Anionic Polymerization of Tetraphenylgermole-*spiro*-cyclogermatetrasilane. A Striking Contrast in the Mechanism to the Corresponding Silole Case[1]

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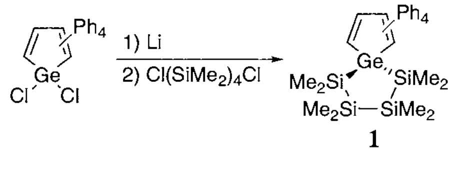
Germole-incorporated polygermatetrasilanes are prepared by ring-opening anionic polymerization of tetraphenylgermole-*spiro*-cyclogermatetrasilane. Interesting contrasts in the polymerization mechanism between silole- and germole-incorporated polymers are discussed. Properties of novel polymers are described.

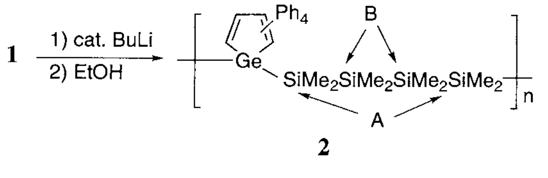
In a previous paper,[2] we have reported a novel silole-incorporated polysilanes with interesting properties due to the combination of electron-donating polysilane and electron-accepting silole.[3,4] Germoles have similar electronic structures having relatively high-lying HOMO and low-lying LUMO.[5] Therefore, it is expected that germole-incorporated polysilanes can have similar interesting properties.

Similar to the previous study, our synthetic strategy for the germole incorporated polymer is based on a ring opening polymerization of tetraphenylgermole-*spiro*-cyclogermatetrasilane (**1**) which can be prepared, as shown in eq. 1,[6] by the reaction of the germole dianion and 1,4-dichlorooctamethyltetrasilane in a similar manner as applied for tetraphenylsilole-*spiro*-cyclopentasilane.



(1)

Anionic ring opening polymerization of **1** (0.30 g, 0.45 mmol) with a catalytic amount of butyllithium (0.092 mmol) as an initiator in THF (5.0 ml) at -40 °C for 2 h proceeded smoothly (eq. 2), the polymer **2**[7] being obtained in 60% yield (0.18 g, Mn = 11000, Mw/Mn = 1.8). The structure of the polymer was highly ordered as estimated by NMR analyses.



(2)

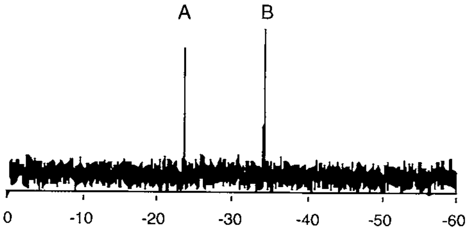
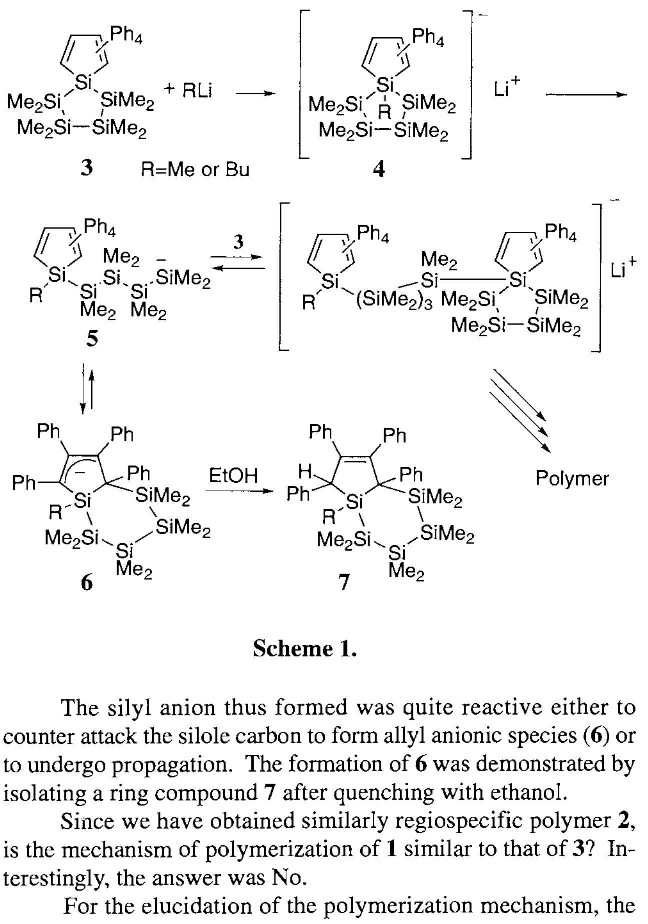


Figure 1. ^{29}Si NMR spectrum of the polymer **2**.

