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Synthesis of Polygermanes by Ligand Substitution Polymerization of the 1,4-Dioxane Complex of Germanium Dichloride with Organolithium Compounds

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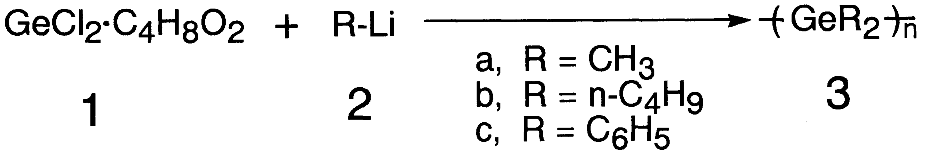
Higher molecular weight polygermanes were synthesized by a ligand substitution polymerization of the 1,4-dioxane complex of germanium dichloride with organolithium compounds at a lower reaction temperature. Different from the conventional Wurtz-type coupling reaction, the present polymerization gives rise much higher yields of polygermanes.

Polymers composed of only metal atoms in the backbone have been attracted interests for many years since the first investigation on polyorganosilanes by Kipping in 1924.1) Not only polysilanes, organogermane2,3) and organostannane4,5) polymers of the 14th elements in the periodic table were also synthesized in a similar manner. While the Wurtz-type coupling and its modified methodology usually led to the low yield of the organometallic polymers, in which the tetravalent organometallic dihalides were used as the starting materials. Unlike divalent silicone halides, divalent germanium halides (germylenes) can be prepared as a stable species. The preparation of the 1,4-dioxane complex of germanium dichloride (**1**) has been well established6) and used for the synthesis of germylenes having bulky ligands7) by the ligand substitution with organolithium compounds. On the other hand, the reaction of **1** or germanium diiodide with less bulky organolithium compounds was reported to produce mainly cyclogermane oligomers.8-10)

In the course of our investigations on the polymer synthesis using germylenes as comonomer, we have recently found new copolymerizations involving an oxidation-reduction process.11-13) We report here our recent findings on the ligand substitution reaction of **1** with organolithium compounds (**2**), by which polygermanes (**3**) with higher molecular weight are formed in high yields (*ligand substitution polymerization*). The present reaction implies a new concept of ligand substitution polymerization in polymer chemistry, which provides a general methodology for the synthesis of new polymers.



$$\underset{\mathbf{1}}{GeCl_2\cdot C_4H_8O_2} + \underset{\mathbf{2}}{R\text{-}Li} \xrightarrow[\substack{a,\ R = CH_3 \\ b,\ R = n\text{-}C_4H_9 \\ c,\ R = C_6H_5}]{} \underset{\mathbf{3}}{\left(GeR_2 \right)_n}$$

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In a typical experiment (Entry 4 in Table 1), 563 mg (2.43 mmol) of **1** was suspended in 20.0 mL of diethyl ether under argon and cooled to -78 °C. To this suspension, 4.86 mmol of n-butyllithium (1.6 M solution in hexane as commercially supplied) was slowly added within 15 min. After stirring for 1 h at -78 °C, the reaction mixture was condensed under reduced pressure to evaporate the volatiles and extracted by 40 mL of toluene, followed by filtration over celite to separate LiCl and by evaporation of toluene thoroughly under reduced pressure. Then, 445 mg of a very viscous materials (**3 b**) with pale yellow color were obtained (98% yield). The product was analyzed by using NMR, IR and UV spectroscopy as well as gel permeation chromatography (GPC).

Table 1. Ligand substitution polymerization of **1**

Reaction[a]					Polymers				
Entry	**1** (mmol)	**2**	T °C	Time h	Structure	Yield[b] %	*Mw* [c] /10^3	*Mw/Mn* [c]	Composition(%)[d]
1	1.74	**2a**	-78	2	**3a**	45	31.0	7.76[e]	47
							1.3	1.31	53
2	2.62	**2b**	0	2	**3b**	95	1.3	1.09	
3	2.78	**2b**	0	2	**3b**	39	1.5	1.31	
4	2.43	**2b**	-78	1	**3b**	98	17.9	2.88	39
							1.4	1.12	61
5	1.81	**2c**	0	1	**3c**	83	0.7	1.17	
6	1.72	**2c**	-78	3	**3c**	58	1.0	1.21	

a) The feed molar ratio **2**/**1** = 2.0 in 20.0 mL of diethyl ether. b) The yields for Entries 1, 3 and 6 are the isolated ones by precipitation from methanol and the yields for Entries 2, 4, and 5 are the isolated ones by extraction using toluene. Precipitation from methanol usually brought about the product loss of the lower molecular weight portion. c) Determined by GPC based on polystyrene standard using chloroform as eluent. d) Based on GPC trace profile. e) The higher *Mw/Mn* value is probably due to two reasons; one is the poor solubility of the higher molecular weight portion in chloroform, and the other is the photoinduced degradation of the polymer.

