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Synthesis and Properties of Novel Germole-Containing Polymers by Reaction of Bis(cyclopentadienyl)titanacyclopentadiene-Containing Polymer with Germanium Tetrachloride

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Summary

The synthesis and properties of novel germole-containing polymers are described. A polymer possessing bis(cyclopentadienyl)titanacyclopentadiene unit in the main chain was prepared by the polymerization of 1,4-bis(1-hexynyl)benzene and a low-valent bis(cyclopentadienyl)titanium(II) complex, generated in situ from bis(cyclopentadienyl)titanium(IV) dichloride and *n*-butyllithium (2 equiv). The organotitanium polymer thus obtained was converted into a 1,1-dichlorogermole-containing polymer by the reaction with $GeCl_4$, and its further reaction with methyllithium gave a 1,1-dimethylgermole-containing polymer. Optical and electrochemical properties of the resulting 1,1-dimethylgermole-containing polymer were studied by the UV-vis spectra and the cyclic voltammetric analyses, from which the germole-containing polymer was supposed to have a low-lying LUMO level.

Introduction

Polymers containing metallacycle units in main chain are attractive candidates of novel reactive polymers, which can yield main chain-functional polymers through the transformation of the metallacycles units into organic and/or other organometallic building blocks. Previously, we reported the synthesis of polymers containing cobaltacyclopentadiene [1], titanacyclobutene [2], and titanacyclopentadiene [3] units in their main chain. It is expected that their reactions with organic and inorganic reagents give polymers having various functional groups in their main chain. Concerning the organocobalt polymers, their versatile and effective transformation processes made it possible to prepare organic polymers containing thiophene, 2-pyridone, selenophene, phenylene, dithiolactone, and diketone units [4] and organometallic polymers having other organocobalt units [5]. Likewise, Tilley et al. have independently described the synthesis of polymers having zirconacyclopentadiene units in the main chain [6]. Their polymer reactions proved to give polymers containing diene, thiophene, and phosphole moieties.

In view of the diverse reactivity and the potential further progress of the chemistry of titanacyclopentadiene derivatives [7], polymers containing the corresponding organotitanium units may also serve as unique main chain-reactive polymers. In the course of our studies on the main chain reactive organometallic polymers, we are currently trying to find out new reaction routes of the titanacyclopentadienes and their applications to the transformations of the main chain structure of the organotitanium polymers. On the basis of the fact that the reactivity of the titanacyclopentadienes is somewhat similar to that of zirconacyclopentadiene derivatives and that germole derivatives are obtainable by the reaction of the zirconacyclopentadienes [8], we herein describe a new transformation route of the titanacyclopentadiene derivatives into germole derivatives by the reaction with germanium(IV) tetrachloride ($GeCl_4$), and its application to the polymer reaction leading to organogermanium polymers.

Experimental

Measurements

Nuclear magnetic resonance (NMR) spectra were measured on a JEOL ECP-300 instrument using tetramethylsilane as an internal standard (300 MHz and 75 MHz for ^1H NMR and ^{13}C NMR, respectively). Fourier transform infrared (FT-IR) spectra were measured on a JASCO FT/IR-5300 instrument. EI mass spectrum was recorded on a JEOL JMS-700 mass spectrometer. Gel permeation chromatography (GPC) measurements were performed on a Shimadzu LC-10AS liquid chromatograph equipped with Tosoh TSK-gel GMH_{HR}–M tandem columns using chloroform ($CHCl_3$) as an eluent at 35°C. Polystyrene standards were used for calibration. UV-vis spectra were recorded on a Shimadzu UV-3100PC spectrometer in $CHCl_3$. Electrochemical measurements were performed on a computer-controlled electrochemical system (ALS/CHI 750a) using a one-compartment Pyrex® glass container with Pt disk working electrode (d =1.6 mm, BAS, Japan), a spiral platinum (Pt) wire auxiliary electrode, and a silver wire reference electrode under nitrogen stream.

