ORIGINAL ARTICLE

Oxidation-reduction alternating copolymerization of germylene and *N*-phenyl-*p*-quinoneimine

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The germylenes bis[bis(trimethylsilyl)amido]germanium (1a) and bis[*t*-butyl-trimethylsilyl]amido]germanium (1b) were reacted with *N*-phenyl-*p*-quinoneimine (2) to give copolymers (3a and 3b) with alternating tetravalent germanium and *p*-aminophenol units. The copolymerization took place smoothly at 0 °C without added catalyst or initiator. 1 acted as a reductant monomer, and 2 acted as an oxidant monomer (oxidation-reduction alternating copolymerization). Product copolymers were obtained in very high yields and had high molecular weights. The copolymers were soluble in toluene, benzene, *n*-hexane and chloroform, whereas they were insoluble in acetonitrile and acetone. Additionally, they were stable toward hydrolytic degradation. Electron spin resonance (ESR) spectroscopic studies of the reaction suggested a structure of a stable germyl radical and a plausible mechanism of biradical copolymerization.

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INTRODUCTION

Divalent germanium compounds (germylenes) and their tin analogs (stannylenes) continue to attract much interest in the organometallic chemistry area as heavy carbene analogs in the 14th group elements.^{1–5} In the polymerization chemistry field, there are few examples of their use as a monomer or a catalyst (initiator) because of the difficulty faced in handling them, such as inducing self-oligomerization, such difficulties are caused by the compounds' instability. Germylenes have a strong reducing ability and are generally observed as a short-lived reaction intermediate. The leading work by Lappert and co-workers,⁶ however, enabled the synthesis of stable germylenes. They showed that bulky alkyl, amino and phenoxy groups are effective substituents to prevent oligomerization and/or dimerization. Germanium-containing polymers were once derived from the substitution reaction of germanium dichloride, which led to polygermanes,⁷ and from the polyaddition reaction of a bisgermylene to an organic halide.⁸

These stable germylenes show potential to be very convenient and useful as monomers to prepare germanium-containing polymers because they are highly reactive as a reductant monomer to form two new bonds on the germanium atom. In fact, we have extensively developed new polymerization reactions by using a stable germylene (GeR₂, 1) as the monomer, as observed in the following examples. An acyclic germylene, bis[bis(trimethylsilyl)amido]germanium (1a), was copolymerized with various *p*-benzoquinones to give alternating copolymers that had high molecular weights in very high yields. The copolymerization took place at –78 °C without added catalyst.⁹ The biradical copolymerization mechanism was decidedly established through detailed nuclear magnetic resonance (NMR), electron spin resonance (ESR) and ultraviolet-visible (UV-VIS) spectroscopic

investigations.¹⁰ Five- and six-membered cyclic germylenes, conversely, were copolymerized with *p*-benzoquinone derivatives in similar reaction conditions to afford novel 2:1 periodic copolymers with high molecular weights in very high yields.¹¹ Interestingly, monomer 1 gave a poly(germanium enolate) with high molecular weight in high yield at 0 °C by the reaction of 1 with α,β -unsaturated ketone.^{12–14} Monomer 1 and either ethylene sulfide or propylene sulfide underwent copolymerization at 0 °C, giving rise to 1:1- α -periodic copolymers with eliminating ethylene or propylene.¹⁵ When thietane (four membered) was used in place of ethylene sulfide (three membered), 1 or a cyclic germylene was copolymerized with thietane in a 1:1 alternating fashion.¹⁶ Monomer 1 was also copolymerized with an acetylene monomer, leading to a copolymer at room temperature. This reaction required an Rh catalyst.¹⁷ A cyclic stannylene was similarly copolymerized with *p*-benzoquinone derivatives at –42 °C, giving rise to 1:1 alternating copolymers in very high yields and having a molecular weight range from 1.1×10^5 to 5.7×10^3 .¹⁸ In all of these copolymerizations, a germylene or stannylene acted as a reductant monomer, whereas a *p*-benzoquinone, α,β -unsaturated ketone, acetylene, or cyclic sulfide behaved as an oxidant monomer (oxidation-reduction copolymerization).^{9–21} Of interest in the organometallic chemistry field, germylenes showed interesting reactivity toward α,β -unsaturated carbonyl compounds and 2-vinylpyridine.^{22,23}

In the present study, we report a new 1:1 oxidation-reduction alternating copolymerization of germylene (1a and 1b) with *N*-phenyl-*p*-quinoneimine (2), in addition to a very brief oral presentation in part.²⁴ 1 acted as a reductant monomer, whereas 2 acted as an oxidant monomer, similar to a *p*-benzoquinone derivative. The resulting copolymers (3a and 3b) had a tetravalent germanium unit and a

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Scheme 1 Alternating copolymerization of germylene (**1**) with *N*-phenyl-*p*-quinoneimine.