From the experimental results summarized in Table 1, the polymerization involving ligand substitution proceeded fast, which completed within 2 h even at a lower reaction temperature (-78 °C). Product polymers **3** showed roughly two molecular weight distributions with higher and lower portions when the reaction was carried out at -78 °C with an alkyllithium (Entries 1 and 4). This bimodal molecular weight distribution is similar to the polygermanes formed by the Wurtz-type coupling reactions.[2,3] The higher portion was not formed when the reaction was carried out at 0 °C with both phenyllithium (Entry 5) and n-butyllithium (Entries 2 and 3) and at even -78 °C with phenyllithium (Entry 6). It is reasonable to assume that cyclic oligomers were formed as a lower molecular weight portion in competition with linear polymers of higher molecular weight. A lower temperature was favorable for the linear polymer formation. The broad molecular weight distribution of the higher portion was probably due to the photoinduced degradation (*vide infra*).

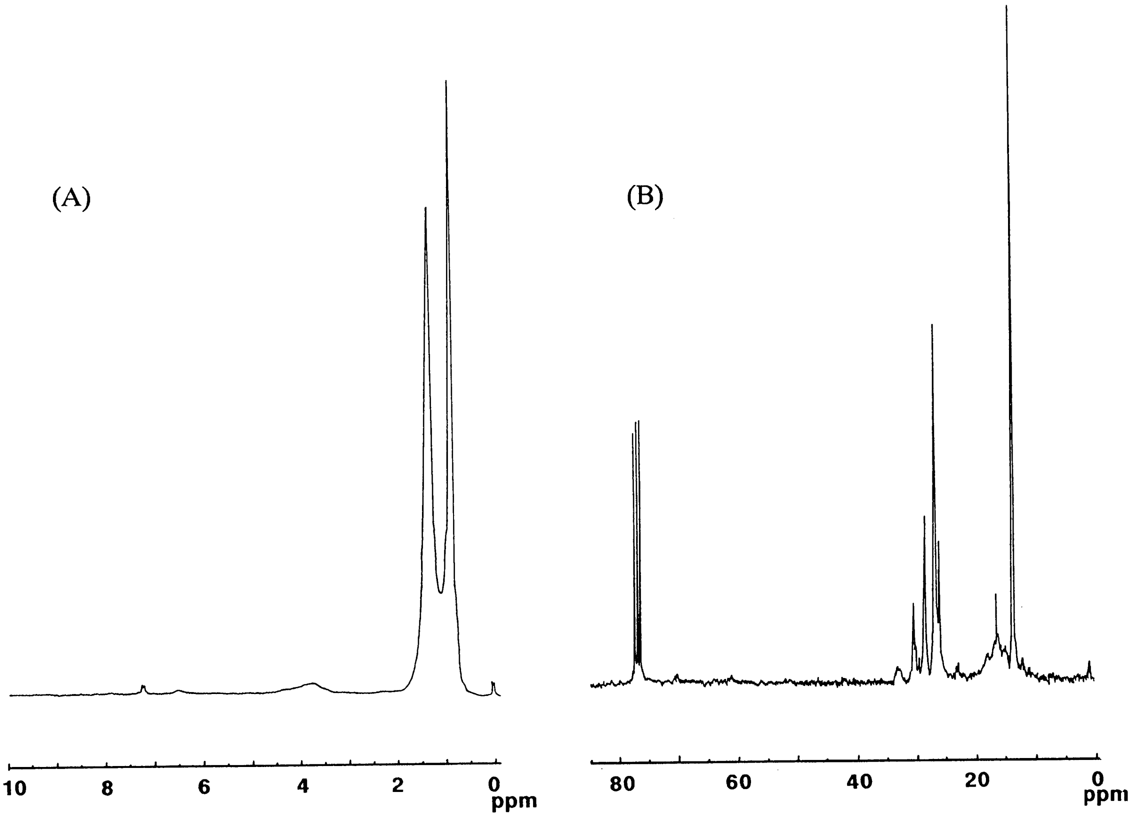

Fig. 1. ^{1}H (A) and ^{13}C (B) NMR spectra of poly(di-*n*-butylgermane) **3b** (both in $CDCl_3$).

