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Effect of Disilane Additives on the Electroreductive Polymerization of Organodichlorosilanes

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The electroreduction of dichloromethylphenylsilane was carried out in the presence of the disilane additives such as 1,1,1-trimethyl-2,2,2-triphenyldisilane under constant current conditions by using Mg electrodes to give the corresponding polysilanes in 24–88% yield. The disilane additives were found to promote the electroreductive polymerization of dichloromethylphenylsilane and control the molecular weight distribution of the resulting polysilanes. The number average molecular weights of the resulting polysilanes were determined by GPC to be 2100–3800, and the molecular weight distributions, 1.05–1.25. The resulting polymers synthesized in the presence of the disilanes showed narrower molecular weight distributions than that synthesized without the additives. In particular, the resulting polymer prepared using an equal amount of the disilane additive to the dichlorosilane monomer, the number average molecular weight was 3200, the molecular weight distribution was 1.25, and the yield was found to be remarkably increased (88%). The mechanism of the electroreductive polymerization of dichloromethylphenylsilane in the presence of 1,1,1-trimethyl-2,2,2-triphenyldisilane was discussed.

Keywords electroreductive polymerization, Mg electrodes, 1,1,1-trimethyl-2,2,2-triphenyldisilane, molecular weight distribution

Introduction

Polysilanes (1) have attracted considerable attention of researchers in various fields because of their unique properties (2–7). They have usually been prepared by the Wurtz type condensation of dichlorosilanes with alkali metals. However, this method requires rather drastic reaction conditions, and hence, has a disadvantage in controlling the unit-structure and molecular weight. Several modified or alternative methods have been proposed. Sonochemical coupling of dichlorosilane promoted by alkali metal (8) is a good example of alternative methods, which can be carried out under milder conditions. Other approaches have been also reported for the synthesis of polysilane, for instance, the transition metal catalyzed reaction of hydrosilane, (9) the anionic polymerization of masked disilenes, (10) and ring-opening polymerization (11). The electroreductive

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condensation of dichlorosilanes is a promising alternative method, and the electroreductive coupling of organodichlorosilanes with mercury electrode has been reported by Hengge (12) in 1976 as a method to form disilane, but this method is not effective in the preparation of polysilane (13, 14).

On the other hand, it has been reported in our previous papers (15–19) that the electroreduction of organic compounds with Mg electrode promotes a variety of unique reactions that cannot be attained without using the Mg electrode, and a typical example reported preliminarily (15) is the formation of a Si-Si bond and its application to the synthesis of high molecular weight polysilane that shows monomodal molecular weight distribution. This electroreductive polymerization has several advantages such as mild reaction conditions, good yields, and the monomodal molecular weight distribution of the resulting polysilanes. However, in the electroreductive polymerization, especially at higher temperature ($>18^{\circ}\text{C}$), the backbiting reaction of the propagating polymer (19) is a serious side reaction, which causes the broadening of the molecular weight distribution of the resulting polysilanes.

In this paper, we wish to describe the electroreductive polymerization of dichloromethylphenylsilane in the presence of several disilanes and discuss the additive effect of the disilanes on the yields and molecular weights of the resulting polysilanes.

Experimental

General

IR spectra were obtained on Perkin-Elmer FT-IR 1760X spectrometer. $^1\text{H-NMR}$ NMR spectra were measured on a Varian OXFORD NMR300 (300 MHz) spectrometer and the chemical shift values (δ) were expressed in ppm downfield from the internal TMS standard. Gel permeation chromatography (GPC) analyses of polysilanes were carried out on a Hitachi L-6000 high performance liquid chromatograph, L-3350 RI detector and Shodex[®] GPC A-803 column. Tetrahydrofuran was used as the eluent with a flow rate of 1.0 mL/min, and molecular weight values are relative to the polystyrene standards (Shodex[®] STANDARD (SM-105) polystyrene).

