perature factors, an empirical absorption correction (μ = 10.3 cm^{-1})[16] were applied. The structure was solved by the Patterson method. R indices after refinement with anisotropic temperature factors were R = 0.037 and $R_w(F)$ = 0.039. A total of 1225 independent reflections with $F_o \geq 2\sigma(F_o)$ was used in the calculations. Methyl hydrogen atoms could not be located, but the three hydrogen atoms of the ethylene part appeared in a final difference Fourier map. The SHELX program package was used for the calculations.[17]

For the space group *Fdd*2 one has to consider two polarities of the crystal structure. In view of the limited data set, we did not attempt to determine the polarity, however. Final atomic parameters are listed in Table II. Additional data (listings of anisotropic temperature factors, F_o/F_c listings, additional bond distances and angles) may be obtained from the Fachinformationszentrum, Ges. für technisch-wissenschaftl. Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting CSD 55601, the names of the authors, and the journal.

Acknowledgment. This work was supported by the "Deutsche Forschungsgemeinschaft" and by the "Fonds der Chemischen Industrie", Frankfurt/Main, FRG. We are indebted to Dr. H. Runsink, Institute for Organic Chemistry, Technical University of Aachen, for recording high-field NMR spectra. A loan of ruthenium chloride from Johnson Matthey, Reading, England, is gratefully acknowledged.

Supplementary Material Available: Tables of bond distances and angles, least-squares planes, and thermal parameters for **2** (3 pages). Ordering information is given on any current masthead page.

OM910403V

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Electrochemistry of Organosilicon Compounds. 3. Synthesis of Poly(disilanylene)ethylenes by Electrolysis of Bis(chlorosilyl)ethanes[1]

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Received January 3, 1992

Electrolysis of 1,2-bis(chloromethylphenylsilyl)ethane (**1**) and 1,2-bis[chloromethyl(*p*-tolyl)silyl]ethane (**6**) in 1,2-dimethoxyethane using copper as the electrodes and tetrabutylammonium tetraphenylborate as the supporting electrolyte afforded poly(disilanylene)ethylenes with high molecular weights, in which no silicon–oxygen bonds in the polymer backbone are included. The effect of supporting electrolytes and solvents on the silicon–silicon bond formation is discussed.

Introduction

In recent years, much interest has been focused on the chemistry of polymeric organosilicon compounds that have silicon–silicon bonds in the polymer backbone. In this field, the silicon–silicon bond formation is of considerable importance for building up these molecules. Many papers concerning studies on the formation of the Si–Si bond have been reported to date.[2–14]

Recently, we have demonstrated that the electrochemical reduction of chlorosilanes in an undivided cell is effective for the formation of silicon–silicon bonds and affords polysilane oligomers in high yields.[1a,b] In this paper, we wish to report that poly(disilanylene)ethylenes with high molecular weights can be obtained by the reduction of 1,2-bis(chlorosilyl)ethanes with the use of copper as the electrodes and tetrabutylammonium tetraphenylborate as the supporting electrolyte in 1,2-dimethoxyethane.

Results and Discussion

As described in the previous paper,[1b] lower homologues of polysilanes such as disilanes, trisilanes, tetrasilanes, and

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Table I. Effect of Supporting Electrolytes and Solvents on Electrolytic Reduction of Chloromethyldiphenylsilane (3)

amt of 3 (mmol)	electrolyte (amt, g)	solvent	current (F mol^{-1})	isolated product (% yield)	
4.74	(TBA)ClO$_4$ (1.26)	DME	1.18	4 (83)	5 (trace)
3.86	LiCl (0.05)	DME	9.43	4 (61)	5 (10)
4.77	LiCl (0.24)	DME–DMF (5:1)	1.00	4 (11)[a]	5 (56)[a]
5.58	(TBA)ClO$_4$ (1.26)	DME–PC (6:1)	1.23	4 (5)[a]	5 (16)[a]
6.29	(TBA)ClO$_4$ (1.27)	MeCN	0.53	no reacn	
4.06	(TBA)BF$_4$ (0.25)	DME	1.26	4 (48)	
4.32	(TBA)OCOCF$_3$ (1.30)	DME	2.38	4 (15)[a]	5 (2)[a]
3.69	(TBA)BPh$_4$ (0.41)	DME	1.93	4 (84)	

[a] Yield determined by GLC.