Table 1 Alternating copolymerization of **1** with **2**^a

Code	Germylene	Copolymer	Yield (%) ^b	<i>M_w</i> ^c	<i>M_w</i> / <i>M_n</i> ^c
1	1a	3a	88	4.98 × 10 ⁴	2.17
2	1b	3b	94	2.76 × 10 ⁴	2.38
3 ^d	1a	3a	quantity.	7.05 × 10 ⁴	2.80

^aCopolymerization was carried out in toluene at 0 °C for 2 hours under argon, with the feed of an equimolar amount of **1** and **2**.

^bIsolated yields.

^cDetermined by gel permeation chromatography (GPC).

^dCopolymerization was performed in toluene at 0 °C for 2 hours under argon, with the feed molar ratio **1a**:**2** = 100:90.

p-aminophenol unit alternating in the main chain (Scheme 1). An analogous type of copolymerization was also reported using cyclic and acyclic phosphorus(III) compounds as reductant monomers involving the oxidation of the P(III) monomer to a P(V) monomer unit in the product copolymer.^{25–27}

EXPERIMENTAL PROCEDURE

Materials

1a and **1b** were prepared by the reaction of a GeCl₂1,4-dioxane complex with the appropriate lithium amides, as reported.^{9,10} **2** was prepared by the oxidation of *p*-hydroxydiphenylamine with Ag₂CO₃ and then purified by sublimation.²⁸ 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) was obtained from Aldrich (Tokyo, Japan). Toluene and diethyl ether were commercial reagents that were distilled from sodium-benzophenone before use. Acetonitrile was distilled from calcium hydride. Other solvents were commercially available and used as obtained.

Copolymerization

The copolymerization of **1a** with **2** was carried out as follows. A solution of **2** in toluene (0.635 g of **2**, 3.47 mmol in 10 ml of toluene) was added to a toluene solution (5 ml) containing **1a** (1.370 g, 3.48 mmol) under argon at 0 °C while stirring. After stirring at 0 °C for 2 h, the reaction mixture was poured into 150 ml of acetonitrile while stirring. White precipitates were obtained, collected by filtration, and dried in vacuo, this reaction yielded 1.749 g (88%) of copolymer **3a**: ¹H NMR (CDCl₃, δ) 0.24 (s, SiMe₃, 36H), 6.6–7.0 (br. two peaks, Ar, 9H); ¹³C NMR (CDCl₃, δ) 6.0 (SiMe₃), 120.1, 121.7, 128.1, 129.0 (CH of Ar), 137.1 (C-NPh), 149.5 (C-N), 154.1 (C-O); infrared spectroscopy (IR; cm⁻¹) 2950, 2890, 1590, 1496, 1248, 1195, 873, 848. Anal, calculated for (C₂₄H₄₅N₃OSi₄Ge)_n: C, 49.99; H, 7.87; N, 7.29. Found: C, 49.57; H, 7.59; N, 7.49.

The copolymerization of **1b** with **2** was performed in a similar manner as described above. Copolymer **3b** was obtained in a 94% yield, **3b**: ¹H NMR (CDCl₃, δ) 0.28 (br, SiMe₃, 18H), 1.53 (br, Bu, 18H), 6.77 (br. Ar, 9H); ¹³C NMR (CDCl₃, δ) 7.9 (SiMe₃), 34.4 (Me₃C), 56.2, 58.3 (Me₃C) 118.7, 120.2, 127.6, 130.4 (CH of Ar), 136.3 (C-NPh), 150.8 (C-N), 154.8 (C-O); IR (cm⁻¹) 2955, 1593, 1500, 1238, 1179, 853, 751. Anal, calculated for (C₂₆H₄₅N₃OSi₂Ge)_n: C, 57.36; H, 8.33; N, 7.72. Found: C, 57.03; H, 8.20; N, 7.49.

