for thermally stable ceramics⁴ or a material for microlithography⁵ and also due to their potentiality⁶ in the preparation of new types of material showing semiconducting,⁷ photoconducting,⁸ or nonlinear optical⁹ property. In contrast to the growing interest with the polysilane, the method of preparation hitherto known is highly limited. So far, the only practical method is the condensation of organodichlorosilane with alkali metal (the Kipping method). This method, however, requires drastic reaction conditions and, hence, is very much limited in the type of substituent that is allowed to be located on the monomer. Although several modified or alternative methods such as sonochemical coupling of dichlorosilane promoted by alkali metal,¹⁰ transition metal catalyzed reaction of hydrosilane,¹¹ anionic polymerization of masked disilane,¹² and ring opening polymerization of cyclic or-

ganosilane¹³ have been proposed, they are not always extensively effective as preparative methods.

The electroreductive coupling of dichlorosilane with mercury electrode was reported by Hengge^{14a} in 1976 as a method to form disilane, but this method was not effective in the preparation of polysilane.^{14b,c}

On the other hand, it has been reported in our previous papers^{15–18} that the electroreduction of organic compounds with Mg electrode promotes a variety of unique reactions that cannot be attained without using the Mg electrode. A typical example reported preliminarily^{15a} is the formation of a Si–Si bond and its application to the synthesis of high molecular weight polysilane that shows monomodal and rather sharp molecular weight distribution.

In this paper, the details of the electroreductive synthesis of high molecular weight polysilane,^{15a} and some types of functionalized polysilanes,^{15b} and also polygermanes¹⁶ are described, including additional information about the effects of electrode material and monomer concentration. We also wish to report that our electroreduction system is successfully applied for the synthesis of oligosilanes, silane–germane copolymers, and polycarbosilanes.

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Scheme 1

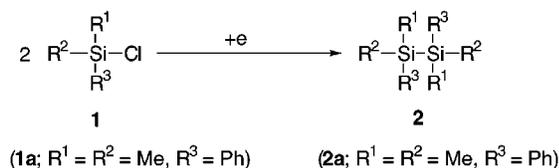


Table 1. Effect of Electrode Materials in the Electroreductive Formation of 1,1,2,2-Tetramethyl-1,2-diphenyldisilane (2a)^a

entry	anode	cathode	alternation ^b	yield, % ^c
1	Mg	Mg		92
2	Pt	Pt		0
3	C	C		0
4	Zn	Zn		trace
5	Pt	Mg	×	0
6	Mg	Pt	×	93 ^d

^a The electroreduction was carried out under the constant current condition (current density = 30 mA/cm², supplied electricity = 2.0 F/mol). ^b The anode and cathode were alternated with an interval of 1 min. ^c Material yield based on **1a**. ^d Ultrasound was applied to the reaction.

Results and Discussion

Preliminary Study on Electroreductive Formation of Si–Si bond. The electroreduction of chlorodimethylphenylsilane (**1a**) was studied as the model reaction (Scheme 1) and carried out under a variety of reaction conditions. First, the cathodic reduction was performed in a divided cell because Si–Si bond is electrochemically oxidized at the potential range of 0.7–1.6 V vs SCE.¹⁹ The yield of 1,1,2,2-tetramethyl-1,2-diphenyldisilane (**2a**) was, however, unexpectedly low under these reaction conditions. Then, the idea of using a sacrificial electrode was studied in order to avoid the undesirable anodic oxidation of the Si–Si bond in an undivided cell. It was found that the electroreduction of **1a** with Mg electrode was highly effective for the formation of the Si–Si bond, and **2a** was obtained in an excellent yield.

As shown in Table 1, the electrode material is one of the most important factors to control the formation of the Si–Si bond. When a solution of **1a** in dry THF containing LiClO₄ as a supporting electrolyte was electrochemically reduced with Mg cathode and anode with a constant current (current density = 30 mA/cm², supplied electricity = 2.0 F/mol), the coupling product **2a** was obtained in 92% isolated yield (entry 1). The results that Pt, carbon, or Zn is not an effective electrode in the formation of the Si–Si bond (entry 2–4) clearly indicate that Mg plays some important roles in the formation of the Si–Si bond.¹⁹ Although details of the role of Mg in the mechanism of formation of the Si–Si bond are not always clear at present, the unique reactivity of Mg electrode is undoubtedly shown in this reaction.^{17,18}

The effects of supporting electrolyte and solvent are summarized in Table 2 in which it is shown that the use of THF as the solvent and LiClO₄ as the supporting electrolyte gave the best result. The supporting electrolytes containing fluorine, such as LiBF₄ and BuNBF₄, were not suitable for this reaction because the reaction of **1a** with fluoride ion from decomposition of the electrolyte gave fluorosilane, which was not electrochemically reduced under the present reaction conditions.²⁵

Table 2. Effect of Supporting Electrolytes and Solvents in the Electroreductive Formation of 2a^a

electrolyte	yield of 2a , % ^b		
	THF	DME	dioxane
LiClO ₄	92	70	0
LiBF ₄	2	10	
<i>n</i> -Bu ₄ NClO ₄	75	50	0
<i>n</i> -Bu ₄ NBF ₄	12	2	

^a The electroreduction was carried out under the constant current condition, and Mg anode and cathode were alternated.

