

SYNTHESIS OF ORGANOGERMANE OLIGOMERS VIA LIGAND SUBSTITUTION POLYMERIZATION FROM 1, 4-DIOXANE COMPLEX OF GERMANIUM DICHLORIDE*

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ABSTRACT

Some organogermanium oligomers with different side groups were synthesized via ligand substitution polymerization from 1, 4-dioxane complex of germanium dichloride with different organolithium compounds. The oligomers were isolated through either precipitation from methanol or extraction using toluene with a yield of no less than 50%. The weight average molecular weight (M_w) of the oligomers is ranging from 1.4×10^3 to 5.9×10^3 depending on the type and alkyl length of the organolithium compounds used.

INTRODUCTION

Along with the progress and wide applications of organosilicone polymers, organogermanium polymers have attracted much attention in recent years, not only for the theoretical interests, but also for the potential application possibility. Some germanium-containing polymers have been found to possess photosensitive, semiconductive, bleaching and thermochromic properties^[1-4]. On the other hand, for the synthesis of organogermanium polymers, methods described in literatures were mainly polycondensations from a tetravalent organogermanium dihalide with bifunctional alcohol or carboxylic acid^[3]. A Wurtz-type coupling reaction has also been used leading to polygermanes, but the yield of the polymers was fairly low^[1,2]. An oxidation-

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reduction polymerization methodology has been established in recent years^[5,6] using germylene, a subvalent germanium species, as monomer giving organogermanium polymers with unique molecular structure and high molecular weight. A ligand substitution polymerization process has been investigated by using the 1,4-dioxane complex of germanium dichloride as starting material at low reaction temperature (-78°C) to give polygermanes having methyl, *n*-butyl and phenyl side groups, respectively, with much higher yield^[4] in comparison with those formed from the Wurtz-type coupling reaction. The present paper deals with our extended investigation on this ligand substitution polymerization process.

EXPERIMENTAL

Material

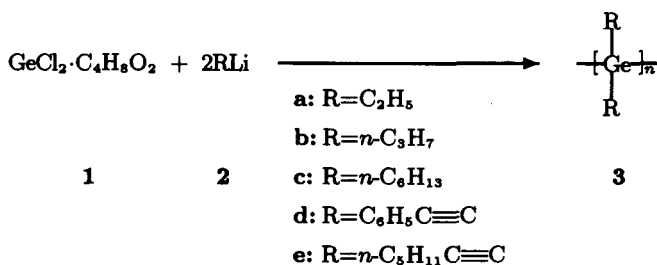
The 1, 4-dioxane complex of germanium dichloride was prepared according to literature procedures from germanium tetrachloride^[7]. Germanium tetrachloride was obtained from Nacalai Chemical Co. (Japan) and used without further purification. Hexane solution of *n*-butyllithium or *t*-butyllithium was obtained from Aldrich and directly used. Acetylene compounds and organic halides were as commercial products without further purification. Diethyl ether and toluene were predried conventionally and distilled under argon in the presence of sodium-benzophenone before use. All of the organolithium compounds were prepared in diethyl ether and directly used for ligand substitution polymerization without isolation. Compounds **2a**, **2b** and **2c** were synthesized from corresponding organic iodide with double molar amount of *t*-butyllithium, and compounds **2d** and **2e** were prepared from corresponding acetylene compounds with equimolar amount of *n*-butyllithium.

Measurements

^1H and ^{13}C NMR spectra were recorded on a 250 MHz Bruker AC-250T spectrometer. IR spectra were taken from a Shimadzu-435 spectrophotometer with KBr pellets. Gel permeation chromatography (GPC) was performed by using TOSO SC8010 apparatus with chloroform as eluent at a flow rate of 1.0 ml/min based on polystyrene standard.

Polymerization

All chemical reactions were carried out under argon atmosphere to exclude trace amount of moisture involved in the reaction system. The ligand substitution reaction is illustrated as follows:



In a typical polymerization (sample 2 in Table 1), 500 mg (2.16 mmol) of **1** was suspended in 10 ml of diethyl ether under argon and cooled to -78°C . 4.32 mmol of **2b** was prepared by the reaction of 4.32 mmol of *n*-propyl iodide with 8.64 mmol of *t*-butyllithium in 15 ml of diethyl ether at -78°C for 3 h. The diethyl ether solution of **2b** thus prepared was then directly added slowly into the suspension of **1**. After stirring for 3 h at -78°C , the reaction mixture was poured into 60 ml of methanol to precipitate the polymeric product. The precipitate was filtered and dried in vacuo, 200 mg of viscous material (**3b**) with pale yellow color were obtained (58% yield). The product was analyzed by using NMR and IR spectroscopies as well as gel permeation chromatography (GPC). The polymerization results are listed in Table 1.

