Electroreductive Synthesis of Polygermane and Germane–Silane Copolymer

Tatsuya Shono,* Shigenori Kashimura* and Hiroaki Murase

*Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606-01, Japan
b Advanced Technology Center, Osaka Gas. Co., Ltd., 5-7-1-61 Torishima, Konohana, Osaka 554, Japan

Formation of Ge–Ge and Ge–Si bonds has been achieved by electroreduction with an Mg electrode and this method has been successfully applied to the preparation of polygermane and germane–silane copolymer.

Polygermane and germane–silane copolymer have recently attracted considerable attention owing to their promising physical properties such as semiconductivity, photoconductivity, photoluminescence and third-order nonlinear effects.1–3 Although reduction of organodichlorogermanes with alkali metals is the only known method effective for the preparation of polygermane,4 this method inevitably suffers from the difficulties that the reaction conditions are rather drastic and the product polymer usually shows polymodal molecular weight distribution. We have recently found that electroreduction of organodichlorosilane with Mg electrode was highly effective for the preparation of polysilane under mild reaction conditions and the product polymer showed a monomodal molecular weight distribution.5

It has been found in the present study that Ge–Ge and Ge–Si bonds are effectively formed by electroreduction with an Mg electrode, and this method has been successfully applied to the preparation of polygermane and germane–silane copolymer. Thus, hexamethyldigermane 2 was obtained in 84% yield by the electroreduction of chlorotrimethylgermane 1. The electroreduction of 1 was carried out with an Mg rod cathode and anode in an undivided cell under sonication (47 MHz), and the cathode and anode were alternated at an interval of 15 s. Moreover, the electroreduction of a mixture of 1 and chlorotriphenylsilane 3a or chlorodimethylphenylsilane 3b (molar ratio of 1:3, 1:2) under similar conditions afforded the corresponding germylsilane 4a or 4b as the main product (Scheme 1).

\[ \text{Me}_3\text{GeCl + C_3\text{SiPhR}_2} \rightarrow \text{Me}_3\text{GeSiPh}_2 + (\text{Me}_2\text{Ge})_2 \]

\[ a: \text{R = Ph} \]
\[ b: \text{R = Me} \]

Scheme 1 Conditions: 3 F mol⁻¹ electricity based on 1; LiClO₄ in tetrahydrofuran (THF); Mg cathode and anode; sonication. Yields (%) based on 1: 30%; 4a, 60%; 4b, 52%.

These results clearly indicate that the electroreductive method is useful for the formation of Ge–Ge and Ge–Si bonds. Accordingly, the synthesis of high molecular weight polygermane and germane–silane copolymer was studied by using the same electrochemical reduction as the key reaction. A typical polygermane obtained by the electroreduction of dichlorophenylbutylgermane 5 showed a molecular weight of \( M_n = 19900 \) (λ_max 355 nm; yield 10%). Under similar
Scheme 2 Conditions: 3.8 F mol⁻¹ electricity; LiClO₄ in THF. Mg cathode and anode, sonication.

Table 1 Preparation of germane-silane copolymer

<table>
<thead>
<tr>
<th>Molar ratio of monomer (5/6)</th>
<th>Yield (%)ᵃ</th>
<th>Ge content in copolymer R = [x(x + y)]ᵇ Mₓ</th>
<th>ƛₘₐₓ/nmᵈ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.39</td>
<td>34</td>
<td>0.16</td>
<td>17 000  330</td>
</tr>
</tbody>
</table>

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

Conditions, a mixture of 5 and dichloromethylphenylsilane 6 gave a germane-silane copolymer (Scheme 2). Typical results are shown in Table 1; the atomic ratio (Ge/Si) in the copolymers was roughly proportional to the molar ratio of the monomers 5/6, and an almost linear correlation was observed between ƛₘₐₓ and the germanium content [R = x(x + y)] in the polymer including polygermane (R = 1; ƛₘₐₓ = 355 nm) and polysilane (R = 0; ƛₘₐₓ = 325 nm). These results provide support for our assumption that the copolymerization of 5 and 6 actually took place under the conditions of the electroreduction.

Received, 24th March 1992; Com. 2/01578A

References