Materials

Tetrahydrofuran (THF) (Wako Pure Chemical Industries, Ltd., 1-2, Doshomachi 3-Chome, Chuo-Ku, Osaka 540-8605, Japan) was distilled from Na-benzophenoneketyl under an argon atmosphere. Chlorotrimethylsilane (TMS-Cl) (Shin-Etsu Chemical Co. Ltd., 6-1, Otemachi 2-Chome, Chiyoda-ku, Tokyo 100-0004, Japan) was distilled under an argon atmosphere. Dichloromethylphenylsilane (Shin-Etsu Chemical Co. Ltd., 6-1, Otemachi 2-Chome, Chiyoda-Ku, Tokyo 100-0004, Japan) was distilled under reduced pressure. Hexaphenyldisilane (Shin-Etsu Chemical Co. Ltd., 6-1, Otemachi 2-Chome, Chiyoda-Ku, Tokyo 100-0004, Japan) was used without purification. 1,1,1-Trimethyl-2,2,2-triphenyldisilane was prepared by electroreductive coupling reaction of chlorotrimethylsilane with chlorotriphenylsilane (18).^a Lithium perchlorate (LiClO_4) as a supporting electrolyte (Wako Pure Chemical Industries, Ltd., 1-2, Doshomachi 3-Chome, Chuo-Ku, Osaka 540-8605, Japan) was used without purification. Magnesium ingot (Rare Metallic Co. Ltd., 20-1, Misakicho 3-Chome, Chiyoda-Ku, Tokyo 101-0061, Japan) was cut into rods

^aThe 1,1,1-trimethyl-2,2,2-triphenyldisilane was recrystallized from ethanol to give 85% yield.

($\Phi = 9$ mm, length = 40 mm) for electrodes. Mg electrodes were treated with conc. HCl, and then washed with water and acetone.

Electroreductive Polymerization of Dichloromethylphenylsilane

In a 30 mL three-necked flask equipped with Mg cathode and anode. Into this cell was placed 1.0 g of LiClO_4 and 1,1,1-trimethyl-2,2,2-triphenyldisilane. The cell was dried at room temperature *in vacuo* for 3 h. Chlorotrimethylsilane (0.05 mmol) and 20 mL of dry THF were then added under an argon atmosphere. After the solution was magnetically stirred for 3 h to remove residual water as hexamethyldisiloxane, 140°C of electricity was passed through the cell (pre-electrolysis) under the constant current condition (50 mA), and the polarity of the electrodes was alternated at an interval of 15 sec. using a commutator. During the electrolysis, the ultrasound (47 kHz) was sonicated with cooling by running water. This pre-electrolysis is needed to consume the residual chlorotrimethylsilane. Into the cell were then syringed 10 mmol of dichloromethylphenylsilane as monomers in a stream of argon, and the solution was further electrolyzed. After 4F/mol of electricity (based on dichloromethylphenylsilane) was passed, the reaction mixture was poured into ice cold 1 N HCl (50 mL) and the aqueous solution was extracted with diethylether (50 mL \times 3), and washed with saturated NaHCO_3aq and NaClaq . The combined organic layer was dried over anhydrous MgSO_4 , and concentrated. The resulting crude polymer was dissolved in a trace amount of benzene and reprecipitated from ethanol. The molecular weight of the polymer was determined by GPC with THF as an eluent.

Poly(methylphenylsilane)

IR (KBr) 3050, 2960, 1428, 1250, 1100 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ -0.95–0.70(br-m, 3H), 6.30–7.70(br-m, 5H).

Results and Discussion

Electroreduction of Dichloromethylphenylsilane in the Presence of Several Chlorosilanes

It has been reported in our previous papers that the electroreduction of organochlorosilanes using a Mg electrode was effective to the formation of a Si-Si bond, and its application to the synthesis of polysilanes (15–20). In these electroreductive polymerizations, a small amount of chlorotrimethylsilane was added into the electrolysis solution and stirred to remove residual water as hexamethyldisiloxane before the monomers (organodichlorosilanes) was added. The excess chlorotrimethylsilane was then electrolyzed (pre-electrolysis) and converted to hexamethyldisilane, which did not act as a terminator of the electroreductive polymerization.