Materials

Bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) was purified by recrystallization from a mixed solvent of $CHCl_3$ and hexane. Germanium(IV) tetrachloride ($GeCl_4$) was obtained from Cica and distilled under nitrogen. *n*-Butyllithium (*n*-BuLi, 1.60 M in hexane solution) and methyllithium (MeLi, 1.04 M in diethyl ether) were obtained from Cica. Tetrahydrofuran (THF) and diethyl ether were dried over sodium benzophenone ketyl, methanol (MeOH) was dried over magnesium methoxide, and dichloromethane (CH_2Cl_2) was dried over P_2O_5, and they were distilled under nitrogen. 1-Heptynylbenzene and 1,4-bis(1-hexynyl)benzene were prepared as previously described [9]. The polymerization, polymer reactions, and their model reactions were carried out under argon.

Synthesis of **5**

The synthesis of intermediate titanacyclopentadiene derivatives (**3**) was carried out as described [10]. To a two-necked flask containing Cp_2TiCl_2 (0.27g, 1.10 mmol), THF

(20 mL), and 1-heptynylbenzene (0.35 g, 2.03 mmol), was added *n*-BuLi (1.60 M, 1.40mL, 2.24 mmol) at -78°C. After stirring for 15 min at that temperature, the mixture was warmed to room temperature and kept stirring overnight to obtain a mixture containing the titanacyclopentadiene derivatives (**3**). After evaporation of THF, diethyl ether (20 mL) and then $GeCl_4$ (0.24 g, 1.10 mmol) were added at ambient temperature and the mixture was kept stirring overnight to give a mixture containing 1,1-dichlorogermole derivatives (**4**). After filtration, MeLi (1.04 M in diethyl ether, 7.0 mL, 7.28 mmol) was added to the filtrate at -78°C, and the mixture was allowed to warm to room temperature. After stirring overnight, MeOH (5.0 mL) was added to the reaction mixture, and the resulting mixture was filtered under argon. After removal of the volatile fractions under reduced pressure, CH_2Cl_2 (20 mL) was added to the residue and the CH_2Cl_2-soluble part was collected by filtration. After evaporation of CH_2Cl_2, the products (**5**) were obtained in a 94% yield (0.43 g, 0.96 mmol) as an essentially pure form (yellow oil). If **5** were purified further by alumina column chromatography (activity III, eluent: hexane), the isolated yield of **5** decreased to 67% (0.30 g, 0.67 mmol).

^{1}H-NMR ($CDCl_3$, ppm): 0.48-2.16 (-GeC*H*$_3$, -(C*H*$_2$)$_4$-C*H*$_3$, 28 H), 7.10-7.35 (aromatic, 10 H). ^{13}C-NMR ($CDCl_3$, ppm): -3.8, -3.1, 13.8, 14.0, 21.9, 22.3, 22.5, 22.6, 29.0, 29.1, 29.4, 30.6, 31.4, 31.5, 31.6, 31.8, 32.1, 124.9, 125.9, 126.2, 127.1, 127.5, 127.7, 127.8, 128.1, 128.2, 128.5, 129.4, 139.3, 140.2, 142.5, 145.5, 150.4, 150.9, 151.2. IR (KBr, cm^{-1}): 3025, 2961, 2926, 2858, 1678, 1599, 1493, 1450, 1412, 1377, 1296, 1261, 1095, 1024, 804, 700, 592, 501. HR-MS m/z calcd for $C_{28}H_{38}Ge$: 448.2185; Found: 448.2199.