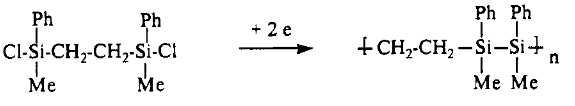
Table II. Polymers Obtained by Electrolysis of 1 and 6 with Copper Electrodes[16]

chlorosilane (amt, mmol)	supporting electrolyte	current (F mol^{-1})	polymer	M_r (M_r/M_n)	yield (%)	ce[a] (%)
1 (2.96)	(TBA)ClO$_4$	12.0	2	14000 (6.6)	39	7
1 (3.54)	(TBA)BPh$_4$	3.5	2	61000 (16)	13	7
1 (3.01)	(TBA)BPh$_4$	12.4	2	120000 (8.0)	17	3
6 (2.24)	(TBA)BPh$_4$	10.5	7	10000 (4.6)	45[b]	9
6 (2.12)	(TBA)BPh$_4$	12.8	7	18000 (10)	54	8
6 (2.76)	(TBA)BPh$_4$	17.9	7	25000 (10)	44	5

[a] Current efficiency. [b] Besides 7, an oligomer of M_r = 2600 was isolated in 52% yield.

pentasilanes are readily obtained in high yields by cathodic reduction of chlorosilanes in an undivided cell with the use of a copper anode. For example, 3-phenylundecamethylpentasilane was obtained in a 79% yield by the reduction of a mixture of dichloromethylphenylsilane and chloropentamethyldisilane in 1,2-dimethoxyethane (DME) in the presence of tetrabutylammonium (TBA) perchlorate using copper electrodes as both the cathode and anode.

We attempted to apply the electrochemical condensation of chlorosilanes to the synthesis of silicon-containing polymers in which regular alternating arrangement of a disilanylene unit and an ethylene unit is included in the polymer backbone (eq 1).[15] When the electrolysis of



$$\mathrm{Cl{-}Si(Ph)(Me){-}CH_2{-}CH_2{-}Si(Ph)(Me){-}Cl} \xrightarrow{+2\,e} \left[\mathrm{CH_2{-}CH_2{-}Si(Ph)(Me){-}Si(Ph)(Me)}\right]_n \qquad (1)$$

1 2

1,2-bis(chloromethylphenylsilyl)ethane (1) was carried out using the electrolytic system as specified above, poly[(1,2-dimethyl-1,2-diphenyldisilanylene)ethylene] (2) with molecular weight of 14000 was produced in 38% yield (see Table II).[16] In the IR spectrum of this polymer, however, a strong absorption attributed to silicon–oxygen bonds was observed. The formation of siloxane bonds in the polymerization of 1 may be ascribed to the use of perchlorate as the supporting electrolyte. We therefore attempted to find more suitable supporting electrolytes and solvents for the formation of disilanylene-containing polymers. Reduction of chloromethyldiphenylsilane (3) was chosen as the model reaction (eq 2). The progress of the reaction was monitored by GLC. Results are summarized in Table I.

$$\underset{3}{2\,\mathrm{Ph_2MeSiCl}} \xrightarrow{+2\,e} \underset{4}{\mathrm{Ph_2MeSi{-}SiMePh_2}} \qquad (2)$$

As reported previously, the use of (TBA)ClO$_4$ in DME is quite effective for the dimerization of 3 to give 1,2-dimethyltetraphenyldisilane (4) in 83% yield, but this system is not appropriate for the polymerization of 1. When lithium chloride was used instead of (TBA)ClO$_4$, disilane 4 was obtained in 61% yield. Lithium chloride is less soluble in DME than (TBA)ClO$_4$ resulting in rather low conductivity of the electrolytic solution. This probably decreases the current efficiency of the reaction and hence results in lower yield of 4.[17] The electrolysis with lithium chloride was, therefore, carried out in a mixed solvent of DME and dimethylformamide (DMF) (5:1) in order to increase the solubility. The disilane 4 was, however, obtained only in 11% yield, and 1,3-dimethyltetraphenyldisiloxane (5) was formed as a main product (56% yield). Similarly, when the electrolysis was carried out in a 6:1 mixture of DME and propylene carbonate (PC) containing (TBA)ClO$_4$, the yield of the dimer 4 was only 5%. These results clearly indicate that the carbonyl oxygen in the solvents causes the formation of an appreciable amount of disiloxane. The electrochemical reduction of 3 did not take place at all in an acetonitrile solution containing (TBA)ClO$_4$, and thus no dimer was produced.[18]

Next we used (TBA)BF$_4$ in DME. However, the disilane 4 was obtained only in 48% yield, owing to the fast exchange of the chlorine atom of compound 3 with a fluorine atom of the supporting electrolyte. The fluorinated 3 thus formed in the electrolytic solution was remained unchanged, after all of the remaining chlorosilane were consumed. Similarly, the use of (TBA)CF$_3$CO$_2$ in DME resulted in the fast exchange between chlorine and fluorine atoms.

The best result was obtained with the use of (TBA)BPh$_4$. Namely, the chlorosilane 3 was electrolyzed in DME using (TBA)BPh$_4$, as the supporting electrolyte until 1.93 F mol^{-1} of the electricity was supplied. Under these conditions, all of 3 was electrolyzed quite smoothly and the dimer 4 was isolated in 84% yield as the sole product. The formation of disiloxane was not found at all during the

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(15) Recently, synthesis of poly(tetramethyldisilanylene)ethylene by alkali-metal condensation of 1,2-bis(chlorodimethylsilyl)ethane at 80 °C has been reported: Hayashi, T.; Kawamoto, A. M.; Kobayashi, T.; Yamashita, H.; Tanaka, M. Presented at the 36th Symposium on Organometallic Chemistry, Japan, 1989; Abstr. No. A214.

