Electroreductive Synthesis of Silylene-Germylene Copolymers with Ordered Sequences

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The silylene-germylene copolymer with the SISiGe ordered sequences was successfully synthesized in 49% yield by the electroreductive polymerization of bis(chlorodimethylsilyl)dibutylgermane, which was prepared by the electroreductive cross-coupling reaction of chlorodimethylsilane with dichlorodibutylgermane followed by the chlorination of the Si-H bonds. The resulting copolymer having 3900 of the number average molecular weight showed a characteristic strong UV absorption bands ($\lambda_{\text{max}}$) at 300 nm, and the extinction coefficients ($\epsilon_{\text{max}}$) per dibutylgermylene and dimethyilsilylene units were calculated to be 14000. On the other hand, the electroreductive homo- and copolymerization of dibutyldichlorosilane or dibutyldichlorogermaine with chlorodimethylsilane were also carried out using Mg electrodes to give the corresponding copolymers in 6-44% yield. The number average molecular weights were 3000-1600. The copolymers showed $\lambda_{\text{max}}$ at 308 and 286 nm. The $\epsilon_{\text{max}}$ per dibutylsilylene, dibutylgermylene or dimethyilsilylene units were calculated to be 6300 and 1600. The $\epsilon_{\text{max}}$ value of copolymer with SISiGe sequences was found to be much higher than those of copolymers having random sequences. A large difference of the $\epsilon_{\text{max}}$ values between the silylene-germylene copolymers is probably due to the conformational difference of the polymer main chain.

Key Words: Electroreductive Copolymerization, Mg Electrodes, Dibutylsilylene, Dibutylgermylene

1 Introduction

Polysilanes have recently attracted considerable attention due to their usefulness as precursors for thermally stable ceramics or a material for microlithography and also due to their potentiality in the preparation of new types of material showing semiconducting, photoconducting, or nonlinear optical properties. In contrast to the growing interest with the polysilanes, the method of preparation hitherto known is highly limited. Almost only practical method, so far, is the condensation of organodichlorosilanes 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, and has a disadvantage in controlling the unit-structure. Several modified or alternative methods have been proposed. Sonocatalytic coupling of dichlorosilane promoted by alkali metal 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, the anionic polymerization of masked disilenes, and ring-opening polymerization. The anionic polymerization of masked disilenes has provided a useful method for preparing some poly (disilanylene)s whose units are ordered in two sequences. The anionic ring-opening polymerization of cyclic oligosilanes is another method for obtaining structure-controlled polysilanes.

The electroreductive coupling of organodichlorosilanes with mercury electrode was reported by Hengge in 1976 as a method to form disilane, but this method was not effective in the preparation of polysilane. It has been reported in our previous papers 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 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. The same reaction system was also remarkably effective for the synthesis of polydisiloxanes, polygermanes, and related polymers.

Most recently we have been studying the electroreductive synthesis of the silicon-containing $\sigma$-conjugation copolymers with an ordered units sequence. The $\sigma$-conjugation character of the dialkyl (both symmetrically and unsymmetrically substituted) substituted and phenyl substituted polysilanes have been widely studied including the copolymers. And the structure-controlled $\sigma$-conjugation polysilanes were synthesized by M. Fujino, however, not always effective as a preparative method. Our electroreductive method using Mg electrodes, on the other hand, has a considerable potentiality for the synthesis of various kinds of structure-controlled silicon-containing polymers since the reaction can be
carried out at ambient or lower temperature, and also can be easily controlled by the control of the electrochemical parameters such as electric current, potential, and supplied electricity. In this paper we wish to describe the electroreductive synthesis of the copolymers which consist of distubylsilylene or dibutylgermylene with dimethyldisilane units and the structure-controlled silylene-germylene copolymer. The units composition and the photochemical properties of these copolymers are also discussed.

2 Experimental

2.1 Measurement

IR spectra were obtained on Parkin-Elmer FT-IR 1760X spectrometer. $^1$H 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 polymers were carried out on a Hitachi L-6000 high performance liquid chromatograph, L-8350 RI detector and Shodex $^\text{a}$ 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 $^\text{a}$ STANDARD (SM-105) polystyrene). UV absorption spectra were recorded on a Hitachi U 4000 spectrophotometer.