The effect of the pre-electrolysis was remarkable in the electroreduction of dichloromethylphenylsilane. Moreover, the kinds of the chlorosilane additives were found to influence the yields and molecular weight of the resulting polysilanes. Table 1 summarized the effects of the pre-electrolysis using several kinds of chlorosilanes, such as chlorotrimethylsilane, and the mixture of chlorotrimethylsilane and chlorotriphenylsilane, on the electroreductive polymerization of dichloromethylphenylsilane.

Table 1
Electroreduction^a of dichloromethylphenylsilane in the presence of disilane additives

Entry	Monomer (mol/L)	Disilane additives ^{b,c} (mol/L) ^d	\bar{M}_n^e	\bar{M}_w/\bar{M}_n^e	Yield ^f (%)
1	0.50	—	3200	1.65	38
2	0.50	A 0.03	3700	1.39	54
3	0.50	B 0.04	3000	1.10	56
4	0.50	C 0.04	2600	1.08	59

^aElectroreduction was carried out by using Mg electrodes under sonication (47 kHz), the polarity of electrodes was alternated with interval of 15 sec under sonication. The electricity was 4 F/mol based on dichloromethylphenylsilane.

^bThe disilane additives were prepared *in situ* by the pre-electrolysis.

^c**A**: hexamethyldisilane, **B**: 1,1,1-trimethyl-2,2,2-triphenyldisilane, **C**: hexaphenyldisilane.

^dTotal concentration of chlorosilanes.

^eDetermined by GPC using polystyrene standard.

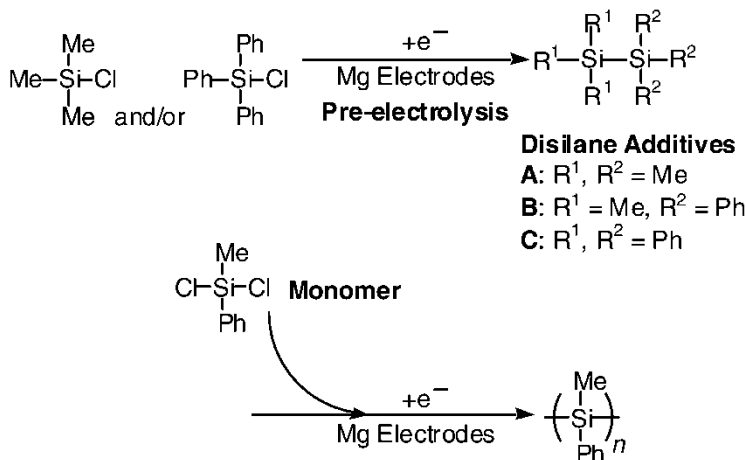
^fIsolated by reprecipitation from benzene-ethanol.

The electroreduction of dichloromethylphenylsilane was carried out using Mg electrodes to give the corresponding polymers in 38–59% yield (Scheme 1 and Table 1). All the polymers were obtained as white powders.

The molecular weight of the resulting products after purification by reprecipitation from benzene-ethanol, was determined by GPC with THF as the eluent to be 2600–3700 depending on the unit compositions, and all elution profiles showed a monomodal molecular weight distribution.

The conversion of the electroreductive polymerization without the pre-electrolysis was low, and the resulting polymer showed lower molecular weight and broader molecular weight distribution than that prepared with the pre-electrolysis using chlorotrimethylsilane (Entries 1, 2 in Table 1).

The electroreductive polymerization of dichloromethylphenylsilane was then carried out after the pre-electrolysis using chlorotrimethylsilane and chlorotriphenylsilane, which



Scheme 1. Electroreductive polymerization of dichloromethylphenylsilane with the pre-electrolysis.

produced 1,1,1-trimethyl-2,2,2-triphenyldisilane as a disilane additive, and using chlorotriphenylsilane, which produced hexaphenyldisilane. In the presence of these phenyl group containing disilane additives, the polymerization proceeded in higher yield, and the molecular weight distribution of the resulting polysilanes was much narrower ($M_w/M_n = 1.08-1.10$) than that obtained in the electroreductive polymerization in the presence of hexamethyldisilane (Entries 2–4 in Table 1). These results indicated that chlorosilanes added in the pre-electrolysis were not only the drying reagent to remove residual water as the corresponding disiloxanes but some kind of promoter of the electroreductive polymerization of the dichlorosilane monomer.