(16) In all of the experiments given in Table II, the electrolyzed solutions were treated with LiAlH$_4$ before isolating products in order to avoid hydrolysis of the chlorosilyl residue at the polymer end (see Experimental Section).

(17) The addition of 12-crown-4 into the electrolytic solution did not improve the solubility of LiCl, and hence the yield of 2 was low.

(18) Electroplating of copper from the anode to the cathode took place as the main reaction, since copper(I) ions become soluble by complexation with acetonitrile and therefore accumulate in the solution.

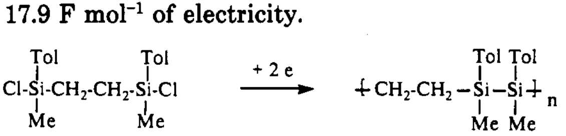
electrolysis. Thus, the nature of the solvents and the supporting electrolytes affects largely the dimerization of **3**.

The electrolytic system was then applied to the condensation of 1,2-bis(chloromethylphenylsilyl)ethane (**1**) (Table II). The electrolysis of **1** was carried out using the copper electrode system, for both the anode and cathode, and (TBA)BPh_4 as the supporting electrolyte in DME until all of **1** was consumed (3.5 F mol^{-1}).[16] Poly(1,2-dimethyl-1,2-diphenyldisilanylene)ethylene (**2**) was isolated in 13% yield after reprecipitation of the products from ethanol. The molecular weight of **2** was determined to be $M_r = 61\,000$ ($M_r/M_n = 16$), relative to polystyrene standards. The polymer **2** with higher molecular weight was obtained by prolonged electrolysis. Namely, the electrolysis of **1** with a supply of 12.4 F mol^{-1} of electricity gave polymer **2** with a molecular weight of $M_r = 120\,000$ ($M_r/M_n = 8.0$) in 17% yield.

Polymer **2** thus obtained is an elastic solid and is soluble in common organic solvents such as THF, benzene, and halocarbons. The structure of **2** was verified by IR, ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectroscopic techniques as well as by elemental analysis. The ^{1}H NMR spectrum of **2** at 270 MHz reveals two singlet resonances at δ 0.15 and 0.19 ppm due to methylsilyl protons and a singlet resonance at δ 0.56 ppm due to methylene protons as well as multiplet resonances at δ 7.11–7.23 ppm attributed to aromatic ring protons. The ^{13}C NMR spectrum of **2** reveals two resonances at δ −6.34 (methylsilyl carbons) and 6.33 ppm (methylene carbons) as well as five resonances appearing at δ 127.6–138.0 ppm (aromatic ring carbons). The ^{29}Si NMR spectrum of **2** shows a single resonance at δ −18.40 ppm due to the disilanylene unit, while the starting compound **1** reveals a signal at δ 21.77 ppm. All of the spectral data are consistent with the proposed structure. For comparison, condensation of **1** was carried out with sodium dispersion in benzene at low temperature under ultrasonic irradiation for 10 h to give a polymer with molecular weight of $M_r = 265\,000$ ($M_r/M_n = 2.5$). ^{1}H NMR and ^{13}C NMR spectra of this polymer were identical with those of **2** obtained by electrolysis.

The electrochemical condensation of **1** with the use of (TBA)ClO_4 in DME certainly produces the polymer ($M_r = 14\,000$), but absorptions attributed to an Si–O bond are always observed in its IR spectrum.[19] In contrast to this, no absorptions due to an Si–O bond are found in the polymer which was obtained by electrolysis using (TBA)BPh_4 as the supporting electrolyte.

The present method can also be applicable to the condensation of 1,2-bis[chloromethyl(*p*-tolyl)silyl]ethane (**6**). Thus, when **6** was electrolyzed in the similar manner until 12.8 F mol^{-1} of electricity was supplied, poly[1,2-dimethyl-1,2-bis(*p*-tolyl)disilanylene]ethylene (**7**) with molecular weight of $M_r = 18\,000$ was obtained in 54% yield (eq 3). Polymer **7** with molecular weight of $M_r = 25\,000$ was obtained in 44% yield by electrolysis with supply of 17.9 F mol^{-1} of electricity.



$$\underset{\textbf{6}}{\mathrm{Cl{-}\overset{Tol}{\underset{Me}{Si}}{-}CH_2{-}CH_2{-}\overset{Tol}{\underset{Me}{Si}}{-}Cl}} \xrightarrow{+2\,e} \underset{\textbf{7}}{\mathrm{\left[CH_2{-}CH_2{-}\overset{Tol}{\underset{Me}{Si}}{-}\overset{Tol}{\underset{Me}{Si}}\right]_n}} \quad (3)$$

In this electrolysis, products with low molecular weight were also produced. Thus, after the electrolysis of **6** with 10.5 F mol^{-1} of electricity, a polymeric part was separated by reprecipitation from ethanol to give polymer **7** (M_r 10 000, $M_r/M_n = 4.6$, 45% yield), and an oligomeric part was purified by recycling GPC to give the oligomer of **7** as an oil ($M_r = 2600$, $M_r/M_n = 2.7$, 52% yield). The oligomer shows the presence of a hydrosilyl group as indicated from its infrared (2109 cm^{-1}) and ^{1}H NMR (δ 4.33 ppm) spectra. The average number of the repeating unit in the oligomer, $(C_{18}H_{24}Si_2)_n$, was calculated to be $n = 8.8$ on the basis of the GPC analysis. The value is approximately the same as that estimated from the relative intensity of the terminal SiH group in the ^{1}H NMR spectrum ($n = 7.1$), suggesting that the oligomer has mainly linear structure.