2.2 Materials

Tetrahydrofuran (THF) (Wako Pure Chemical Industries, Ltd.) was distilled from Na-benzophenoneketyl under an argon atmosphere. Chlorotrimethylsilane (TMS-Cl), chlorodimethylsilane and dichlorodimethylsilane (Shin-Etsu Chemical Co. Ltd.) were distilled under an argon atmosphere. Dichloromethylphenylsilane, dibutyldichlorosilane, (Shin-Etsu Chemical Co. Ltd.) and dibutyldichlorogermane (Gelset Inc.) were distilled under reduced pressure. Lithium perchlorate (LiClO$_4$) as a supporting electrolyte (Wako Pure Chemical Industries, Ltd.) was used without purification. Magnesium ingot (Rare Metallic Co. Ltd.) was cut into rods $\phi = 9$ mm, length = 40 mm) for electrodes. Mg electrodes were treated with conc. HCl, and then washed with water and acetone.

2.3 Electroreductive cross-coupling reaction of dibutyl dichlorosilane (1a) or dibutyl dichlorogermane (1b) with chlorodimethylsilane (2)

In a 30 mL threenecked flask equipped with Mg cathode and anode was placed 1.0 g of LiClO$_4$, and the content of the cell was dried in vacuo at room temperature for 3 h. Chlorodimethylsilane (2) (21 mmol) and 20 mL of dry THF were then added under an argon atmosphere. After the solution was magnetically stirred for 3 h, dibutylchlorosilane (1a) or dibutyl dichlorogermane (1b)) was syringed into the cell in a stream of argon, and the solution was further electrolyzed. The electrolysis was carried out under the constant current condition (50 mA) and the polarity of the electrodes was alternated at an interval of 15 sec using a comutator. During the electrolysis, the ultrasound (42 kHz) was sonicated with cooling by running water. After 4 F/mol of electricity (based on 1a or 1b) 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×3), and washed with saturated NaHCO$_3$ (aq.) and NaCl (aq.). The combined organic layer was dried over anhydrous MgSO$_4$, and concentrated. The residue was purified by a silica gel column eluting with hexane.

1,3-Dihydro-1,1,3,3-tetramethyl-2,2-dibutyltrisilane (3a) (b.p. 84-87°C/1 mmHg) $^1$H NMR (CDCl$_3$) $\delta$ 0.20 (d, 12H, $J = 3.0$ Hz), 0.43-1.40 (m, 18H), 4.71-1.75 (m, 2H).

Bis(chlorodimethylsilyl) dibutylgermane (3b) (b.p. 84-90°C/1 mmHg) $^1$H NMR (CDCl$_3$) $\delta$ 0.20 (d, 12H, $J = 4.5$ Hz), 0.43-1.40 (m, 18H), 4.71-1.75 (m, 2H).

2.3.2 Chlorination of 1,3-dihydro-1,1,3,3-tetramethyl-2,2-dibutyltrisilane (3a) and bis(chlorodimethylsilyl) dibutylgermane (3b)

A solution of 1,3-dihydro-1,1,3,3-tetramethyl-2,2-dibutyltrisilane (3a) or bis(chlorodimethylsilyl) dibutylgermane (3b) (30 mmol) and benzoyl peroxide (0.6 mmol) as a initiator in CCl$_4$ (30 mL) was refluxed for 2 h. The resulting oil was then concentrated and distilled under reduce pressure.

1,3-Dichloro-1,1,3,3-tetramethyl-2,2-dibutyltrisilane (4a) (b.p. 80-83°C/0.5 mmHg) $^1$H NMR (CDCl$_3$) $\delta$ 0.46 (s, 12H), 0.86-1.40 (m, 18H). Bis(chlorodimethylsilyl) dibutylgermane (4b) (b.p. 85-88°C/0.5 mmHg) $^1$H NMR (CDCl$_3$) $\delta$ 0.62 (s, 12H), 0.86-1.52 (m, 18H).