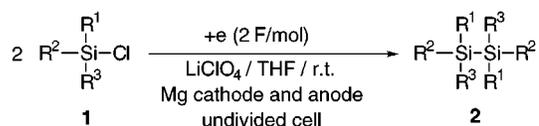
^b Material yield based on **1a**.

Table 3. Electroreductive Formation of Disilanes (2)

entry	chlorosilanes 1			yield of 2 , % ^a
	R ¹	R ²	R ³	
1	1b	Me	Me	2b , 82
2	1c	Me	Ph	2c , 77
3	1d	Ph	Ph	2d , 85

^a Isolated material yield based on **1**.

Scheme 2



The cathodic coupling of other organochlorosilanes was carried out under the best reaction condition, that is, Mg cathode and anode were alternated with an interval of 1 min., supporting electrolyte was LiClO₄, solvent was THF, and the electricity passed was 2.0 F/mol (Scheme 2). The results summarized in Table 3 show the high potentiality of this method in the synthesis of a variety of disilanes. Moreover, it is remarkable that the extent of contamination with siloxane (Si–O–Si) was less than 2%.²⁷

Two types of mechanism may be proposed for this electroreductive Si–Si bond forming reaction. Namely, one is a radical coupling reaction in which a silyl radical formed by one electron reduction of the starting chlorosilane couples with another silyl radical to give the disilane. In the second mechanism, two-electron reduction of the chlorosilane yields an active species equivalent to a silyl anion that reacts with chlorosilane to give the dimer. To have an insight into the mechanism, the products obtained in the mixed system of chlorotrimethylsilane (**1b**) and chlorotriphenylsilane (**1d**) (**1b**:**1d** = 1:1) were studied in detail. As shown in Scheme 3, the mixed

(20) The same type of electroreductive Si–Si bond formation was reported independently by using aluminum²¹ sacrificial anode, and after the present study the use of silver^{22,23} and copper²⁴ electrodes was reported to be effective for the electroreductive coupling of organochlorosilanes.

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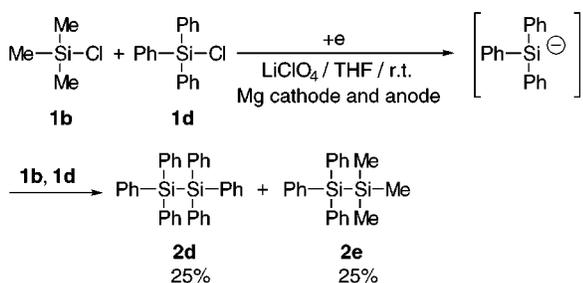
(25) The reductive potential of fluorosilane is generally more negative than that of the corresponding chlorosilane.²⁶

(26) Corriu, R. J. P.; Dabosi, G.; Martineau, M. *J. Organomet. Chem.* **1980**, *188*, 63.

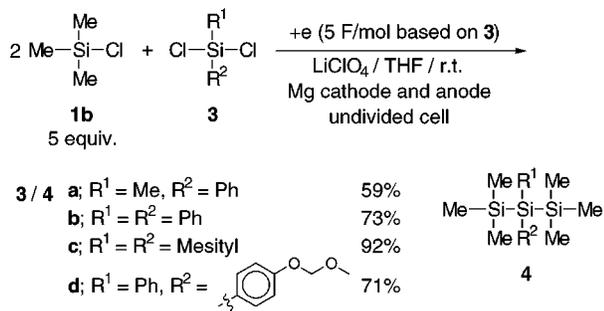
(27) The contamination of siloxanes was apparently caused by residual H₂O in the electrolysis solution. To attain a highly dry condition, the electrolysis system was pre-electrolyzed in the presence of a catalytic amount of chlorotrimethylsilane (see Experimental Section).

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Scheme 3



Scheme 4

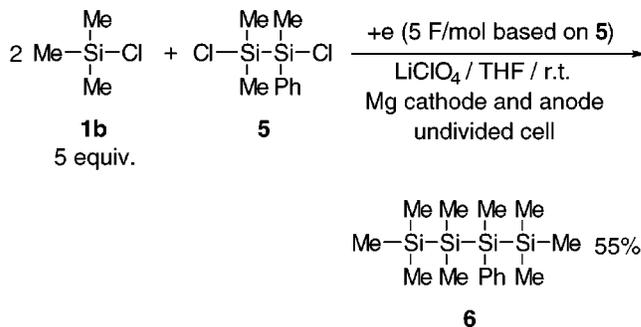


coupling product (**2e**) and the homocoupling product of **1d**, that is, hexaphenyldisilane (**2d**), were formed in the ratio of 1:1, whereas the homocoupling product of **1b**, that is, hexamethyldisilane (**2b**), was not found in the products at all. This result seems to agree with the anion mechanism. Namely, **1d** is first reduced to triphenylsilyl anion that reacts with **1b** and **1d** to afford disilanes **2e** and **2d**, respectively. The electrophilicity of chlorosilanes **1b** and **1d** is high enough to be attacked equally by the triphenylsilyl anion at the half conversion (supplied electricity = 1 F/mol based on the total amount of **1b** and **1d**). In the radical mechanism, however, if only **1d** is reduced to yield a radical, the formation of **2e** is not reasonable, whereas if two types of radical are formed by the reduction of both **1b** and **1d**, the absence of **2b** in the products is unreasonable. Thus, the anion mechanism is the most reasonable in this coupling reaction. The fact that the reduction potential of **1d** is much more positive than that of **1b** also supports the above-mentioned reaction mechanism.^{25,28}