Additive Effects of 1,1,1-Trimethyl-2,2,2-triphenyldisilane

The disilane additives containing triphenylsilyl group, which were generated *in situ* in the pre-electrolysis, was found to be effective for the promotion of the electroreductive polymerization of dichloromethylphenylsilane and the control of the molecular weight distribution of the resulting polysilanes. However, these experiments included complex parameters such as the effect of chlorosilanes as drying reagents and the by-products of the pre-electrolysis. Then, 1,1,1-trimethyl-2,2,2-triphenyldisilane was separately prepared, and the electroreduction of dichloromethylphenylsilane in the presence of the disilane additive was carried out using Mg electrodes. As a result, the polymer was obtained as a white powder and the yield was 56% (Entry 2 in Table 2). The molecular weight of the resulting product after purification by reprecipitation from benzene-ethanol, was determined by GPC with THF as the eluent to be 2200, and the elution profile showed a monomodal molecular weight distribution. The electroreductive polymerization in the presence of hexaphenyldisilane was also tried, however, the commercially available hexaphenyldisilane was barely soluble into the THF electrolyte.

S. M. Chen reported that the reduction of dichloromethylphenylsilane by the Wurtz type condensation using metal lithium in the presence of the catalytic amount 1,1,1-trimethyl-2,2,2-triphenyldisilane afforded five- and six-members ring products (20). On the other hand, the cyclosilanes were not detected under our electroreductive conditions. The polymers synthesized electroreductively in the presence of 1,1,1-trimethyl-2,2,2-triphenyldisilane showed a narrower molecular weight distribution than that prepared without the disilane additive (Table 2).

The effect of the disilane concentration was summarized in Table 3. The addition of 0.3 to 1.5 mol% (0.002–0.008 mol/L) of the disilane based on the dichlorosilane

Table 2
Electroreduction^a of dichloromethylphenylsilane in the presence of Me₃SiSiPh₃

Entry	Monomer (mol/L)	Me ₃ SiSiPh ₃ (mol/L)	\bar{M}_n^b	\bar{M}_w/\bar{M}_n^b	Yield ^c (%)
1	0.50	—	3700	1.39	54
2	0.50	0.008	2200	1.10	56

^aElectroreduction was carried out by using Mg electrodes under sonication (47 kHz) and the polarity of electrodes was alternated with interval of 15 sec. The electricity was 4 F/mol based on dichloromethylphenylsilane.

^bDetermined by GPC using polystyrene standard.

^cIsolated by reprecipitation from benzene-ethanol.

Table 3
Electroreduction^a of dichloromethylphenylsilane in the presence of Me₃SiSiPh₃

Entry	Monomer (mol/L)	Me ₃ SiSi Ph ₃ (mol/L)	\bar{M}_n^b	\bar{M}_w/\bar{M}_n^b	Yield ^c (%)
1	0.50	—	3700	1.39	54
2	0.50	0.001	3800	1.25	60
3	0.50	0.002	2100	1.05	24
4	0.50	0.008	2200	1.10	56
5	0.50	0.045	3100	1.19	53
6	0.50	0.451	3200	1.23	88

^aElectroreduction was carried out by using Mg electrodes under sonication (47 kHz) and the polarity of electrodes was alternated with interval of 15 sec. The electricity was 4F/mol based on dichloromethylphenylsilane.

^bDetermined by GPC using polystyrene standard.

^cIsolated by reprecipitation from benzene-ethanol.