2.3.3 Electroreductive copolymerization of 1,3-dichloro-1,1,3,3-tetramethyl-2,2-dibutyltrisilane (4a) or bis(chlorodimethylsilyl) dibutylgermane (1b)

In a 30 mL threenecked flask equipped with Mg cathode and anode was placed 1.0 g of LiClO$_4$, and the content of the cell was dried in vacuo at room temperature 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 comutator. During the electrolysis, the ultrasound (42 kHz) was sonicated with cooling by running water. This pre-electrolysis is needed to consume the residual chlorotrimethylsilane. 1,3-Dichloro-1,1,3,3-tetramethyl-2,2-dibutyltrisilane (4a) or bis(chlorodimethylsilyl) dibutylgermane (4b)) as monomers were then syringed into the cell in a stream of argon, and the solution was further electrolyzed. After 4 F/mol of electricity (based on monomers) 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×3), and washed with saturated NaHCO$_3$ (aq.) and NaCl (aq.). The combined organic layer was dried over anhydrous MgSO$_4$, and concentrated. The resulting crude polymer was dissolved in a small amount of $n$-hexane andreprecipitated from ethanol. The molecular weight of the polymer was determined by GPC with THF as an eluent.

Polymer SI (Oligomeric products): $^1$H NMR (CDCl$_3$) $\delta$ 0.00-0.40 (br-m, 12H), 0.46-1.50 (br-m, 18H). Polymer G1: $^1$H NMR (CDCl$_3$) $\delta$ -0.04-0.54 (br-m, 12H), 0.60-1.45 (br-m, 18H).

2.3.4 Electroreductive copolymerization of dibu-
tyldichlorosilane (1a) or dibutyl dichlorogermane (1b) with dichlorodimethylsilane (5) In a 30 mL threenecked flask equipped with Mg cathode and anode was placed 1.0 g of LiClO₄, and the content of the cell was dried in vacuo at room temperature 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, the pre-electrolysis was carried out in the same procedure described above. Dibutyldichlorosilane (1a) (or dibutyl dichlorogermane (1b)) and dichlorodimethylsilane (5) as monomers were then syringed into the cell in a stream of argon, and the solution was further electrolyzed (see Table 3). After 4 mol of electricity (based on monomers) was passed, the reaction mixture was poured into ice cold 1 N HCl (50 mL) and the aqueous solution was extracted with diethyl ether (50 mL × 3), and washed with saturated NaHCO₃(aq) and NaCl(aq). The combined organic layer was dried over anhydrous MgSO₄, and concentrated. The resulting crude polymer was dissolved in a small amount of n-hexane and reprecipitated from ethanol. The molecular weight of the resulting polymer was determined by GPC with THF as an eluent.

Poly(dibutylsilylene) (S2) : IR (KBr) 2957, 2925, 1216, 754, 669 cm⁻¹; ¹H NMR (CDCl₃) δ 0.74-1.64 (br-m, 18H).

Poly(dibutylsilylene-co-dimethylsilylene) (S3) : IR (KBr) 2957, 2925, 2871, 1216, 754, 669 cm⁻¹; ¹H NMR (CDCl₃) δ 0.04-0.62 (br-m, Si-Me), 0.64-1.48 (br-m, Si-Bu).

Poly(dibutylgermylene) (G2) : IR (KBr) 2957, 2925, 2871, 1216, 754, 670 cm⁻¹; ¹H NMR (CDCl₃) δ 0.76-1.68 (br-m, 18H). Poly (dibutylgermylene-co-dimethylsilylene) (G3) : IR (KBr) 2957, 2926, 2871, 1216, 745, 669 cm⁻¹; ¹H NMR (CDCl₃) δ 0.02-0.64 (br-m, Si-Me), 0.62-1.58 (br-m, Ge-Bu).

3 Results and Discussion

3.1 Synthesis of poly (dibutylsilylene-co-dimethylsilylene) and poly (dibutylgermylene-co-dimethylsilylene) with ordered sequences

M. Fujino reported the synthesis of silylene-germylene copolymer with ordered SiSiGe sequences, however the preparation of the monomer having the SiSiGe structure was not always versatile as a preparative method. On the other hand, it has been already reported in our previous paper that 1,3-dihydrotrisilanes are prepared by the electroreductive cross-coupling of dichlorosilanes with chlorohydrosilanes by using Mg electrodes, and these trisilanes are useful as the precursors of the monomers in the electroreductive polymerization and also usable for the monomers of the dehydrogenation polymerization.