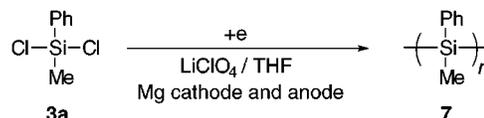
This method is also applicable to the synthesis of trisilanes and tetrasilanes. For example, the electroreductive cross-coupling of organodichlorosilanes (**3**) with chlorotrimethylsilane (**1b**) (5 equiv to **3**) gave the corresponding trisilanes **4** in moderate to good material yields (Scheme 4), and that of 1,2-dichloro-1,1,2-trimethyl-2-phenyldisilane (**5**) and **1b** (5 equiv to **5**) gave tetrasilane **6** in 55% yield (Scheme 5). Trisilane **4c** is a key intermediate for the photochemical synthesis of tetramesityldisilene, which is known as an isolable disilene.²⁹

Electroreductive Polymerization of Dichloromethylphenylsilane (3a). Electroreduction of dichloromethylphenylsilane (**3a**) (Scheme 6) carried out under the above-mentioned reaction conditions gave polymethylphenylsilane (**7**) in low yield (Table 4, entry 3). Sonication with ultrasound was found to be necessary for the

Scheme 5



Scheme 6

Table 4. Electroreductive Synthesis of Poly[methylphenylsilane] (**7**)^{a,b}

entry	alternation ^c	sonication ^d	M _n ^e	M _w /M _n	yield of 7 , % ^{f,g}
1	×	×			
2			5200	1.5	43
3	×		3900	1.4	17
4		×	4000	1.4	7

^a Concentration of monomer **3a** is 0.33 mol/L. ^b Supplied electricity is 4 F/mol. ^c Anode and cathode were alternated with an interval of 1 min. ^d Ultrasound (47 kHz) was applied during the electroreduction. ^e Determined by GPC based on polystyrene standard. ^f Purified by reprecipitation from benzene–EtOH. ^g Material yield based on **3a**.

Table 5. Effect of Electrode Material in the Electroreductive Synthesis of Polymethylphenylsilane (**7**)^a

entry	electrode	M _n ^b	M _w /M _n	yield of 7 , % ^c
1	Mg	5200	1.5	43
2	Cu	700	1.1	<i>d</i>
3	Ni	640	1.1	<i>d</i>
4	Al	4700	1.5	15

^a Conditions: [monomer **3a**] = 0.33 mol/L/ supplied electricity = 4 F/mol; ultrasound (47 kHz) was applied during the electroreduction. Anode and cathode were alternated with an interval of 15 sec. ^b Determined by GPC based on polystyrene standard. ^c Purified by reprecipitation from benzene–EtOH. ^d Material yield based on **3a**. ^e No precipitate was obtained after usual reprecipitation procedure.

electroreductive polymerization of **3a** (entry 1). The low yield of **7** may be explained by the difficulty of keeping the electric current at a suitable level due to the increase of the voltage between anode and cathode with progress of the reaction. This difficulty was overcome by the alternation of anode and cathode with a suitable interval (Table 4, entry 2), and the material yield of **7** was remarkably improved.

Magmesoi, is a remarkably effective electrode material for the formation of **7**, whereas Al gave low yield (entry 4) and other materials such as Cu and Ni were rather ineffective (Table 5, entries 2 and 3). Although the electroreduction of **3a** with Al electrode (supporting electrolyte, Bu₄NCl; solvent, DME)³⁰ has been reported by another group, the molecular weight of product obtained in this case was too low to be used as a high molecular weight polymer.

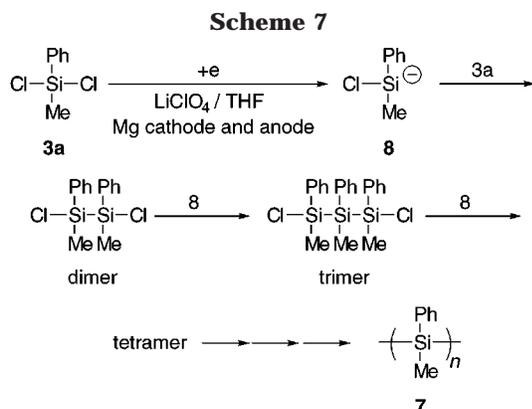
(28) (a) Corriu, R. J. P.; Dabosi, G.; Martineau, M. *J. Organomet. Chem.* **1981**, *222*, 195. (b) Dessy, R. E.; Kitching, W.; Chivers, T. *J. Am. Chem. Soc.* **1966**, *88*, 453.

(29) For a review on disilenes, see: West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201.