Polymer **7** is an elastic solid and soluble in common organic solvents such as THF, benzene, and halocarbons. The ^{13}C NMR spectrum of **7** reveals two singlet resonances at δ −6.18 and −5.98 ppm, attributed to silylmethyl carbons, and a resonance at δ 6.53 ppm, attributed to methylene carbons in the polymer chain, as well as seven resonances appearing at δ 21.45 ppm and in the region of δ 128.46–137.80 ppm, due to methyl and ring carbons. The ^{29}Si NMR spectrum of **7** shows a single resonance at δ −18.67 ppm, at higher magnetic field than that of the starting compound **6** (21.83 ppm). All spectral data obtained for **7** were consistent with the proposed structure. Again, no Si–O bonds in the polymer backbone were observed in its infrared spectrum.

In conclusion, (disilanylene)ethylene polymers with high molecular weights, which involve no siloxy units, were obtained by electrolysis using copper as the electrodes, (TBA)BPh_4 as the supporting electrolyte, and DME as the solvent. The present approach may be used as the general method for the synthesis of the polymers having disilanylene unit.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were determined on JEOL JNM EX-270 and JNM FX-90A spectrometers. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Analysis of the products and monitoring of the reaction were performed by gas–liquid chromatography (GLC) using columns packed with OV-17 and SE-30 resin. Molecular weights of polymers were determined by gel-permeation chromatography using Shodex KF-806 and KF-804 resin for the columns and tetrahydrofuran (THF) as the eluent and are relative to polystyrene standards.

Chloromethyldiphenylsilane (**3**) was supplied by Shin-Etsu Chemical Co. Ltd. and was used after distillation. Chlorosilanes **1** and **6** were synthesized. Tetrabutylammonium (TBA) salts of perchlorate, tetrafluoroborate, trifluoroacetate, and tetraphenylborate were prepared from (TBA)Br by treatment with perchloric acid, tetrafluoroboric acid, trifluoroacetic acid, and sodium tetraphenylborate, respectively. These salts were purified by recrystallization from acetone–water 3–5 times and dried in vacuo for several days. 1,2-Dimethoxyethane (DME) was purified and dried in a manner described in the previous paper.[1a,b] Dimethylformamide (DMF), propylene carbonate (PC), and acetonitrile (MeCN) were distilled over phosphorous pentaoxide and dried over molecular sieves (4 Å).

Preparation of 1,2-Bis(chloromethylphenylsilyl)ethane (1). A solution of bromoethylene (20 mL, 0.28 mol) in THF (20 mL) was added dropwise into a mixture of magnesium (6.1 g, 0.25 mol) and THF (180 mL) over 1 h under ice cooling, and then the mixture was stirred at room temperature for 2 h. The resulting Grignard solution was added dropwise to a solution of dichloromethylphenylsilane (70 g, 0.37 mol) in THF (350 mL) under ice cooling. After being stirred at room temperature for 12 h, the solution was filtered and concentrated on a rotary evaporator. A distillate (45.1 g) boiling at 203–217 °C under an atmospheric pressure was collected. The distillate consisting of chloromethylphenylvinylsilane was mixed with chloromethylphenylsilane

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[19] The carbon content of this polymer was found to be lower than the calculated value, showing contamination of Si–O bonds in the polymer chain.

(31.2 g, 0.20 mol) and a catalytic amount of hexachloroplatinic acid, and the mixture was stirred at room temperature for 24 h. The mixture was distilled under a reduced pressure (135–137 °C/5 mmHg) to give crude 1 (25.6 g), which solidified on standing. Recrystallization from hexane gave pure 1 (22.56 g, 66.5 mmol, 29% yield): IR 3070, 1428, 1255, 1116, 1054, 784, 734 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 0.69 (s, 6 H, SiMe), 1.12 (s, 4 H, CH_2), 7.43–7.64 (m, 10 H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) –0.36 (SiMe), 9.77 (CH_2), 128.1, 130.4, 131.6, 133.0, 133.4, 134.6 (phenyl ring carbons); ^{29}Si NMR ($CDCl_3$) δ 21.77; mass *m/e* 338 (M^+), 303 (M^+ – Cl), 261 (M^+ – Ph). Anal. Calcd for $C_{16}H_{20}Si_2Cl_2$: C, 56.62; H, 5.94. Found: C, 56.61; H, 5.82.