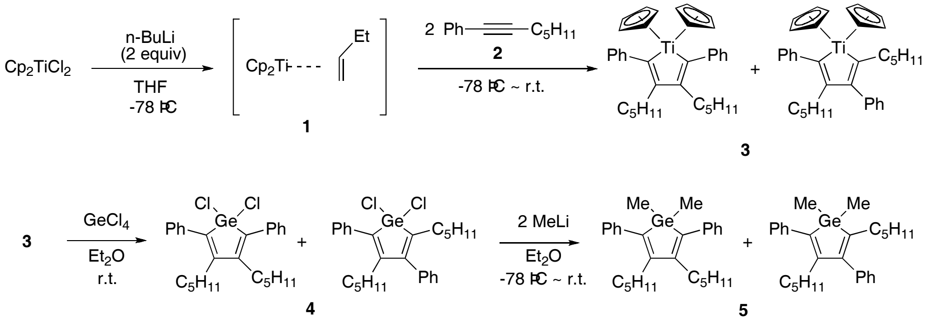
Synthesis of ***9***

To a two-necked flask containing Cp_2TiCl_2 (0.27 g, 1.10 mmol), dry THF (20 mL), and 1,4-bis(1-hexynyl)benzene (0.24 g, 1.00 mmol), was added *n*-BuLi (1.60 M in hexane, 1.40 mL, 2.24 mmol) at -78°C under argon. After stirring for 15 min at that temperature, the mixture was warmed to room temperature and kept stirring overnight. After evaporation of THF, diethyl ether (30 mL) and the $GeCl_4$ (0.24 g, 1.10 mmol) were added at ambient temperature and the mixture was kept stirring overnight to give a mixture containing a polymer having germole units (**8**). After filtration, MeLi (1.04 M in diethyl ether, 7.0 mL, 7.28 mmol) was added to the filtrate at -78°C. The mixture was allowed to warm to room temperature and kept stirring overnight. After addition of MeOH (5.0 mL), all the volatile fractions were evaporated to dryness and the residue was dissolved with CH_2Cl_2 (3.0 mL). The CH_2Cl_2–soluble part was precipitated into MeOH to obtain a polymer (**9**) as yellow solid in a 50% yield (0.17 g 0.50 mmol unit).

^{1}H-NMR ($CDCl_3$, ppm): 0.48-2.40 (-GeC*H*$_3$, -(C*H*$_2$)$_3$-C*H*$_3$, 24 H), 6.70-7.41 (aromatic, 4 H). ^{13}C-NMR ($CDCl_3$, ppm): -3.6, 13.1, 13.4, 18.6, 19.0, 21.5, 22.2, 25.5, 28.0, 28.8, 29.2, 30.4, 30.6, 31.1, 31.7, 32.6, 121.3, 122.8, 127.2, 127.9, 128.1, 128.8, 130.5, 130.8, 138.5-145.3, 150.3, 150.8. IR (KBr, cm^{-1}): 2964, 1685, 1655, 1560, 1541, 1523, 1508, 1458, 1412, 1261, 1093, 1020, 864, 798, 684, 518.

Results and discussion

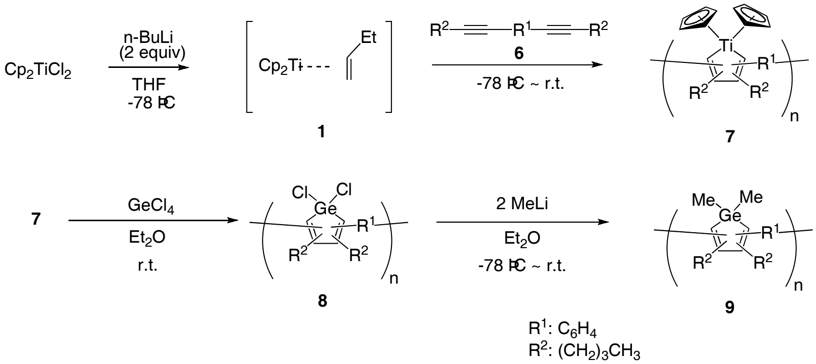
On the basis of the metallacyclization of two acetylene molecules with low-valent titanium complexes, two kinds of the titanacyclopentadiene derivatives, 1,1-bis(cyclopentadienyl)diphenyldipentyltitanacyclopentadienes (**3**) [10] and a titanacycle which is supposed to have 1,1-diisopropoxy-2,5-diphenyl substituents [11], were prepared in situ and they were subjected to the reaction with $GeCl_4$. Within the examined conditions, the latter could not yield objective products due to its insufficient thermal stability under ambient temperature. In the case of **3**, the reaction was found to proceed smoothly under appropriate conditions. That is, the titanacyclopentadiene derivatives (**3**) were prepared by the reaction of heptynylbenzene (**2**) and a low-valent titanocene (**1**, generated from Cp_2TiCl_2 and *n*-BuLi) and its reaction with $GeCl_4$ was carried in some solvents such as THF and diethyl ether. It was of fortunate that the reaction was found to occur in diethyl ether at ambient temperature to give objective 1,1-dichlorogermole derivatives (**4**). The treatment of the moisture-sensitive **4** with an excessive amount of MeLi gave 1,1-dimethylgermole derivatives as yellow oil (**5**) in an almost quantitative fashion (94% yield as an essentially pure form). The products seem not to be stable enough under ambient conditions and the isolation by the alumina column chromatography (activity III, eluent: hexane) accompanied a substantial loss (67% isolated yield).