Stability of the copolymer toward moisture

Water (0.8 ml) was added to a 16 ml solution of **3a** (0.082 g) in tetrahydrofuran (THF) under air, and the mixture was stirred for 25 hours. No decrease in

molecular weight of the recovered **3a** was observed by gel permeation chromatographic analysis. IR and ¹H NMR spectra were identical to those of the starting copolymer sample **3a**.

ESR measurement of the germyl radical

The solutions of **1a** and **2** in toluene were separately set into a U-type reaction vessel with an ESR tube connected. The system was degassed by four freeze–thaw cycles and sealed at reduced pressure at liquid nitrogen temperature. The solution of **2** was added at 20 °C to the solution of **1a**, during which the addition was controlled with a two-way stopcock.

Analytical methods

¹H and ¹³C NMR measurements were conducted on a Bruker AC-250T spectrometer (Karlsruhe, Germany). IR spectra were obtained on a SHIMADZU IR-460 spectrometer (Kyoto, Japan). UV-VIS spectra were recorded on a SHIMADZU UV-160 spectrophotometer using a 10 mm quartz cell with a teflon silicon septum cap. Gel permeation chromatographic analysis was carried out using chloroform as the eluent and polystyrene as the standard. ESR spectra were measured on a Bruker ESP300 spectrometer. The spin concentration of the germyl radical was determined by comparison with the ESR signal intensity of a solution of TEMPO in toluene with a known concentration.

RESULTS AND DISCUSSION

Copolymerization reaction

The present copolymerization is shown in Scheme 1. The germylenes seemed air sensitive, and therefore, the copolymerization was carried out under argon atmosphere as previously reported.^{9–11} Monomer **1** reacted very rapidly in toluene at 0 °C with an equimolar amount of monomer **2**, giving rise to an alternating copolymer (**3**). The copolymerization results are given in Table 1.

The copolymerization of monomers **1a** and **2** gave copolymer **3a** in an 88% yield and having a high molecular weight *M_w* = 4.98 × 10⁴ (Code 1). The ¹H NMR spectrum of copolymer **3a** (Figure 1a) shows a large singlet peak a at δ 0.24 due to Si(CH₃)₃ (36H) and broad multiplet peaks b at δ 6.6–7.0 due to the aromatic protons (total 9H). In the ¹³C NMR spectrum of copolymer **3a** (Figure 1b), a large singlet peak a is apparent at δ 6.0 due to Si(CH₃)₃, specific singlet peaks b appear at δ 137.1 due to Ge–C–NC₆H₅, c appears at 149.5 due to Ge–N–C–, d appears at δ 154.1 due to Ge–O–C–, and other aromatic CH carbon peaks appear at δ 120–129. For the peak assignment, ¹³C NMR spectra of monomer **2** and of *N*-phenyl-*p*-aminophenol were taken as reference (data not shown). These NMR spectral data supported the structure of copolymer **3a** having an alternating arrangement of a tetravalent germanium unit and *N*-phenyl-*p*-aminophenol unit in the main chain.

Furthermore, the IR spectrum and elemental analysis of **3a** clearly supported the structure of **3a**. A significant feature of the IR spectrum of monomer **2** was the absence of ν (C=O) and ν (C=N), which were observed at 1642 cm⁻¹ and 1615 cm⁻¹, respectively. The absorption due to stretching of aromatic rings was observed at 1590 and 1496 cm⁻¹ for copolymer **3a**, being similar to those of

Figure 1 ¹H NMR spectrum (a) and ¹³C NMR spectrum (b) of copolymer **3a** (both in CDCl₃).

p-hydroxydiphenylamine (1591 cm⁻¹ and 1501 cm⁻¹, respectively). *Anal.*, calculated for (C₂₄H₄₅N₃OSi₄Ge)_n: C, 49.99; H, 7.87; N, 7.29. Found: C, 49.57; H, 7.59; N, 7.49.

Similarly, the copolymerization of **1b** with **2** was carried out (Code 2), giving rise to the alternating copolymer **3b** in a high yield with high molecular weight. Compared with comonomer **1a**, **1b** possessed a more sterically hindered *t*-butyl group, yet produced the alternating copolymer **3b** in a similar manner.