Preparation of 1,2-Bis[chloromethyl(*p*-tolyl)silyl]ethane (6). (a) Methyl(*p*-tolyl)vinylsilane. A solution of bromoethylene (25 mL, 0.35 mol) in THF (30 mL) was added dropwise into a mixture of magnesium (9.4 g, 0.39 mol) and THF (200 mL) under ice cooling over a period of 1 h, and then the mixture was stirred at room temperature for 2 h. The resulting Grignard solution was added to a solution of chloromethyl(*p*-tolyl)silane (54.7 g, 0.32 mol) in THF (150 mL) under ice cooling over a period of 2.5 h. After being stirred at room temperature for 6 h, the solution was concentrated on rotary evaporator and filtered. Distillation of the filtrate under reduced pressure afforded 30.0 g (0.18 mol) of methyl(*p*-tolyl)vinylsilane (bp 90–95 °C/27 mmHg): ^{1}H NMR ($CDCl_3$) δ 0.32 (d, 3 H, SiMe, J = 3.6 Hz), 2.26 (s, 3 H, *p*-Me), 4.44–4.50 (m, 1 H, SiH), 5.75 (dd, 1 H, olefinic proton, J = 19.6 Hz, J = 4.1 Hz), 6.02 (dd, 1 H, olefinic proton, J = 14.3 Hz, J = 4.1 Hz), 6.18 (ddd, 1 H, olefinic proton, J = 14.3 Hz, J = 19.6 Hz, 2.8 Hz), 7.09 (d, 1 H, aromatic proton, J = 7.8 Hz), 7.35 (d, 1 H, aromatic proton, J = 7.8 Hz); ^{13}C NMR δ ($CDCl_3$) –5.55 (SiMe), 21.48 (*p*-Me), 128.77, 131.61, 134.57, 134.88, 135.02, 139.34 (phenyl and olefinic carbons); IR 2965, 2120 (Si–H), 1602, 1403, 1250, 1109, 1008, 955, 877, 838, 798 cm^{-1}; mass *m/e* 162 (M^+), 147 (M^+ – CH_3), 135 (M^+ – C_2H_3), 91. Anal. Calcd for $C_{10}H_{14}Si$: C, 74.00; H, 8.69. Found: C, 73.75; H, 8.64.

(b) 1-[Chloromethyl(*p*-tolyl)silyl]-2-[methyl(*p*-tolyl)silyl]ethane. Methyl(*p*-tolyl)vinylsilane (19.0 g, 0.12 mol) was mixed with chloromethyl(*p*-tolyl)silane (20.5 g, 0.12 mol) and a catalytic amount of hexachloroplatinic acid, and the mixture was stirred at room temperature for 48 h. The mixture was distilled under a reduced pressure to give 1-[chloromethyl(*p*-tolyl)silyl]-2-[methyl(*p*-tolyl)silyl]ethane (16.1 g, 48 mmol), (bp 137–142 °C/4 mmHg): ^{1}H NMR ($CDCl_3$) δ 0.265 (d, 3 H, SiH*Me*, J = 3.6 Hz), 0.29 (s, 3 H, SiCl*Me*), 0.73 (br m, 4 H, CH_2), 2.35 (s, 6 H, *p*-Me), 4.22–4.37 (br m, 1 H, SiH), 7.10–7.51 (m, 8 H, aromatic ring protons); ^{13}C NMR δ ($CDCl_3$) –6.07 (SiHMe), –1.53 (SiClMe), 5.07 (CH_2SiH), 10.12 (CH_2SiCl) 21.48 (*p*-Me), 128.48, 128.63, 128.75, 132.70, 133.42, 133.48, 134.38, 135.04 (phenyl ring carbons); IR 2957, 2109 (Si–H), 1603, 1252, 1110, 785 cm^{-1}; mass *m/e* 332 (M^+), 297 (M^+ – Cl), 241 (M^+ – Tol), 135. Anal. Calcd for $C_{18}H_{25}Si_2Cl$: C, 64.92; H, 7.57. Found: C, 65.21; H, 7.47.

(c) 1,2-Bis[chloromethyl(*p*-tolyl)silyl]ethane (6). A mixture of 1-[chloromethyl(*p*-tolyl)silyl]-2-[methyl(*p*-tolyl)silyl]ethane (16.1 g, 48 mmol), carbon tetrachloride (50 mL), and a catalytic amount of palladium chloride was stirred under ice cooling for 3 h. The solvent was evaporated, and the residue was distilled under a reduced pressure to give 6 (9.82 g, 27 mmol) (bp 143–147 °C/5 mmHg) in 13% yield based on chloromethyl(*p*-tolyl)silane: ^{1}H NMR ($CDCl_3$) δ 0.65 (s, 6 H, SiMe), 1.07 (s, 4 H, CH_2), 2.38 (s, 6 H, *p*-Me), 7.22–7.51 (m, 8 H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ –0.27 (SiMe), 9.89 (CH_2), 21.53 (*p*-Me), 128.68, 128.93, 131.07, 133.46, 140.57 (phenyl ring carbons); ^{29}Si NMR ($CDCl_3$) δ 21.83; IR 3012, 1603, 1392, 1253, 1111, 915, 777 cm^{-1}; mass *m/e* 366 (M^+), 331 (M^+ – Cl), 169, 91. Anal. Calcd for $C_{18}H_{24}Si_2Cl_2$: C, 58.83; H, 6.58. Found: C, 58.80; H, 6.50.