Table 1 Ligand substitution polymerization of 1,4-dioxane complex of germanium dichloride (**1**)

Reaction				Product			
Sample	1 (mmol)	2	<i>t</i> (h)	Structure	Yield ^{a)} %	$\bar{M}_w$ ^{b)} /10 ³	$\bar{M}_w/\bar{M}_n$ ^{b)}
1	1.09	2a	2	3a	53	1.7	1.22
2	1.08	2b	3	3b	58	5.9	2.06
3	2.23	2c	2	3c	99	2.6	1.84
4	2.57	2d	1	3d	94	1.4	1.42
5	1.90	2e	2	3e	95	2.1	1.10

^{a)} Isolated yield for sample 1 and 2 by precipitation from methanol and sample 3, 4 and 5 by extraction using toluene

^{b)} Determined by GPC. The polymer **3a** from sample 1 shows bimodal molecular weight distribution with 10% portion having a $\bar{M}_w$ of 2.2×10^4 and a $\bar{M}_w/\bar{M}_n$ of 1.72

RESULTS AND DISCUSSION

From Table 1, it can be found that the polymerization involving a ligand substitution process took place very fast. In all cases except sample 1, the products were oligomers with $\bar{M}_w$ not higher than 5.9×10^3 . Product isolation with extraction

using toluene (sample 3, 4 and 5) gave much higher yield than that with precipitation from methanol (sample 1 and 2), which suggested that the product loss during precipitation was very serious owing to the lower molecular weight. Product **3a** from sample 1 showed bimodal molecular weight distribution with a 10% higher weight portion having a $\bar{M}_w$ of 2.2×10^4 and a $\bar{M}_w/\bar{M}_n$ of 1.72, which is similar to the results reported previously^[4]. Polymerizations with organolithium compounds **2** having shorter alkyl chain were favorable to give higher molecular weight product. Longer alkyl chain may hinder the polymerization to form ring-shaped oligomers as assumed in Ref. [4]. Meanwhile, polymerizations with organolithium compounds **2** having an acetylene group only gave lower molecular weight oligomers (sample 4 and 5) at the present reaction conditions.

All products are easily soluble in common organic solvents like chloroform, hexane, toluene and THF, their NMR analysis was conducted by using CDCl_3 as solvent. Product **3a** and **3b** are viscous solids with pale yellow colour. Only one broad signal centered at δ 1.11 ppm is found in the ^1H NMR spectrum of product **3a**. The methylene protons adjacent to the germanium atom ($\text{Ge}-\text{CH}_2$) may show a signal at around δ 1.1 ppm and is overlapped by the signal of methyl protons^[1]. Two signals are found at δ 12.13 and 10.05 ppm in the ^{13}C NMR spectrum, respectively. The ^1H NMR spectrum of product **3b** shows two broad signals at δ 0.86 and 1.30 ppm representing methyl and methylene protons respectively, and the ^{13}C NMR spectrum gives three signals at δ 13.88, 16.95 and 27.60 ppm respectively. Product **3c**

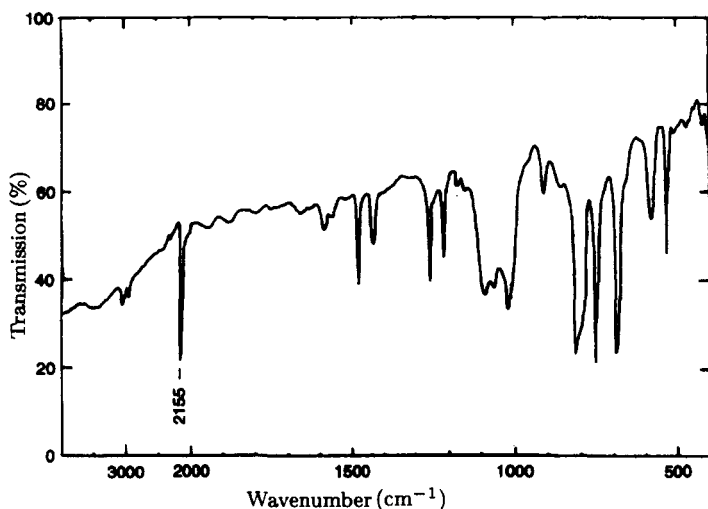


Fig.1 IR spectrum of oligomer **3d**, poly[di(phenyl acetylenyl)-germane]