During the copolymerization, **1** (reductant monomer) was oxidized from Ge(II) to Ge(IV), whereas **2** (oxidant monomer) was reduced from a *p*-quinoneimine structure to a *p*-aminophenol unit structure. Thus, the present reaction is a typical example of 'oxidation-reduction copolymerization' as reported before.^{9–24} The high reactivity of **1** toward **2** involving a carbon-nitrogen double bond toward a carbon-carbon double bond was noted in α,β-unsaturated carbonyl compounds.^{22,23}

The copolymers were white fine powders and were soluble in *n*-hexane, benzene and chloroform, whereas they were insoluble in acetonitrile and acetone. They were stable in air and the molecular weight did not decrease after being kept in air for several months, indicating that they can tolerate oxidation by oxygen and hydrolysis by

Figure 2 ESR spectrum of the reaction mixture of **1a** with 60 mol% of **2** measured at 20 °C.

moisture. The Si-N, Ge-N and Ge-O bonds are usually dipolar and readily cleaved by a protic solvent.²⁹ For example, hexamethyldisilazane is immediately hydrolyzed in aqueous methanol.³⁰ An attempt to hydrolyze copolymer **3a** was made by keeping it in THF-water mixture for 25 hours. Gel permeation chromatographic analysis of the sample **3a** showed no molecular weight decrease. Additionally, its IR spectrum showed the absence of absorption for ν(N-H), indicating that hydrolysis of the bis(trimethylsilyl)amino group did not occur. These facts strongly indicate that bulky substituents on the germanium in **3a** prevent the water molecule from approaching the dipolar bonds.

ESR study

Oxidation-reduction reactions normally involve an electron transfer process to give a radical ion pair or a biradical species. Reduction of a carbonyl group with a Grignard reagent is a typical example.³¹ In our previous study on the alternative copolymerization of germylene **1** and a *p*-benzoquinone derivative, copolymerization via a biradical mechanism was verified by ESR spectroscopy and trapping experiments.¹⁰

For the present reactions, the copolymerization mechanism was similarly considered owing to the similarity in structure between **2** and *p*-benzoquinone. To investigate this point in more detail, an ESR study was performed. When **2** (60 mol% toward **1a**) was added to the toluene solution of **1a**, the color of the solution turned from yellow to deep violet. In the ESR spectrum of the reaction mixture (Figure 2), a 1:3:6:7:6:3:1 septet signal was clearly observed, which was ascribed to the germyl radical (**4**) located at both propagating polymer ends. The germyl radical was bonded to two equivalent bis(trimethylsilyl)amino groups and selectively bonded to the third nitrogen atom of the terminal *p*-aminophenol unit, whose structure is indicated as (a) in Scheme 2. Another possible germyl radical bonded to the oxygen atom of the *p*-aminophenol unit was not observed, indicating that germyl

Scheme 2 (a) Germyl radicals (**4**) bonded to three nitrogen atoms formed from the reaction of **1a** and **2** (100 : 60 molar ratio), and (b) germyl radicals (**5**) bonded to two nitrogen atoms and one oxygen atom.¹⁰

Table 2 ESR parameters for germyl radicals

Germyl radical	hfc value $A(^{73}\text{Ge})/\text{G}$	<i>g</i> -value	Ref.
•GeMe ₃	83	2.0104	10
•Ge[C ₆ H ^{<i>t</i>} Bu-2-Me ₃ -4,5,6] ₃	85	2.0049	36
•Ge[CH(SiMe ₃) ₂] ₃	92	2.0078	36
Germyl radical 4 (A)	158	1.9988	Present study
Germyl radical 5a (B)	166	1.9986	10
Germyl radical 5b (B)	167	1.9985	10
•Ge[N(SiMe ₃) ₂] ₃	171	1.9991	32,33
•Ge[N(SiMe ₃) ^{<i>t</i>} Bu] ₃	173	1.9998	32,33
•GeCl ₃	220	—	35