Scheme 1. Synthesis of germole derivatives (**4** and **5**) from titanacyclopentadienes (**3**).

The structure of the products (**5**) was supported by its ^{1}H NMR, ^{13}C NMR, and HR-MS analyses. In the ^{13}C NMR spectrum of **5**, two peaks appeared at high magnetic fields (-3.1 ppm and -3.8 ppm), which can be attributed to the methyl substituents on the germanium atom. According to the preceding report by Takahashi et al. [10], the 2,4- and 2,5-diphenyl isomers are produced in the ratio of 90:10 by the metallacyclization step. In the ^{13}C NMR NNE spectrum of **5**, the integral ratio of these two peaks at -3.1 ppm and -3.8 ppm were 90:10, which are hence presumably attributed to the germoles having 2,4- and 2,5-diphenyl substituents.

On the basis of the results obtained in the model experiment, the reaction of a titanacyclopentadiene-containing polymer (**7**) [12] with $GeCl_4$ and the subsequent methylation were carried out under the analogous conditions (Scheme 2). That is, the organotitanium polymer (**7**) was prepared by the reaction of a diyne (**6**) with a low-valent titanocene (**1**) and its reaction with $GeCl_4$ was carried out overnight at ambient temperature. After the treatment with MeLi, a germole-containing polymer (**9**) was obtained in a 50% yield. The polymer (**9**) is soluble in organic solvents such as $CHCl_3$, CH_2Cl_2, and THF. The number-average molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of **9** were estimated as 3400 and 2.12, respectively, by GPC.



Scheme 2. Transformation of titanacyclopentadiene-containing polymer (**7**) into germole-containing polymers (**8** and **9**).

In the ^{1}H NMR spectrum of **9**, no peak for the cyclopentadienyl (Cp) moieties was observed which appeared at 6 ppm in that of the starting polymer (**7**), indicating that the polymer reactions proceeded effectively under the examined conditions (Figure 1). Concerning the ratio of the 2,4- and 2,5-connections at each metallacycle unit of **9**, spectroscopic methods such as ^{1}H NMR and ^{13}C NMR spectra were not informative due to the poor resolution of the peaks. However, we assume that the polymer (**9**) is also composed of the predominant 2,4-linkages, as was the case of the model compounds (**5**).

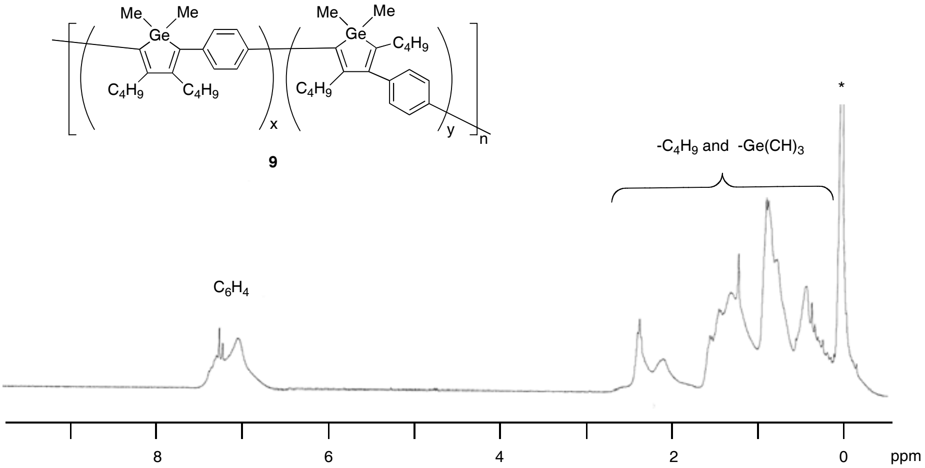


Figure 1. ^{1}H NMR spectrum of germole-containing polymer (**9**).