Table 6. Effect of Monomer Concentration in the Electroreductive Synthesis of 7^a

entry	[3a], mol/L	electricity, F/mol	M_n^b	M_w/M_n	yield of 7, % ^{c,d}
1	0.33	4.0	5200	1.5	43
2	0.67	4.0	9900	2.1	79
3	2.5	2.2	18000	2.1	43
4	6.3	0.8	19000	2.8	15
5	12	0.5	31000	1.8	8

^a The electroreduction was carried out with Mg electrodes and ultrasound (47 kHz), and anode and cathode were alternated with an interval of 15 sec. ^b Determined by GPC based on polystyrene standard. ^c Purified by reprecipitation from benzene–EtOH. ^d Material yield based on 3a.

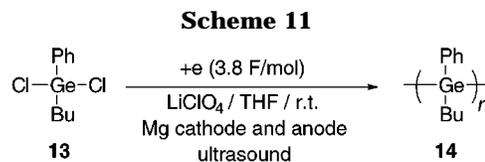
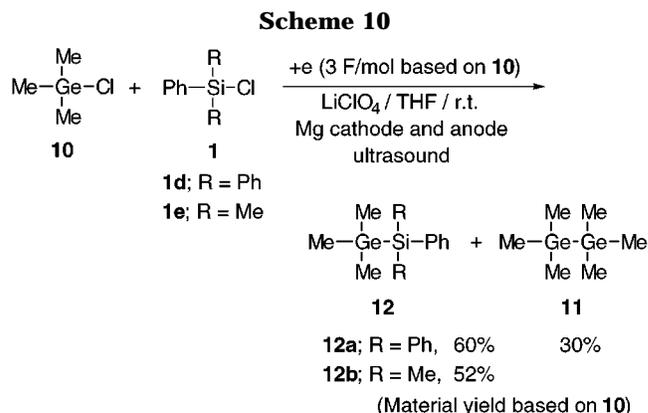
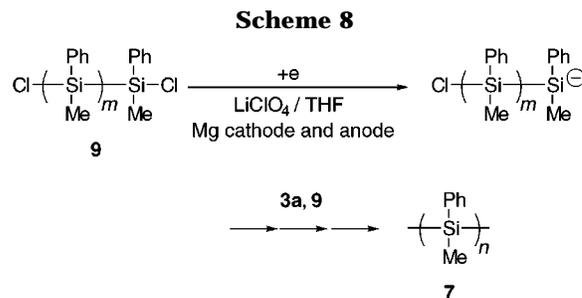


The effect of monomer concentration was investigated in order to obtain a high molecular weight polysilane. As shown in Table 6, the molecular weight of 7 becomes higher with increase in the concentration of 3a. The molecular weight (M_n) of 7 was, for instance, 31 000 when the electroreduction of 3a was carried out with high concentration (1.2 mol/L) and low amount of supplied electricity (0.5 F/mol), though the material yield of 7 remarkably decreased.

The most satisfactory result in which material yield was 79% and molecular weight (M_n) was 9900 was obtained when the concentration of 3a was 0.67 mol/L (entry 2). The polysilane 7 obtained here showed relatively sharp monomodal distribution of molecular weight in its elution profile by gel permeation chromatography, whereas the polysilanes prepared by the alkali metal condensation method usually showed broad bimodal distribution.¹⁰

The mechanism of electroreductive formation of polysilane is not always perfectly clear, though the initial step of reaction is obviously the reduction of 3a to an active species (8) equivalent to a silyl anion. Two types of reaction patterns may be proposable for the propagation step. In the first case, the reaction of 8 with 3a gives a dimer that yields trimer, tetramer, and finally polymer upon repeated reaction with 8 (Scheme 7).

In another pattern of the propagation, the oligomers such as dimer, trimer, and the like (9) are reduced to give the oligomeric active species, which then react with oligomer 9 or 3a to give finally the polymer. (Scheme 8). Although it is not always possible to specify the extent of contribution of each pattern to the propagation step,

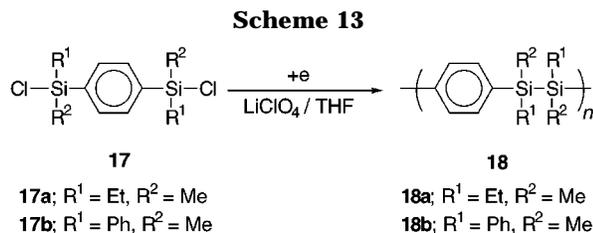
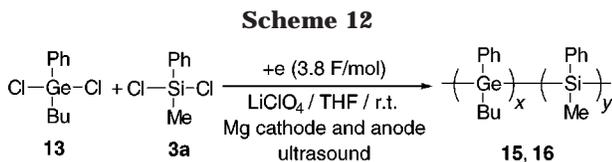


the former seems the main pattern, since the electrochemical reduction of oligomeric silyl chloride 9 may be a rather difficult reaction when it is analogized with the electroreduction of long chain alkyl chlorides.