Figure 1 shows the ^{29}Si NMR spectrum of the polymer where only two different kinds of signals exist. These signals are assigned to the terminal silicon adjacent to the germole ring (A) and the central silicon (B), respectively. Thus the ^{29}Si NMR spectrum is consistent with the polymer chain of highly regulated structure. The ^1H and ^{13}C NMR spectra also supported the conclusion. These results indicate that the anionic ring opening polymerization process itself must be highly regioselective.

In the case of the formation of silole-incorporated polysilane, we have indicated that the initial step of the reaction is the attack of alkyllithium to the silole silicon atom of **3** to form a pentacoordinate silicate intermediate (**4**). Then the silicon-silicon bond was cleaved to form a silyl anion (**5**) as shown in Scheme 1.



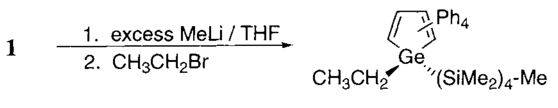
Scheme 1.

The silyl anion thus formed was quite reactive either to counter attack the silole carbon to form allyl anionic species (**6**) or to undergo propagation. The formation of **6** was demonstrated by isolating a ring compound **7** after quenching with ethanol.

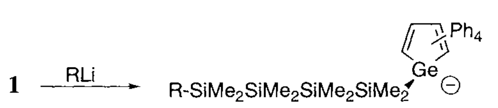
Since we have obtained similarly regiospecific polymer **2**, is the mechanism of polymerization of **1** similar to that of **3**? Interestingly, the answer was No.

For the elucidation of the polymerization mechanism, the reaction of **1** with large excess of methyllithium at -40 °C, followed by addition of bromoethane, was examined. The reaction gave **8** exclusively as shown in eq 3.

The formation of **8**[8] indicates that the initial attack of MeLi occurs at the silicon atom adjacent to the germanium atom in the germole to give an anionic intermediate **9**.



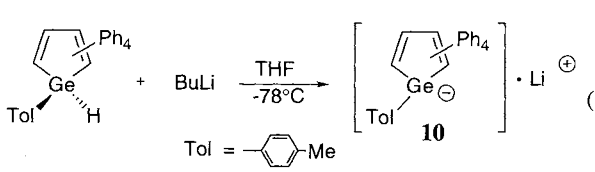
8 (3)



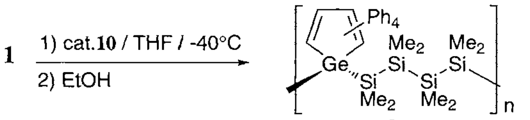
9 (4)

Then the intermediate **9** reacts with bromoethane to give **8**. In the propagation step, **9** must be the key intermediate. Interesting difference in the reaction mode between silole[9] and germole toward the attack of nucleophiles is further demonstrated by a similar model experiment with 1,1-bis(pentamethyldisilanyl)-2,3,4,5-tetraphenylgermole. 1-Ethyl-1-pentamethyldisilanyl-2,3,4,5-tetraphenylgermole was obtained in 52% isolated yield (LC yield > 80%). The formation of hexamethyldisilane was also confirmed qualitatively by GC-MS. Clearly, a germolyl anion similar to **9** should play an important role in these reactions.

To substantiate the matter further, we have then examined initiation of the ring-opening polymerization of **1** (0.27 g, 0.40 mmol) with a germolyl anion **10** (0.04 mmol).[10] As a result, polymer **2** (0.26 g, Mn = 12000; Mw / Mn = 1.6) was obtained in 90% yield as shown below. Thus in the polymerization of **1**, the germolyl anion functions as the propagating species contrary to the case of the corresponding silole monomer **3**.