is a tacky solid with pale yellow colour, its ^1H NMR spectrum shows two broad signals centered at δ 0.88 and 1.28 ppm representing methyl and methylene protons respectively, and its ^{13}C NMR spectrum shows five signals at δ 14.11, 22.69, 29.68, 31.58 and 33.58 ppm, respectively, the signal of the methylene carbon attached to the germanium atom ($\text{Ge}-\text{CH}_2$) is not so identical. In all cases of products **3a** to **3c**, there is no signal from *t*-butyl group that may derive from *t*-butyllithium on their NMR spectra.

Polygermanes **3d** and **3e** having acetylenic side groups were prepared for the first time by the present ligand substitution polymerization. Product **3d** is a yellow solid, its ^1H NMR spectrum shows only a group of multiple signals ranging from δ 6.50 to 8.00 ppm representing the phenyl protons. Its ^{13}C NMR spectrum shows six signals representing the phenyl carbons at δ 122.60, 127.83, 128.13, 128.27, 129.38 and 132.35 ppm, respectively, and two signals representing the acetylene carbons at δ 84.72 and 107.84 ppm, respectively. The IR spectrum of **3d** shows clearly the absorption of the $\text{C}\equiv\text{C}$ triple bond at 2155 cm^{-1} (Fig.1). Product **3e** is a yellowish oil, its ^1H NMR spectrum shows four signals at δ 0.88, 1.32, 1.54 and 2.24 ppm respectively, and the signal assignment is shown in Fig.2(A). The ^{13}C NMR spectrum of product **3e** shows only six signals, in which the signal at δ 13.96 ppm is

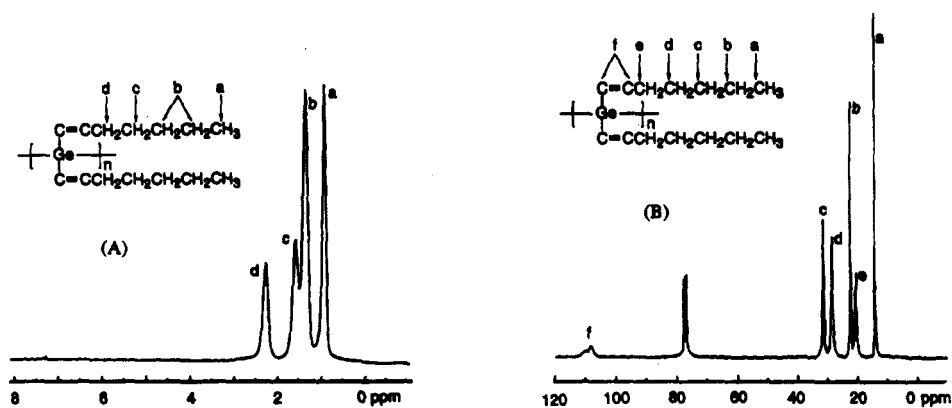


Fig.2 ^1H (A) and ^{13}C (B) NMR spectra of oligomer **3e**, poly[di(1-heptynyl)-germane] (both in CDCl_3)

attributed to the methyl carbon, and the four signals at δ 20.42, 22.25, 29.64 and 31.28 ppm are representing the methylene carbons as assigned in Fig.2(B). The two acetylene carbons appear as one broad signal centered at δ 108.00 ppm, which is a very interesting experimental phenomenon and is much different from its parent compound 1-heptyne. In the ^{13}C NMR spectrum of 1-heptyne in CDCl_3 , the two sig-

nals of acetylene carbons appear at δ 67.95 ($-\text{C}\equiv\text{CH}$) and 84.54 ($-\text{C}\equiv\text{CH}$) ppm, respectively. This phenomenon may need further investigation.

Keywords:

Organogermanium oligomer; Polygermane; Ligand substitution polymerization; Germanium dichloride; Organolithium compounds

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