Electroreductive Formation of Ge–Ge and Ge–Si Bonds. The Mg electrode was also found to be effective for the formation of Ge–Ge and Ge–Si bonds.¹⁶ Hexamethyldigermene (11) was, for example, obtained in 84% material yield by the electroreduction of chlorotrimethylgermane (10) (Scheme 9). The electroreduction of a mixture of 10 and chlorotriphenylsilane (1d) or chlorodimethylphenylsilane (1e) (molar ratio of 10:1d or 1e = 1:2) under similar reaction conditions afforded the corresponding germylsilane (12a or 12b) as the main product (Scheme 10).

These results clearly indicate that the potentiality of the electroreductive method is remarkable for the formation of Ge–Ge and Ge–Si bonds. In fact, the synthesis of high molecular weight polygermane and germane–silane copolymer was effectively achieved by this novel method. As shown in Scheme 11, the electroreduction of dichlorobutylphenylgermane (13) gave polygermane (14) having a molecular weight (M_n) of 19 900 (material yield = 10%). Under similar reaction conditions, a mixture of 13 and dichloromethylphenylsilane (3a) gave germane–

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**Table 7. Preparation of Germane–Silane Copolymer**

	molar ratio of monomer (13/3a)	yield, % ^a	Ge content in copolymer $R = (x/x + y)^b$	M_n^c	$\lambda_{\max}, \text{nm}^d$
15	0.39	34	0.16	17000	330
16	1.04	33	0.45	20600	335

^a Isolated material yields obtained by reprecipitation from benzene–EtOH 1.20. ^b Determined by ¹H NMR (200 MHz). ^c Determined by GPC based on polystyrene standard. ^d UV spectra were measured in THF at 20 °C.

silane copolymers **15** and **16** depending on the molar ratio of monomers (**13/3a**) (Scheme 12).

As it can be seen in the typical results shown in Table 7, the atomic ratio (Ge/Si) in the copolymers was roughly proportional to the molar ratio of monomers (**13/3a**), and an almost linear correlation was observed between UV absorption maximum of the polymer (λ_{\max}) and the germanium content ($R = x/(x + y)$) in polymers including polygermane ($R = 1$; $\lambda_{\max} = 355 \text{ nm}$)³¹ and polysilane ($R = 0$; $\lambda_{\max} = 325 \text{ nm}$).⁶

Electroreductive Synthesis of Poly[*p*-(disilanyl-ene)phenylene]. Poly[*p*-(disilanyl-ene)phenylene] (**18**) has been known for its high etching resistance against oxygen plasma and may be used as the top imaging layer in the double-layer resist system.³² Hence, the electroreductive method of formation of Si–Si bond was applied to the synthesis of **18** (Scheme 13).^{15a}

The effect of electrode materials in the polymerization of **17** was also investigated by using 1,4-bis(chloroethylmethylsilyl)benzene (**17a**) as a model compound. As shown in Table 8, Mg electrode gave **18a** with the best result (Table 8, entry 1), and oligomeric **18a** showing low molecular weight was obtained when Cu,³³ Zn, or Ni was used as the electrode material (Table 8, entries 2–4).

Other factors that control molecular weight and yield of **18a** are summarized in Table 9. The best material yield was obtained when monomer (**17a**) concentration was 0.27 mol/L and the electricity passed was 4 F/mol (entries 1–4). The increase in the concentration of supporting

Table 8. Effect of Electrode Material in the Electroreductive Synthesis of Poly[*p*-(disilanyl-ene)phenylene] **18a^a**

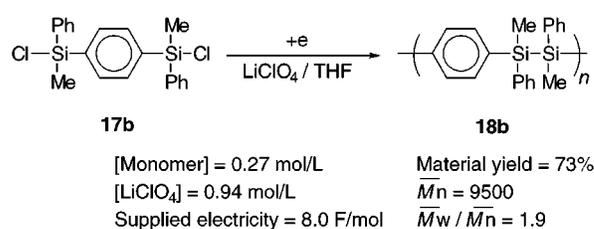
entry	electrode	M_n^b	M_w/M_n	yield of 18a , % ^d
1	Mg	6700	1.6	61
2	Cu	1300	1.8	<i>e</i>
3	Zn	1200	1.3	<i>e</i>
4	Ni	2400	1.7	<i>e</i>

^a Conditions: [monomer **17a**] = 0.27 mol/L; [LiClO₄] = 0.47 mol/L; supplied electricity = 4 F/mol; ultrasound (47 kHz) was applied during the electroreduction. Anode and cathode were alternated with an interval of 15 sec. ^b Determined by GPC based on polystyrene standard. ^c Purified by reprecipitation from benzene–EtOH. ^d Material yield based on **17a**. ^e No precipitate was obtained after usual reprecipitation procedure.

Table 9. Effect of Concentration and Supplied Electricity in the Electroreductive Synthesis of **18a^a**

entry	[17a], mol/L	[LiClO ₄], mol/L	electricity, F/mol	M_n	M_w/M_n	yield of 18a , % ^{b,c}
1	0.27	0.47	2.5	4300	1.6	25
2	0.27	0.47	4.0	6700	1.6	61
3	0.27	0.47	5.0	5200	1.6	32
4	0.27	0.47	7.0	4200	1.6	27
5	0.27	0.94	4.0	7200	1.6	57
6	0.27	0.94	8.0	8600	1.6	50
7	0.27	1.41	12.0	10000	2.0	29
8	5.10	1.90	0.3	14900	1.09	3

^a The electroreduction was carried out with Mg anode and cathode, and ultrasound (47 kHz) was applied during reduction. Anode and cathode were alternated with an interval of 15 sec. ^b Purified by reprecipitation from benzene–EtOH. ^c Material yield based on **17a**.