General Procedure for Electrolysis. Electrolysis of chloromethyldiphenylsilane (3) was carried out in a 30-mL undivided cell equipped with a platinum plate (6 cm^2) as the cathode and a coiled copper wire with a 28-cm^2 surface area as the anode.[20] In the cell was placed 1.26 g of (TBA)ClO_4 (or the other supporting electrolytes given in Table I), and the cell was dried at 50 °C in vacuo for 3 h. The chlorosilane 3 and 25 mL of DME (or the other solvents) were then added to the cell under a dry nitrogen atmosphere. Electrolysis was carried out in a manner of controlled current (30 mA).[21] The progress of the reaction was monitored by GLC. The electrolysis was continued until the starting material disappeared (unless otherwise noted). The resulting solution was concentrated under a reduced pressure. Products were isolated by medium-pressure liquid chromatography on silica gel eluting with a mixture of hexane and benzene (5:1). Current efficiency (ce) was calculated on the basis of [product (mol) × theoretical number of electrons/quantity of electricity (F) supplied] × 100. Results are summarized in Table I.

The procedure for the electrolysis of 1,2-bis(chloromethylphenylsilyl)ethane (1) and 1,2-bis[chloromethyl(*p*-tolyl)silyl]ethane (6) is mostly the same as above, except that the electrolysis was carried out using coiled copper wires as both the cathode (9 cm^2) and anode (31 cm^2). The electrolysis was continued until the starting material disappeared. The electrolyzed solution was transferred into a flask containing $LiAlH_4$ in 30 mL of THF, and the mixture was stirred at 50 °C for 4 h. An excess of $LiAlH_4$ was hydrolyzed as usual (ethyl acetate, ethanol, and then water) and products were extracted with ether. The extracts were concentrated on a rotary evaporator, and the residue was reprecipitated from ethanol. The polymer was collected by filtration and dried under reduced pressure. The structures of polymers 2 and 7 were characterized by spectroscopic method. The spectral data for 2 were compared with the polymer obtained from Na condensation of 1. The molecular weights of these polymers are summarized in Table II.

Electrolysis of 3 with the Use of (TBA)ClO_4 in DME. Electrolysis of 3 (1.103 g, 4.74 mmol) was carried out using (TBA)ClO_4 (1.26 g) in 25 mL of DME and passing 5.57 mF (1.18 F mol^{-1}) of electricity. Products were isolated by liquid chromatography to give 4 (0.78 g, 1.98 mmol, 83% yield, 71% ce).

Electrolysis of 3 with the Use of Lithium Chloride in DME. Electrolysis of 3 (0.899 g, 3.86 mmol) was carried out using lithium chloride (0.05 g) in 25 mL of DME and passing 36.4 mF (9.43 F mol^{-1}) of electricity. Products were isolated by liquid chromatography to give 4 (0.46 g, 1.17 mmol, 61% yield, 7% ce) and 5 (0.083 g, 0.20 mmol, 10% yield).

Electrolysis of 3 with the Use of Lithium Chloride in DME–DMF. Electrolysis of 3 (1.110 g, 4.77 mmol) was carried out using lithium chloride (0.24 g) in a mixed solvent of DME (21 mL) and DMF (4 mL) and passing 4.79 mF (1.00 F mol^{-1}) of electricity. Products were analyzed by GLC to be 3 (32% yield), 4 (11% yield, 11% ce), and 5 (56% yield).

Electrolysis of 3 with the Use of (TBA)ClO_4 in DME–PC. Electrolysis of 3 (1.298 g, 5.58 mmol) was carried out using (TBA)ClO_4 (1.26 g) in a mixed solvent of DME (25 mL) and PC (4 mL) and passing 6.87 mF (1.23 F mol^{-1}) of electricity. Products were analyzed by GLC to be 4 (5% yield, 4% ce) and 5 (16% yield).

Electrolysis of 3 with the Use of (TBA)ClO_4 in MeCN. Electrolysis of 3 (1.464 g, 6.29 mmol) was carried out using (TBA)ClO_4 (1.27 g) in 25 mL of MeCN and passing 3.36 mF (0.53 F mol^{-1}) of electricity. GLC analysis of the electrolytic solution showed that the starting material 3 was not electrolyzed at all under the present conditions.

Electrolysis of 3 with the Use of (TBA)BF_4 in DME. Electrolysis of 3 (0.946 g, 4.06 mmol) was carried out using (TBA)BF_4 (0.25 g) in 25 mL of DME and passing 5.11 mF (1.26 F mol^{-1}) of electricity. Products were isolated by liquid chromatography to give 4 (0.384 g, 0.973 mmol, 48% yield, 38% ce).

