

Electroreductive Synthesis of Polygermane and Germane–Silane Copolymer

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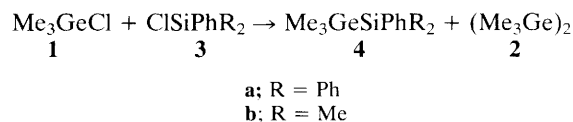
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Formation of Ge–Ge and Ge–Si bonds has been achieved by electroreduction with an Mg electrode and this method has been successfully applied to the preparation of polygermane and germane–silane copolymer.

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 organodichlorogermenes 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

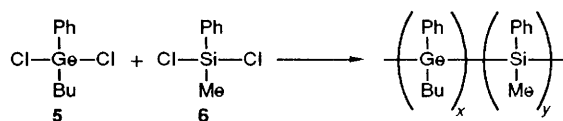
It has been found in the present study that Ge–Ge and Ge–Si bonds are effectively formed by electroreduction with an Mg electrode, and this method has been successfully applied to the synthesis of polygermane⁶ and germane–silane copolymer. Thus, hexamethyldigermene **2** was obtained in 84% yield by 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 germysilane **4a** or **4b** as the main product (Scheme 1).



Scheme 1 Conditions: 3 F mol^{−1} electricity based on **1**; LiClO₄ in tetrahydrofuran (THF); Mg cathode and anode; sonication. Yields (%) based on **1**: **2**, 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 $M_n = 19\,900$ (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

Molar ratio of monomer (5/6)	Yield (%) ^a	Ge content in copolymer $R = [x/(x + y)]^b M_n^c$	$\lambda_{\text{max}}/\text{nm}^d$	
0.39	34	0.16	17 000	330

^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**,^{4,6,7} and an almost linear correlation was observed between λ_{max} and the germanium content [$R = x/(x+y)$] in the polymer including polygermane ($R = 1$; $\lambda_{\text{max}} = 355$ nm) and polysilane ($R = 0$; $\lambda_{\text{max}} = 325$ nm). These results provide support for our assumption that the copolymerization of **5** and **6** actually took place under the conditions of the electroreduction.

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