Scheme 14

electrolyte resulted in the increase in molecular weight and slight decrease in the yield (entries 5–7). High monomer concentration gave the highest molecular weight, though the material yield was poor (entry 8).

The phenyl-substituted monomer **17b** also yielded the corresponding polymer **18b** upon the same electroreduction (Scheme 14).

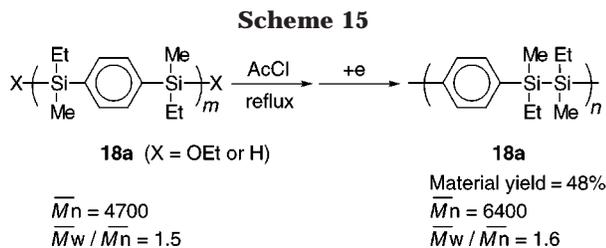
Since the polymerization was quenched with EtOH, a certain extent of the terminal positions of poly[*p*-(disilanyl-ene)phenylene] **18** may have the siloxy group (Si–OEt). This siloxy group may be transformed to a Si–Cl group upon treatment with acetyl chloride, and hence further electroreduction of the resulting polymer may result in the increase in the molecular weight. In fact, as one of the results is shown in Scheme 15, the molecular weight moderately increased.

Conclusion. The formation of Si–Si and Ge–Ge bonds was achievable by the electrochemical reduction of organochlorosilanes and organochlorogermanes with Mg sacrificial electrode. Disilanes, trisilanes, and tetrasilanes were readily obtained in good yield using Mg electrode. Moreover, the same reaction system was also remarkably effective for the synthesis of polysilanes, polygermanes, and related polymers, especially when ultrasound was

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applied to the reaction system. The molecular weight and yield of the polymers was controlled by the concentration of monomer and the amount of supplied electricity. Because the present electroreductive polymerization requires only a single compartment cell and moderate conditions, it is undoubtedly one of the simplest and most powerful tools for synthesis of polysilane, polygermane and related polymers.

Experimental Section

General. ^1H and ^{13}C NMR spectra were obtained at 200 and 50 MHz and were recorded in CDCl_3 . Mass spectra were obtained in the electron-impact (EI) mode. Elemental analyses were performed by the Center for Instrumental Analysis of Kyoto University. Molecular weights of polymers and oligomers were determined by gel permeation chromatography (GPC) using THF as an eluent, relative to polystyrene standards. The constant electrocurrent was supplied with Takasago GPO 50-2 regulated DC power supply. The supplied electricity was counted by a Hokuto Denko Coulomb amperehour meter HF-201. The sonication by ultrasound (47 kHz) was performed by using a Yamato Branson 2200.

Material. Organomonochlorosilanes **1a–e** and organodichlorosilanes **3a,b** are commercially available from Shin-Etsu Chemical Co. Ltd., and they were used after distillation. Dichlorodimesitylsilane (**3c**),³⁵ 1,2-dichloro-1,1,2-trimethyl-2-phenyldisilane (**5**),³⁶ 1,4-bis(chloroethylmethylsilyl)benzene (**17a**),³⁷ and 1,4-bis(chloromethylphenylsilyl)benzene (**17b**)³⁸ were prepared by reported methods. Dichloro-4-(2-oxapropoxy)phenylphenylsilane (**3d**) was prepared by the reaction of a Grignard reagent from 4-bromophenol methoxymethyl ether with phenyltrichlorosilane. Tetrachlorogermane was obtained from Aldrich and used after distillation. Dichlorobutylphenylgermane (**13**) was prepared by a reported method.³¹ Tetrahydrofuran (THF) was distilled from Na–benzophenoneketyl under a nitrogen atmosphere. Magnesium ingot is commercially available from Rare Metallic Co. Ltd. and was cut into rods ($\Phi = 9$ mm, length = 4 cm) for electrodes. The electrodes were treated with concentrated HCl and then washed with water and acetone.

Disilane. The electrolysis of organomonochlorosilanes was carried out in a 30-mL three-necked flask equipped with Mg cathode and anode and a three-way stopcock jointed to a balloon of nitrogen. Into this cell was placed 0.7 g of LiClO_4 , and the content of the cell was dried at 50 °C in vacuo for 3 h. Chlorotrimethylsilane (0.1 mL) and 15 mL of dry THF were then added under a nitrogen atmosphere. After the solution was magnetically stirred for 3 h, the pre-electrolysis was carried out to remove traces of water and residual chlorotrimethylsilane from the electrolysis system; that is, 600 C of electricity was passed through the cell under a constant current condition (current density = 30 mA/cm²) with external

cooling by ice–water bath. During the electroreduction the polarity of the electrodes was alternated with an interval of 15 s using a commutator. The substrate chlorosilane (6 mmol) was then syringed into the cell in a stream of nitrogen, and the solution was further electrolyzed. The progress of the reaction was monitored by GLC or TLC. After the starting material was consumed (supplied electricity = ca. 2 F/mol based on the substrate chlorosilane), the reaction mixture was poured into ice cold 1 N HCl (100 mL), and the aqueous solution was extracted with ether (50 mL \times 3). The combined organic layer was washed twice with 50 mL of brine, dried over MgSO_4 , and concentrated. The residue was purified by a silica gel column, eluting with hexane.