The product **3a** is a white powder slightly soluble in chloroform, which shows a broad signal at δ 0.32 ppm in the ^{1}H NMR spectrum and at δ -1.06 ppm in the ^{13}C NMR spectrum, respectively (both in $CDCl_3$). The higher molecular weight poly(di-n-butylgermane) **3b** (Entry 4) is a very viscous material with a pale yellow color, which is soluble in common organic solvents such as chloroform, toluene and tetrahydrofuran (THF). The ^{1}H NMR spectrum of **3b** of Entry 4 (Fig. 1A) shows two signals at δ 1.34 and 0.89 ppm, assignable to methyl protons (3H) and the protons of the two methylene groups CCH_2CH_2C (4H), respectively. The methylene protons adjacent to the germanium atom (Ge-CH_2) appear around at δ 1.1 as a broad signal,$^{2)}$ which is overlaping with the above two signals. In the ^{13}C NMR spectrum (Fig. 1B), the signal of methyl carbon appears at δ 13.7 ppm. A broad signal centered at δ 17 ppm is assignable to the methylene carbon attached to the germanium atom (Ge-CH_2). Several peaks at δ 26.2-30.6 ppm are ascribed to methylene carbons (CCH_2CH_2C). Similar multiple signals for methylene carbons were also observed in molecules containing n-C_4H_9-Ge group.$^{14)}$ A small signal at δ 33.3 ppm is probably due to the methylene carbon adjacent to the germanium having a chlorine atom.$^{15)}$

Like other oligo- and polygermanes in the literatures,$^{2,3)}$ all of the products **3** showed very strong UV absorbtions owing to the Ge-Ge σ-bond conjugation. The absorbtion maximum in THF at room temperature for product **3b** appeared at 218 nm for Entry 2 and 324 nm for Entry 4, respectively. This proved that the increase of molecular weight leads to the longer Ge-Ge σ-bond conjugation. The higher molecular weight products **3** were very photosensitive, especially in the solution form. Figure 2 shows the UV absorbtion change of product **3b** (Entry 4) in THF in a UV cell under exposure to daylight in the room. The longer the exposion time, the smaller the molecular weight and the shorter the UV absorbtion maximum. After storage in THF for 2 h under exposure to daylight, all of the higher molecular weight portion disapeared by the GPC analysis. The polymer chain sccision behavior was also found in the solid form, but not so pronounced as in the solution form.

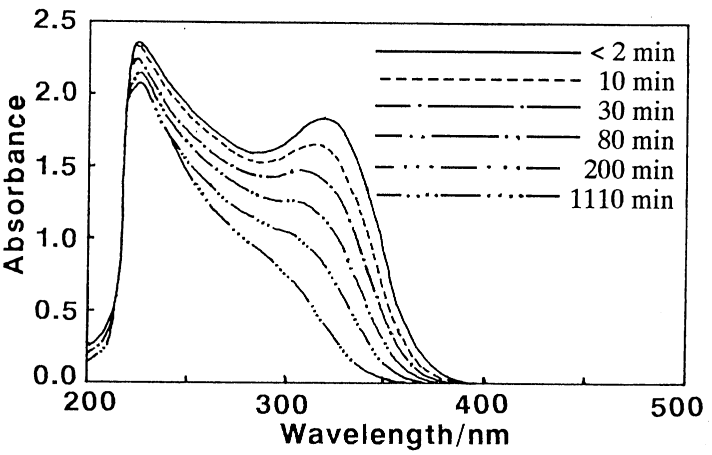

Fig. 2. UV spectral change of the THF solution of poly(di-*n*-butylgermane) **3b** (Entry 4) under exposure to daylight.

Elemental analysis for **3b** (Entry 4) gave values: C, 47.67; H, 8.83 and Cl, 3.32%, respectivelly, from which the caculated fomula would be $[(C_4H_9)_{1.83}Cl_{0.17}Ge]_n$ (C, 48.00; H, 9.06 and Cl, 3.29%). This means that the substitution was almost complete. Further works concerning the polymerization mechanism and the reactions of **1** with other organolithium compounds are under progress.

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