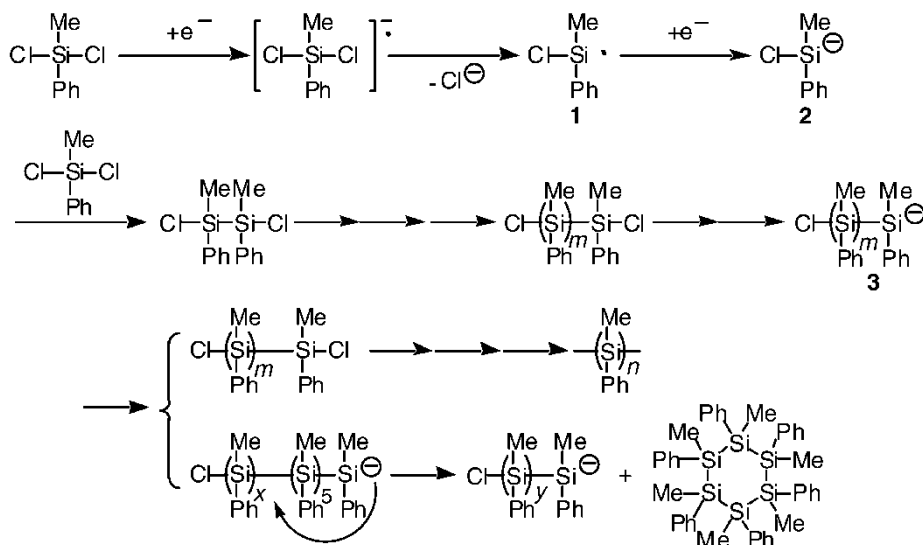
monomer resulted in a slight decrease in the molecular weights of the resulting polysilanes, but gave the narrowest molecular weight distributions ($M_w/M_n = 1.05-1.10$, Entries 3, 4 in Table 3). At higher concentration of the disilane additive, the polysilane, having 3100 of the number average molecular weight, was obtained in good yield (53%). Furthermore, its molecular weight distribution slightly broadened, but was still narrow ($M_w/M_n = 1.19$, Entry 5). The yield of the polysilane was found to be remarkably increased (88%, Entry 6) by using an equal amount of the disilane additive to the dichlorosilane monomer. However, the molecular weight distribution broadened and the formation of the six-membered ring product was observed.

Plausible Mechanism of Electroreduction of Dichlorosilanes in the Presence of 1,1,1-10-2,2,2-triphenyldisilane

The mechanism of the electroreductive polymerization of dichlorosilanes suggested in our previous paper (18) is shown in Scheme 2.

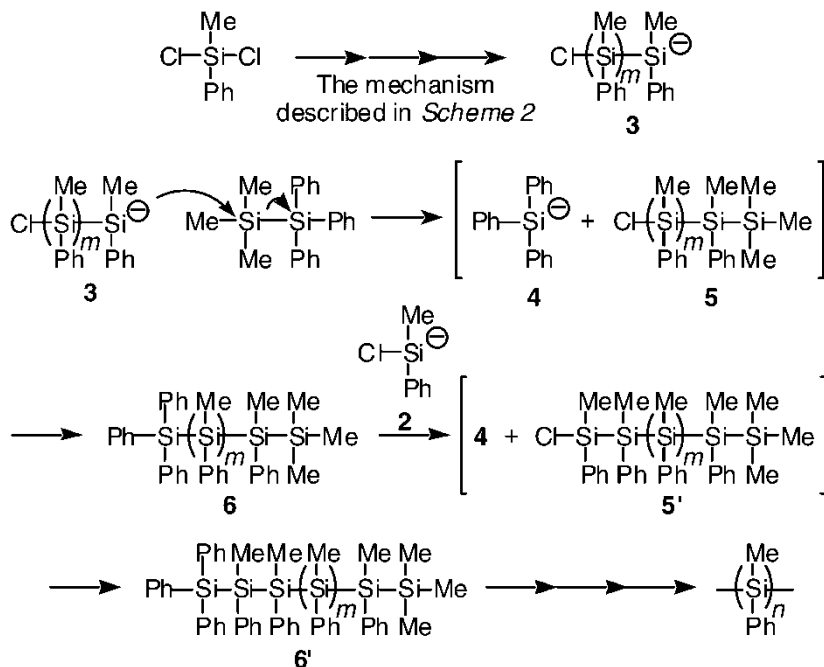
In the first step, dichloromethylphenylsilane is reduced electrochemically to generate the silyl radical **1**, which is further reduced to silyl anion **2** by the second electron transfer. The nucleophilic attack of the silyl anion **2** to the chlorinated silicon centers provides a dimer, oligomer, and finally polymer. During the course of the electroreductive polymerization, the terminal silyl anion species of the propagating polymer **3** often attacks the Si-Si chain forming cyclosilanes as by-products (backbiting reaction), (19) and this side reaction broadens the molecular weight distribution of the resulting polysilanes.