Electrolysis of 3 with the Use of (TBA)(CF_3CO_2) in DME. Electrolysis of 3 (1.005 g, 4.32 mmol) was carried out using (TBA)CF_3CO_2 (1.30 g) in 25 mL of DME and passing 10.3 mF (2.38 F mol^{-1}) of electricity. Products were analyzed by GLC as to be 4 (15% yield, 6% ce) and 5 (2% yield).

Electrolysis of 3 with the Use of (TBA)(BPh_4) in DME. Electrolysis of 3 (0.859 g, 3.69 mmol) was carried out using (TBA)BPh_4 (0.41 g) in 25 mL of DME and passing 7.13 mF (1.93 F mol^{-1}) of electricity. Products were isolated by liquid chromatography to give 4 (0.610 g, 1.55 mmol, 84% yield, 43% ce).

Electrolysis of 1 with the Use of Perchlorate. 1,2-Bis(chloromethylphenylsilyl)ethane (1) (1.005 g, 2.96 mmol) was

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[20] Details for the electrolytic system are mentioned in our previous papers. See ref 1a,b.

[21] In the course of the electrolysis, a copper(I) chloride layer was formed on the anode surface, but the anode did not become passive.

electrolyzed using (TBA)ClO_4 (1.25 g) in 25 mL of DME until 35.44 mF (12.0 F mol^{-1}) of electricity was supplied. Treatment of the electrolyzed solution with $LiAlH_4$ (0.10 g) and reprecipitation of the product from ethanol gave poly(1,2-dimethyl-1,2-diphenyldisilanylene)ethylene (**2**) (0.31 g, 39% yield, 7% ce): M_r = 14000 (M_r/M_n = 6.6); IR 3048, 2112, 1427, 1251, 1051, 773, 733, 699 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.09–0.35 (br m, 6 H, SiMe), 0.57 (br s, 4 H, CH_2), 7.25–7.37 (m, 10 H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −6.43, −6.36, −6.29, −6.16 (SiMe), 6.18, 6.34 (CH_2), 127.6, 127.8, 128.3, 129.1, 133.2, 134.1, 134.3, 137.8, 137.9 (phenyl ring carbons). Anal.[19] Calcd for $(C_{16}H_{20}Si_2)_n$: C, 71.57; H, 7.51. Found: C, 66.63; H, 7.16.

Electrolysis of 1 with the Use of Tetraphenylborate. 1,2-Bis(chloromethylphenylsilyl)ethane (**1**) (1.20 g, 3.54 mmol) was electrolyzed using (TBA)BPh_4 (0.51 g) in 25 mL of DME until 12.4 mF (3.5 F mol^{-1}) of electricity was supplied. Treatment of the electrolyzed solution with $LiAlH_4$ (0.12 g) and reprecipitation of the product from ethanol gave poly(1,2-dimethyl-1,2-diphenyldisilanylene)ethylene (**2**) (0.12 g, 13% yield, 7% ce): M_r = 61000 (M_r/M_n = 16); IR 3047, 2110, 1426, 1247, 1106, 772, 732, 698 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.16, 0.20 (two s, 6 H, SiMe), 0.57 (s, 4 H, CH_2), 7.11–7.37 (m, 10 H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −6.38 (SiMe), 6.31 (CH_2), 127.6, 128.3, 134.0, 137.8, 137.9 (phenyl ring carbons). Anal. Calcd for $(C_{16}H_{20}Si_2)_n$: C, 71.57; H, 7.51. Found: C, 71.13; H, 7.28.

Similarly, the electrolysis of **1** (1.02 g, 3.01 mmol) was carried out with a supply of 37.2 mF (12.4 F mol^{-1}) of electricity. Treatment of the electrolyzed solution with $LiAlH_4$ (0.10 g) and reprecipitation of the product from ethanol gave **2** (0.14 g, 17% yield, 3% ce): M_r = 120000 (M_r/M_n = 8.0); IR 3066, 1426, 1247, 1105, 771, 732, 698 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.15, 0.19 (two s, 6 H, SiMe), 0.56 (s, 4 H, CH_2), 7.11–7.23 (phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −6.34 (SiMe), 6.33 (CH_2), 127.6, 128.3, 134.1, 137.8, 138.0 (phenyl ring carbons); ^{29}Si NMR ($CDCl_3$) δ −18.40.

Electrolysis of 6 with the Use of Tetraphenylborate. 1,2-Bis[chloromethyl(*p*-tolyl)silyl]ethane (**6**) (0.78 g, 2.12 mmol) was electrolyzed using (TBA)BPh_4 (0.51 g) in 25 mL of DME until 27.2 mF (12.8 F mol^{-1}) of electricity was supplied. Treatment of the electrolyzed solution with $LiAlH_4$ (0.18 g) and reprecipitation of the product from ethanol gave poly[1,2-dimethyl-1,2-bis(*p*-tolyl)disilanylene]ethylene (**7**) (0.34 g, 54% yield, 8% ce): M_r 18000 (M_r/M_n = 10); ^1H NMR ($CDCl_3$) δ 0.09–0.35 (br m, 6 H, SiMe), 0.55 (br s, 4 H, CH_2), 2.33 (br s, 6 H, *p*-Me), 6.90–7.60 (br m, 8 H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ −6.12, −6.09 (SiMe), 6.54 (CH_2), 21.46 (*p*-Me), 128.01, 128.50, 133.41, 134.18, 134.36, 137.84 (phenyl ring carbons); ^{29}Si NMR ($CDCl_3$) δ −18.67; IR 2955, 2915, 2110, 1602, 1249, 1100, 770 cm^{-1}.