The electroreductive cross-coupling reaction of dibutyl dichlorosilane (1a) or dibutyl dichlorogermane (1b) with chlorodimethylsilane (2) was then carried out (Scheme 1) under various reaction conditions. Several results of the optimization of reaction conditions were summarized in Table 1. The optimized concentration was found to be 2.26 mol/L of chlorodimethylsilane (2) and 0.36 mol/L of dibutyl dichlorosilane (1a) for the preparation of the trisilane 4a. On the other hand, the concentra-

![Scheme 1](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dichloride 1</th>
<th>Chlorodimethylsilane</th>
<th>Yield of 3(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si</td>
<td>0.16</td>
<td>1.12</td>
</tr>
<tr>
<td>2</td>
<td>Si</td>
<td>0.36</td>
<td>2.26</td>
</tr>
<tr>
<td>3</td>
<td>Ge</td>
<td>0.15</td>
<td>1.15</td>
</tr>
<tr>
<td>4</td>
<td>Ge</td>
<td>0.31</td>
<td>2.31</td>
</tr>
</tbody>
</table>

a) The electroreduction was carried out by using Mg electrodes under sonication (42 kHz) and the polarity of electrodes was alternated with interval of 15 sec. The electricity was 4 mol based on 1. b) Isolated.

The Si-H bond is known to be reactive under radical or anionic conditions, and readily transformed to the Si-Si bond with treatment by a catalytic amount of radical source such as benzoyl peroxide and AIBN in CC1₄. Using this method, 1,3-dihydro-1,1,3,3-tetramethyl-2,2-dibutyltrisilane and bis(hydrodimethylsilyl) dibutylermane were transformed into the corresponding chloride 4 in good to moderate yields (Scheme 2).

We have already reported structure-controlled σ-conjugation copolymers, for example, the electroreductive copolymerization of 1,2-dichloro-1,1,3,3-tetramethyl-2,2-diphenyltrisilane was carried out to afford the corresponding polysilane having 4700 of number average molecular weight and SiSiSi ordered-sequences in 50% yield. Under same polymerization conditions the electroreductive polymerization of 1,2-dichloro-1,1,3,3-tetramethyl-2,2-dibutyltrisilane (4a) was carried out, however, the yield of the resulting polymer was very low. In the electroreduction of 1,2-dichlorotrisilanes the cyclized silane compounds such as silacyclohexanes were often obtained, and this cyclization reaction resulted in the formation of the oligosilane mixture. On the other hand, the electroreductive polymerization of bis(chlorodimethylsilyl)dibutylgermane (4b) gave the desired polymer having SiSiGe sequences in 49% yield and its molecular weight was determined to be 3900. The ¹H NMR spectrum of the copolymer G1 showed broad peaks in the δ region of -0.04-0.54 ppm and 0.64-1.48 ppm, which were attributed to the methyl and butyl protons respectively. The methyl pro-

![Scheme 2](image)
Cl>M-Cl
Me Bu Me

\[ \text{Bu} \text{Cl} \rightarrow \text{Bu} \text{Cl} \text{Me} \text{Me} \]

\[ \text{LiClO}_4/\text{THF} \text{ M} \text{g} \text{ electrodes} \text{ alternation, ultrasound} \]

Cl>M-Cl
Me Bu Me

\[ \text{Me Bu Me} \]

4a: M = Si
4b: M = Ge

Scheme 3

\[ \text{Bu} \text{Cl} \rightarrow \text{Bu} \text{Cl} \text{Me} \text{Me} \]

\[ \text{LiClO}_4/\text{THF} \text{ M} \text{g} \text{ electrodes} \text{ alternation, ultrasound} \]