10 (5)



2 (6)

The origin of this interesting difference in the mechanism between **1** and **3** is not clear at this moment. We thought initially that characters of LUMO of **1** and **3** should be different and performed quantum chemical calculations at several levels. However, no meaningful difference could be deduced at least at this stage. We are investigating on this point further, the results being reported later.

The polymer **2** exhibits intense fluorescence due to the existence of the germole ring. Figure 2 shows absorption, fluorescence, and excitation spectra of the polymer **2**. In the absorption spectrum, the polymer **2** shows two absorption maxima at 320 and 360 (shoulder) nm, assignable to the polysilane skeleton and the germole ring, respectively. The excitation spectrum, monitored at 520 nm reproduced the absorption spectrum for the most part, indicating that an extensive energy transfer between the germole ring and the polymer backbone takes place similarly as silole incorporated polysilanes.

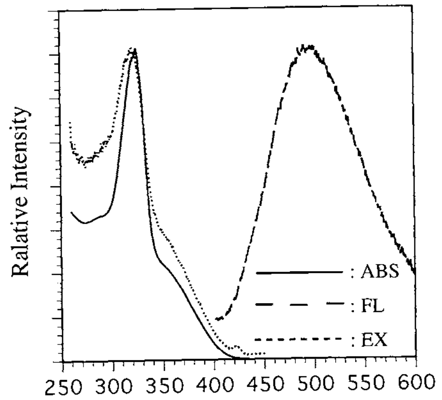


Figure 2. Absorption, fluorescence, and exitation spectra of the polymer **2**.

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References and Notes

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6 Spectral Data of **1**: pale yellow crystals; mp 184-187 °C.^{1}H NMR ($CDCl_3$, δ, 300 MHz) 0.11 (s, 12H, $-SiMe_2-$), 0.17 (s, 12H, $-SiMe_2-$), 6.77-7.05 (brd.m, 20H, Ph); ^{13}C NMR ($CDCl_3$, δ, 75.4 MHz) -6.39, -3.86, 124.9, 125.5, 127.2, 127.6, 129.8, 130.7, 140.3, 142.4, 149.8, 150.7; ^{29}Si NMR ($CDCl_3$, δ, 59.6 MHz) -40.0, -26.8; GC-MS (70 eV) m/z (%) 662 (5, M^+), 473 (14), 248 (100), 173 (46); HRMS Calcd for $C_{36}H_{44}GeSi_4$ 662.1740; Found 662.1737.

7 Spectral Data of **2**: pale yellow powder; Mn = 11000, Mw/Mn = 1.8 (determined by GPC with polystyrene standards), ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 0.17, 6.69-6.98; ^{13}C NMR ($CDCl_3$, δ, 75.4 MHz) -4.08, -1.35, 125.2, 125.6, 127.3, 127.4, 130.1, 130.3, 140.3, 141.3, 150.6, 151.0; ^{29}Si NMR ($CDCl_3$, δ, 59.6 MHz) -33.9, -23.3.

8 Spectral Data of **8**: yellow oil; ^{1}H NMR ($CDCl_3$, δ, 300 MHz) 0.056 (s, 9H, $-SiMe_3$), 0.085 (s, 6H, $-SiMe_2-$), 0.14 (s, 6H, $-SiMe_2-$), 0.19 (s, 6H, $-SiMe_2-$), 1.17 (t, *J*=7.7, 3H, $-CH_3$), 1.42 (q, *J*=7.7, 2H, $-CH_2-$), 6.53-7.06 (brd.m, 20H, Ph); ^{13}C NMR ($CDCl_3$, δ, 75.4 MHz) -5.77, -4.70, -3.18, -1.30, 7.74, 9.95, 125.2, 125.8, 127.3, 127.6, 129.4, 130.3, 140.0, 141.4, 146.6, 152.0; ^{29}Si NMR ($CDCl_3$, δ, 59.6 MHz) -43.0, -38.6, -30.2, -14.9; MS (45 eV) m/z (%) 706 (0.3, M^+), 677 (0.8), 473 (27), 292 (100), 278 (51), 149(22); HRMS Calcd for $C_{39}H_{52}GeSi_4$ 706.2367; Found 706.2352.

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10 P. Jutzi and A. Karl, *J. Organomet. Chem.*, **215**, 19 (1981).