In the presence of the disilane additives such as 1,1,1-trimethyl-2,2,2-triphenyldisilane, another mechanism is possible for the propagation step in the electroreductive polymerization. The reactivity of Si-Si bond including triphenylsilyl group is relatively high, and the cleavage of the Si-Si bond of 1,1,1-trimethyl-2,2,2-triphenyldisilane is induced by the nucleophilic attack of the silyl anion. In fact, the reaction of triphenylsilyllithium with $\alpha\alpha\alpha\omega\omega$ -triphenyl(polydimethylsilane) was reported by M. Kumada (21). As summarized in Scheme 3, the propagating silyl anion species **3** attack 1,1,1-trimethyl-2,2,2-triphenyldisilane instead of the propagating Si-Si chain to afford triphenylsilyl anion (**4**) and α -chloro- ω -trimethylsilyl-(polymethylphenylsilane) (**5**). Then the coupling



Scheme 2. Electroreduction of dichloromethylphenylsilane.

between **4** and **5** gives α -triphenylsilyl- ω -trimethylsilyl-(polymethylphenylsilane) (**6**), and this reaction inhibits the undesirable backbiting reaction. Moreover, the polysilane **6** has enough polymerizability because the Si-Si(Ph)₃ bond at the terminal



Scheme 3. Electroreduction of dichloromethylphenylsilane in the presence of 1,1,1-trimethyl-2,2,2-triphenyldisilane.

position of **6** cleavages by the nucleophilic attacks of the silyl anion **2** forming α -chloro- ω -trimethylsilyl-(polymethylphenylsilane) **5'** and triphenylsilyl anion (**4**). That is, the triphenylsilyl group, at the terminal position of the propagating polymer, inhibits the backbiting reaction and controls the generation of the silyl anion species.

Conclusions

The disilane additives, such as 1,1,1-trimethyl-2,2,2-triphenyldisilane, were found to promote the electroreductive polymerization of dichloromethylphenylsilane and control the molecular weight distribution of the resulting polysilanes. The electroreduction of dichloromethylphenylsilane in the presence of 1,1,1-trimethyl-2,2,2-triphenyldisilane afforded the corresponding polymers in 24–88% yield depending on the concentration of the disilane. The number average molecular weights and the molecular weight distributions were determined by GPC to be 2100–3800, and 1.05–1.25, respectively. The resulting polymers prepared in the presence of the disilane additive showed narrower molecular weight distributions than the polysilane prepared without the disilane additive. The mechanism for the triphenylsilyl substituted disilane to control the electroreductive polymerization is not always clear at this point, but it is reasonable that the disilane traps the highly reactive silyl anion species at the terminal position of the propagating polymers, forming a relatively stable triphenylsilyl anion and inhibits the undesirable side reactions such as backbiting reaction. Triphenylsilyl anion attacks as a nucleophile to the chlorinated silicon atom at the terminal of the propagating polymer to give α -triphenylsilyl- ω -trimethylsilyl-(polymethylphenylsilane). α -Trimethylsilyl- ω -triphenylsilyl-(polymethylphenylsilane) does not lose its polymerizability completely, and triphenylsilyl group at the terminal position acts as an activator of the terminus of the propagating polymer. At a higher concentration of the disilane, the silyl anion generated by the electroreduction of dichloromethylphenylsilane (the monomer) probably attacks the disilane to form 1,1,1,2-tetramethyl-2,3,3,3-tetraphenyltrisilane in the first step. Then, α -trimethylsilyl- ω -triphenylsilyl-(polymethylphenylsilane)s are elongated stepwise. This type of polymerization does not involve highly active anionic species in the propagating polymers, and the polymerization is well controlled, however, the concentration of the trisilane generated in the first step is relatively high. Therefore, at higher concentration of the disilane, the conversion of the polymerization increased remarkably, and the molecular weight distributions were highly controlled, while the molecular weight slightly decreased in comparison with the electroreductive polymerization without the disilane additives.

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