Similarly, electrolysis of **6** (1.02 g, 2.76 mmol) was carried out with supply of 49.3 mF (17.9 F mol^{-1}) of electricity. Treatment of the electrolyzed solution with $LiAlH_4$ (0.15 g) and reprecipitation of the product from ethanol gave **7** (0.36 g, 44% yield, 5% ce): M_r 25000 (M_r/M_n = 10); ^1H NMR ($CDCl_3$) δ 0.05–0.35 (br m, 6 H, SiMe), 0.56 (br s, 4 H, CH_2), 2.33 (br s, 6 H, *p*-Me), 7.00–7.50 (br m, 8 H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ −6.18, −5.98 (SiMe), 6.53 (CH_2), 21.45 (*p*-Me), 128.46, 128.59, 133.37, 134.16, 134.38, 137.80 (phenyl ring carbons); IR 2953, 2917, 2109, 1602, 1248, 1099, 770 cm^{-1}. Anal. Calcd for $(C_{18}H_{24}Si_2)_n$: C, 72.90; H, 8.16. Found: C, 72.83; H, 8.06.

Analysis of Products with Low Molecular Weight. In order to check oligomers formed during the electrolysis, chlorosilane **6** (0.822 g, 2.24 mmol) was electrolyzed with a supply of 23.6 mF (10.5 F mol^{-1}) of electricity in the same manner as above. After the electrolyzed solution was treated with $LiAlH_4$ (0.10 g), products were extracted with ether and reprecipitated from ethanol to give polymer **7** (0.297 g, 45% yield, 9% ce) of M_r = 10000 (M_r/M_n = 4.6), whose spectral data were the same as those obtained in the above runs. The mother liquid was concentrated, and the resultant mixture (0.421 g) was purified by recycling-GPC. Oligomers of **7** were isolated as oils (0.345 g, 1.16 mmol calculated as $C_{18}H_{24}Si_2$, 52% yield, 9% ce): M_r = 2600 (M_r/M_n = 2.7); ^1H NMR ($CDCl_3$) δ 0.10–0.40 (br m, 6 H, SiMe), 0.70–1.00 (br m, 4 H, CH_2), 2.35 (br s, 6 H, *p*-Me), 4.33 (br s, 0.28 H, SiH), 7.00–7.69 (m, 8 H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ −5.98 (MeSi), 6.54 (CH_2), 21.46 (*p*-Me), 127.7, 128.5, 128.7, 134.2, 134.4, 138.0 (phenyl ring carbons); IR 2956, 2919, 2109 (ν_{Si-H}), 1602, 1250, 1108, 797, 700 cm^{-1}.

Reaction of 1 with Sodium Dispersion. In a 200-mL three-necked flask fitted with a mechanical stirrer, dropping funnel, and reflux condenser was placed sodium metal (0.89 g, 39 mmol) and 50 mL of dry toluene. The contents of the flask were heated to reflux under an atmosphere of nitrogen and stirred vigorously to prepare sodium dispersion. The mixture was cooled, and toluene was replaced with 50 mL of benzene. The flask was immersed into ice water taken in a sonication bath (35 kHz, 225 W), and chlorosilane **1** (6.0 g, 17.7 mmol) was added dropwise to the mixture with stirring and irradiation of ultrasonic waves over a period of 30 min at 10–5 °C. The mixture was stirred under the same conditions for 10 h and then hydrolyzed with ethanol and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined extracts were filtered and concentrated. The resulting solid was purified twice by reprecipitation from chloroform–ethanol and chloroform–2-propanol to give poly(1,2-dimethyl-1,2-diphenyldisilanylene)ethylene (**2**) (2.8 g, 59% yield): M_r = 265000 (M_r/M_n = 2.5); ^1H NMR δ ($CDCl_3$) 0.15, 0.18 (two s, 6 H, SiMe), 0.55 (s, 4 H, CH_2), 7.07–7.26 (m, 10 H, phenyl ring protons); ^{13}C NMR δ ($CDCl_3$) −6.36 (SiMe), 6.29 (CH_2), 127.6, 128.3, 134.1, 137.8, 137.9 (phenyl ring carbons).

Acknowledgment. This research was supported in part by a Grant-in-Aid for Scientific Research (No. 03453104) by the Ministry of Education, Science and Culture, to which our thanks are due. We also express our appreciation to Izumi Science and Technology Foundation, Shin-Etsu Chemical Co. Ltd., Nitto Electric Industrial Co. Ltd., Dow Corning Japan Ltd., and Toshiba Silicone Co. Ltd. for financial support.

OM9200013