1,2-Diphenyltetramethyldisilane (2a):^{22,38} IR (neat) 3050, 2960, 1430, 1250, 1110 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.35 (s, 12H), 7.20–7.65 (m, 10H); ^{13}C NMR (CDCl_3) δ –3.82, 127.71, 128.41, 133.88, 138.98; MS m/z (relative intensity) 270 (5, M^+), 255 (30, $\text{M}^+ - \text{Me}$), 193 (62, $\text{M}^+ - \text{Ph}$), 135 (100, PhMe_2Si^+).

Hexamethyldisilane (2b):³⁹ IR (neat) 2950, 2890, 1250 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.02 (s, 6H); ^{13}C NMR (CDCl_3) δ –2.71; MS m/z (relative intensity) 146 (13, M^+), 131 (18, $\text{M}^+ - \text{Me}$), 73 (100, Me_3Si^+).

1,2-Dimethyltetraphenyldisilane (2c):^{22,38} IR (KBr) 3020, 1420, 1250, 1100 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.69 (s, 6H), 7.15–7.65 (m, 20H); ^{13}C NMR (CDCl_3) δ –4.25, 128.06, 129.16, 135.47, 136.84; MS m/z (relative intensity) 394 (1, M^+), 197 (100, Ph_2MeSi^+).

Hexaphenyldisilane (2d):³⁹ IR (KBr) 3040, 1420, 1100 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.20–7.70 (m, 30H); ^{13}C NMR (CDCl_3) δ 128.15, 130.38, 135.25, 136.75; MS m/z (relative intensity) 518 (2, M^+), 259 (100, Ph_3Si^+).

Cross Coupling of Chlorotrimethylsilane (1b) and Chlorotriphenylsilane (1d). A solution of chlorotrimethylsilane (**1b**) (3 mmol) and chlorotriphenylsilane (**1d**) (3 mmol) in 15 mL of dry THF was electrolyzed by using the same procedure described above (supplied electricity = 580 C) to give **2d** (GLC yield, 25%) and 1,1,1-trimethyl-2,2,2-triphenyldisilane (**2e**) (GLC yield, 25%). **2e:**⁴⁰ ^1H NMR (CDCl_3) δ 0.20 (s, 9H), 7.30–7.50 (m, 15H); ^{13}C NMR (CDCl_3) δ –1.04, 127.95, 128.17, 129.22, 136.17.

Trisilane. A solution of chlorosilane **1** (15 mmol) and dichlorosilane **3** (3 mmol) in dry THF was electrolyzed by using the same procedure for the preparation of disilane to afford trisilane (supplied electricity = ca. 4F/mol based on **3**).

2-Phenylheptamethyltrisilane (4a):^{22,41} IR (neat) 3050, 2940, 2890, 1425, 1245, 1095 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.11 (s, 18H), 0.37 (s, 3H), 7.25–7.34 (m, 3H), 7.36–7.42 (s, 2H).

2,2-Diphenylhexamethyltrisilane (4b):⁴¹ IR (neat) 2950, 2875, 1430, 1250, 1100 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.15 (s, 18H), 7.26–7.37 (m, 6H), 7.40–7.50 (m, 4H); MS m/z (relative intensity) 328 (28, M^+), 255 (67, $\text{M}^+ - \text{SiMe}_3$), 178 (100, $\text{M}^+ - \text{SiMe}_3 - \text{Ph}$); HRMS calcd for $\text{C}_{18}\text{H}_{28}\text{Si}_3$ 328.1499, found 328.1493.

2,2-Dimesitylhexamethyltrisilane (4c):⁴² IR (KBr) 2950, 1440, 1240 1100 cm^{-1} ; ^1H NMR (C_6D_6) δ 0.25 (s, 18H), 2.12 (s, 6H), 2.29 (broad s, 12H), 6.75 (s, 4H); MS m/z (relative intensity) 412 (10, M^+), 397 (4, $\text{M}^+ - \text{Me}$), 339 (100, $\text{M}^+ - \text{SiMe}_3$); HRMS calcd for $\text{C}_{24}\text{H}_{40}\text{Si}_3$ 412.24377, found 412.24542.

2-Phenyl-2-[4-(2-oxapropoxy)phenyl]hexamethyltrisilane (4d): IR (KBr) 2950, 2900, 1500, 1240, 1100 cm^{-1} ; ^1H 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).