Table 2 Electroreductive polymerization\(^{a,b}\) of 4.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>M</th>
<th>Monomers (mol/L)</th>
<th>( M_n^{(b)} )</th>
<th>( M_w/M_n^{(b)} )</th>
<th>Yield(^{(c)} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Si</td>
<td>0.50</td>
<td>-</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>G1</td>
<td>Ge</td>
<td>0.48</td>
<td>3900</td>
<td>1.96</td>
<td>49</td>
</tr>
</tbody>
</table>

\(^{a}\) The electroreduction was carried out by using Mg electrodes under sonication (42 kHz) and the polarity of electrodes was alternated with interval of 15 sec. The electricity was 4 F/mol based on 5. \(^{b}\) Determined by GPC using polystyrene standard. \(^{c}\) Isolated by reprecipitation from \( \alpha \)-hexane-ethanol.  

3.2 Electroreductive random copolymerization of dibutyl dichlorosilane (1a) or dibutyl dichlorogermane (1b) with dichlorodimethylsilane (5)

The electroreductive homo- and co-polymerization of dichlorodibutylsilane (1a) or dichlorodibutylgermane (1b) with dichlorodimethylsilane (5) was carried out to give the corresponding polymers in 6-44% yield (Scheme 3, Table 3). All the copolymers were obtained as white powders. These polymers are soluble into common organic solvents such as THF, benzene, \( \alpha \)-hexane, and chloroform, while poly(dimethylsilylene) is known only as a highly crystalline intractable solid and insoluble into any solvents. The molecular weight of copolymers determined by GPC with THF as the eluent after reprecipitation from hexane-ethanol, was 1300-6100 depending on the units composition, and all elution profiles showed a broad monomodal molecular weight distribution. These copolymers showed the molecular weights near to those in our previous reports. And the molecular weight of the silylene-silylene copolymer S3 was higher than the silylene-germylene copolymer G3. As mentioned above, the reactivity of 1b under the electroreduction conditions is low, and this fact seems to be the main reason for the relatively low yields and molecular weights of G2 and G3. The units composition of the resulting copolymers was determined by integrating the butyl and methyl proton signals in the \(^1\)H NMR spectra. The \(^1\)H NMR spectrum of S3 showed broad peaks in the \(\delta \) region of 0.04-0.62 ppm and 0.64-1.48 ppm and that of G3, 0.02-0.64 ppm and 0.62-1.58 ppm, which were attributed to the methyl and butyl protons respectively. The electroreduction of 1 : 1 mixture of 1a and 5 gave the copolymer having 67% of dibutylsilylene units (Entry 1), and about 1 : 1 mixture of 1b and 5 gave the copolymer having 56% dibutylgermylene units (Entry 2). Dibutylsilylene units were predominantly included in the copolymer S3, while the content of dibutylgermylene units in G3 was almost 1 : 1.

3.3 Photochemical properties of the resulting polymers

The resulting silicon containing polymers showed strong UV absorption bands (\( \lambda_{\text{max}} \)) at 314-286 nm, and the extinction coefficients (\( \varepsilon_{\lambda_{\text{max}}} \)) per dibutylsilylene, dibutylgermylene, or dimethylsilylene units were calculated to be 1600-14000. Both homopolymers (S2 and G2) had longer \( \lambda_{\text{max}} \) values than the corresponding copolymers. These results are consistent with R. West's report, that is, it has been reported \(^1\) that the \( \lambda_{\text{max}} \) values of the same types of copolymers increased with an increase in dibutylsilylene or dibutylgermylene units.

The copolymer with random structure (G3, Si/Ge ratio = 0.79) showed a UV absorption band (\( \lambda_{\text{max}} \)) at 286 nm, and the extinction coefficient (\( \varepsilon_{\lambda_{\text{max}}} \)) per dibutylgermylene units and dimethylsilylene units was calculated to be 1600. The \( \lambda_{\text{max}} \) and \( \varepsilon_{\lambda_{\text{max}}} \) values of G3 are abnormally low in comparison with the values of other homopolymers and copolymers. On the other hand, the \( \lambda_{\text{max}} \) value of the copolymer with ordered sequences (G1, Si/Ge ratio = 2.00) was measured to be 300 nm, and the \( \varepsilon_{\lambda_{\text{max}}} \) per dibutylgermylene units and dimethylsilylene units was calculated to be 14000. High \( \varepsilon_{\lambda_{\text{max}}} \) value of the copolymer G1 can not be explained only by the difference of molecular weight or the content of gemylene units. M. Okano and his coworkers have reported that the irregularity of the units sequences in the silylene-germylene copolymers influences the conformation of the polymer main chain, and the \( \lambda_{\text{max}} \) values greatly depend on the change of the conformation. \(^{22}\)