As shown in Figure 2, both **5** and **9** exhibited shoulder absorption peaks in their UV-vis spectra, whose λ_{onset} were observed at 400 nm and 420 nm, respectively. A small bathochromic shift of the UV-vis absorption of **9** with respect to that of **5** suggested that the π-conjugation may take place partially along the main chain of **9**, although **9** is composed of the predominant 2,4-linkage and sterically demanding 1,1,2,3,4,5-fully substituted germole units which are unfavorable for the effective π-conjugation.

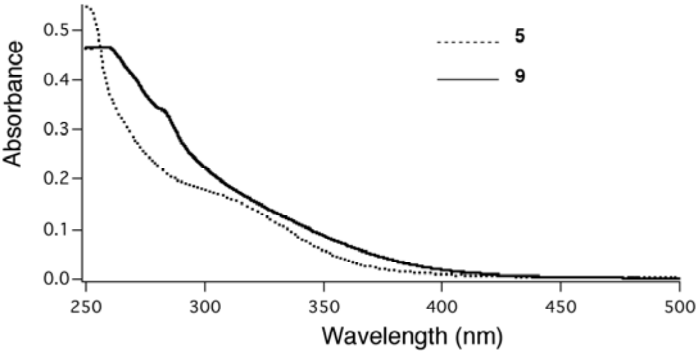


Figure 2. UV-vis absorption spectra of **5** and **9** in $CHCl_3$ solutions ($1.0x10^{-5}$ M).

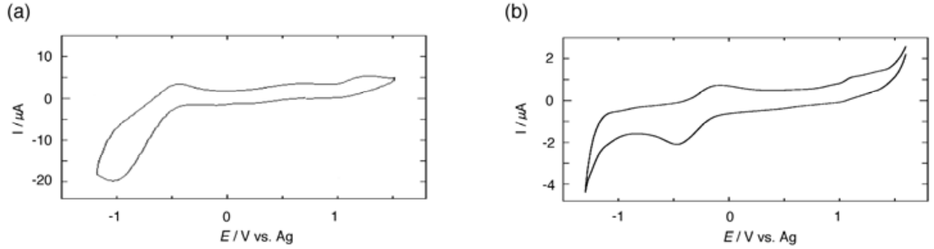


Figure 3. Cyclic voltammograms of **5** (a) and **9** (b) in N_2-saturated THF solutions containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate at a sweeping rate of 100 mV s^{-1}.

The electrochemical properties of the model compounds (**5**) and the polymer (**9**) were evaluated from their cyclic voltammetric (CV) analyses in THF solutions (Figure 3). From the onset reduction potential (E_{red}) observed in their CV measurements, the LUMO energy levels of **5** and **9** were estimated from equation (1) [13] to be -3.65 eV and -3.95 eV, respectively.

$$E_{(\mathrm{LUMO})} = -(E_{red} + 4.40)\ (\mathrm{eV}) \qquad (\mathbf{1})$$

Similar to the silole- and stannole-containing polymers, it should be noted that the LUMO level of **9** (-3.95 eV) is remarkably lower than other heterocycle-containing polymers such as thiophene-containing polymers (-2.59 eV) [14]. As described by Tamao et al. [15] and by Tilley et al. [8], heteroles and heterole-containing π-conjugated materials possessing elements of 14th group have characteristic electronic properties due to their low lying LUMO energy levels. For example, some silole derivatives have been reported to exhibit high electron mobility (10^{-4} cm^2 V^{-1} s^{-1}), which is potentially applicable to advanced materials such as electron-transporting organic semiconductors (ETOS) [16]. In accordance with these preceding studies, the polymer (**9**) obtained in the present study was also found to have a low-lying LUMO energy level. Thus, the molecular design of germole-containing polymers and their applications are currently being investigated.

Conclusions

A polymer having germole repeating unit in the main chain was obtained by the novel synthetic route which involves the chemical transformation of the main chain structure of a titanacyclopentadiene-containing polymer. The polymer (**9**) was supposed to have a low-lying LUMO energy level judging from its CV measurement.

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