2-Phenylnonamethyltetrasilane (6):⁴³ A solution of chlorotrimethylsilane (**1b**) (15 mmol) and 1,2-dichloro-1,1,2-trimethyl-2-phenyldisilane (**5**) in dry THF was electrolyzed by

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using the same procedure described above to give **6** in 55% yield. **6**: IR (neat) 2950, 2890, 1250 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ -0.06 (s, 9H), 0.12 (s, 9H), 0.17 (s, 6H), 0.42 (s, 3H), 7.25–7.31 (m, 3H), 7.35–7.42 (m, 2H); MS m/z (relative intensity) 324 (39, M^+), 251 (60, $\text{M}^+ - \text{SiMe}_3$), 174 (100); HRMS calcd for $\text{C}_{15}\text{H}_{32}\text{Si}_4$ 324.13810, found 324.15502.

Poly[methylphenylsilane] (7).¹⁰ Into the electrolysis cell (30-mL three-necked flask equipped with one 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 h. Chlorotrimethylsilane (0.1 mL) and 15 mL of dry THF were then added under a nitrogen atmosphere. After pre-electrolysis was carried out by using the same procedure as for disilane, dichloromethylphenylsilane (**3a**), the monomer, was syringed into the cell in a stream of nitrogen. The electroreduction was performed under a constant current condition (current density = 30 mA/cm^2), and the polarity of the electrodes was alternated with an interval of 15 s using a commutator. During the electrolysis the mixture was sonicated by ultrasound (47 kHz) under cooling with water. The supplied electricity was counted by a commutator. After the electricity listed in Table 6 was passed through the cell, the reaction was quenched by EtOH (10 mL). The mixture was then poured into ice-cold 1 N HCl (100 mL), and the aqueous solution was extracted with ether (50 mL \times 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. **7**: UV λ_{max} ($\log \epsilon$) (THF) 340 nm (3.95); IR (KBr) 3050, 2960, 1430, 1250, 1100 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ -1.00–0.70 (m, 3H, SiMe), 6.30–7.70 (m, 5H, ring protons).

Digermane. A solution of chlorotrimethylgermane (**10**) (5 mmol) in dry THF was electrolyzed by using the same procedure as for the preparation of disilane to afford hexamethyldigermane (**11**) (supplied electricity = ca. 3F/mol based on **10**). **11**:⁴¹ IR (KBr) 3050, 2960, 1430, 1250, 1100, 1025 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ -1.00–0.70 (m, 3H, SiMe), 6.30–7.70 (m, 5H, ring protons).

Cross-Coupling of Chlorotrimethylgermane (10) and Chlorosilanes 1. A solution of chlorotrimethylgermane (**10**) (3 mmol) and chlorosilane (**1d** or **1e**) (3 mmol) in 15 mL of dry THF was electrolyzed by using the same procedure as for the preparation of disilane.

12a:⁴⁵ IR (neat) 3040, 2950, 2880, 1425, 1105 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.29 (s, 9H), 7.28–7.48 (m, 15H); MS m/z (relative intensity) 378 (5, M^+), 363 (5, $\text{M}^+ - \text{Me}$), 259 (100); HRMS calcd for $\text{C}_{21}\text{H}_{34}\text{SiGe}$ 378.0859, found 378.0834.

12b:⁴⁶ IR (neat) 3040, 2960, 2900, 1425, 1250, 1110 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.14 (s, 9H), 0.38 (s, 6H), 7.31–7.37 (m, 3H), 7.42–7.49 (m, 2H); MS m/z (relative intensity) 254 (7, M^+), 239 (16, $\text{M}^+ - \text{Me}$), 135 (100); HRMS calcd for $\text{C}_{11}\text{H}_{20}\text{-SiGe}$ 254.0546, found 254.0557.

Poly[butylphenylgermane] (14). The electroreductive polymerization of dichlorobutylphenylgermane (**13**) was carried out by the same procedure as for the electroreduction of dichloromethylphenylsilane. **14**: UV λ_{max} ($\log \epsilon$) (THF) 355 nm (4.10); IR (KBr) 3050, 2920, 2850, 1430, 1250, 1080 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.10–1.10 (m, 9H), 6.40–7.35 (m, 5H).

Poly[*p*-(disilanylene)phenylene] (18). 1,4-Bis(chloroethylmethylsilyl)benzene (**17a**) and 1,4-bis(chloromethylphenylsilyl)benzene (**17b**) were electrolyzed by using the same procedure as for the polymerization of dichloromethylphenylsilane (**3a**) to give poly[*p*-(1,2-diethylidimethyl-di-silanylene)-phenylene] (**18a**) and poly[*p*-(1,2-dimethyldiphenyldisilanylene)-phenylene] (**18b**), respectively. The applied reaction conditions were listed in Table 9 and Scheme 14.

18a:³⁷ M_n = 8600; IR (KBr) 3050, 2960, 2875, 1460, 1380, 1250, 1125 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.34 (broad s, 6H, SiMe), 0.91 (broad s, 10H, SiEt), 7.27 (broad s, 4H, ring protons).

18b:³⁷ M_n = 9500; IR (KBr) 3050, 1425, 1250, 1115 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 0.60 (broad s, 6H, SiMe), 7.26 and 7.30 (m, 14H, phenyl and phenylene ring protons).

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Supporting Information Available: $^1\text{H NMR}$ and IR spectra for compounds **4d**, polysilane **7**, polygermane **14**, and poly[*p*-(disilanylene)phenylenes] **18a,b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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