In our case, large difference of the \( \varepsilon_{\lambda_{\text{max}}} \) values between the silylene-germylene copolymers G1 and G3 is also probably due to the conformational difference of the polymer main chain. That is, regularity of units sequences in the copolymer G1 increases the linearity of the polymer main chain, which results in more effective \( \sigma \)-conjugation system.

4 Conclusion

This electroreductive polymerization using Mg elec-
Table 4 Photochemical properties of resulting polymers.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Sequence structure</th>
<th>Me/Bu&lt;sup&gt;a&lt;/sup&gt; ratio&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield&lt;sup&gt;c&lt;/sup&gt; (%)</th>
<th>Mn&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Mw/Mn&lt;sup&gt;d&lt;/sup&gt;</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt; (nm)</th>
<th>ε&lt;sub&gt;max&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>MeMeBu&lt;sup&gt;Si-Si&lt;/sup&gt; and MeMeBu</td>
<td>2.00</td>
<td>trace</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>S2</td>
<td>MeMeBu&lt;sup&gt;Si&lt;/sup&gt; and Bu</td>
<td>—</td>
<td>44</td>
<td>6100</td>
<td>3.61</td>
<td>314</td>
<td>6900</td>
</tr>
<tr>
<td>S3</td>
<td>Me&lt;sup&gt;Si&lt;/sup&gt;Bu&lt;sup&gt;Si&lt;/sup&gt; and Me-Bu</td>
<td>0.49</td>
<td>36</td>
<td>4600</td>
<td>2.24</td>
<td>308</td>
<td>6300</td>
</tr>
<tr>
<td>G1</td>
<td>MeMeBu&lt;sup&gt;Si-Si-Ge&lt;/sup&gt; and MeMeBu</td>
<td>2.00</td>
<td>49</td>
<td>3900</td>
<td>1.96</td>
<td>300</td>
<td>14000</td>
</tr>
<tr>
<td>G2</td>
<td>MeBu&lt;sup&gt;Ge&lt;/sup&gt;Bu and Bu</td>
<td>—</td>
<td>6</td>
<td>1300</td>
<td>1.23</td>
<td>311</td>
<td>6500</td>
</tr>
<tr>
<td>G3</td>
<td>Me&lt;sup&gt;Si&lt;/sup&gt;Bu&lt;sup&gt;Ge&lt;/sup&gt;Bu and Me-Bu</td>
<td>0.79</td>
<td>17</td>
<td>3000</td>
<td>1.84</td>
<td>286</td>
<td>1600</td>
</tr>
</tbody>
</table>

a) Me : Dimethylsilylene unit. Bu : Dibutylsilylene or dibutylgermylene unit. b) Determined by H NMR (300 MHz). c) Isolated by reprecipitation from n-hexane-ethanol. d) Determined by GPC using polystyrenestaraid. e) UV spectra were measured in THF at 20°C.

trodes was successfully applied to the synthesis of the silylene-germylene copolymer (G1) having SiSiGe repeated sequences in good yield. The dimethylsilylene-dibutylsilylene (S3) and dimethylsilylene-dibutylgermylene (G3) random copolymers were also synthesized by this electroreductive method. The resulting copolymers showed characteristic strong UV absorption bands (λ<sub>max</sub>) at 300 (G1), 308 (S3) and 286 (G3) nm. The extinction coefficient (ε<sub>max</sub>) per dibutylgermylene and dimethylsilylene units of the silylene-germylene copolymer G1 was found to be much higher than that of G3. Remarkable difference of ε<sub>max</sub> value between the copolymers G1 and G3 is probably due to the regularity of the units sequences in the silylene-germylene copolymers.

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