radical **4** was linked to three nitrogen atoms.³² If the germyl radical were bonded to the oxygen atom of the terminal *p*-aminophenol unit, the radical would show a 1:2:3:2:1 quintet signal due to the bonding to two bis(trimethylsilyl)amino groups.¹⁰ The coupling constant ($A_N = 9.63$ G) was due to the nitrogen atom ($I = 1$) on the germanium. The fact that only one value of the coupling constant was observed suggests that the values because of the nitrogen atom of the terminal *p*-aminophenol unit and the two equivalent nitrogen atoms of bis(trimethylsilyl)amino groups were almost equal. The A_N value for **4** was approximately 1 G smaller than that ($A_N = 10.6$ G) of the germyl radical •Ge[N(SiMe₃)₂]₃ due to the three equivalent bis(trimethylsilyl)amino groups generated by the photolysis of **1a**.³² The decreased A_N value was most likely due to the decreased spin density on the nitrogen atoms from delocalization of the unpaired electron into the aromatic ring. By comparing the peak intensity with that of the known amount of TEMPO, approximately 0.3% of the germyl radical based on the added **2** was observed at this point.

Among the five isotopes of germanium, only ⁷³Ge has a non-zero nuclei spin value ($I = 9/2$), which gives ten satellite peaks (Figure 2). Because the natural abundance of ⁷³Ge is 7.6%, the satellite's intensity is much smaller than that of the main signal. The hyperfine coupling

Figure 3 UV-VIS spectrum of the reaction mixture of **1a** and 50 mol% of **2** in diethyl ether at 20 °C.

(hfc) constant of **4** ($A_{\text{Ge}} = 158$ G) due to ⁷³Ge was slightly smaller than that of the previously studied radicals having the •Ge[N(SiMe₃)₂]₂ [OAr] structure, as given in **5a** and **5b** (Scheme 2b), $A_{\text{Ge}} = 166$ G and 167 G, respectively.¹⁰ The hfc value of **4** was also smaller than that of the radical •Ge[N(SiMe₃)₂]₃ ($A_{\text{Ge}} = 171$ G).^{32,33} The hfc constant due to the center atom M with a non-zero nuclei spin for the •MX₃ type radical is generally associated with geometry of the radical. The A_M value increases with decreasing *p*-character of the orbital on which the unpaired electron resides. Therefore, the increased A_M value indicated greater deviation from planar geometry of the radical.³⁴ The larger A_{Ge} value for **4** compared with that of the radical •GeMe₃ ($A_{\text{Ge}} = 83$ G) indicated a more pyramidalized radical; however, the A_{Ge} value was less than the almost tetrahedral radical •GeCl₃ ($A_{\text{Ge}} = 220$ G).³⁵ The presence of the electronegative nitrogen atoms and of the *N*-phenyl substituent on the main-chain nitrogen atom, all three bonded to the germanium radical center, would force a geometry more similar to the pyramidal geometry of radical **4**. Additionally, the smaller *g*-value implies the increased tetrahedral character of the germyl radical geometry, although all of the hfc values are in a very narrow range. The *g*-value for **4** ($g = 1.9988$) was close to those for **5a** (1.9986),

Scheme 3 Postulated biradical mechanism for the alternating copolymerization of **1** with **2**.

5b (1.9985) and $\bullet\text{Ge}[\text{N}(\text{SiMe}_3)_2]_3$ (1.9991), suggesting that these four radicals have a similar geometry on the centered germanium.¹⁰ For clarity, these values together with two additional radicals³⁶ are shown in Table 2.

The germyl radical **4** showed great persistency; the half-life time ($t_{1/2}$) was approximately 1.3 hours in toluene at 20°C. The steric hindrance most likely prevented the Ge-Ge bond formation via the coupling of the two germyl radicals, which normally causes the instability.

UV-VIS spectrum

The spectrum of the reaction mixture of **1a** and 50 mol% of **2** in diethyl ether was measured (Figure 3). When **1a** and **2** were mixed, the solution color turned to dark violet. The absorption peak at 362 nm was ascribed to the remaining **1a**, whereas the peak at 446 nm due to **2** was not detected. Thus, the very broad absorption at 543 nm observed in the increased intensity spectrum ($\times 7$) was most likely ascribed to the germyl radical **4**, which was responsible for the dark violet color. When another 50 mol% of **2** was added to the reaction mixture, the color of the solution turned from dark violet to pale yellow orange, and the ESR signal due to **4** completely disappeared.

In the course of this copolymerization, only the germyl radical showed an absorption signal due to reactive species.

Copolymerization mechanism

Based on the above observations, a plausible mechanism of copolymerization of **1** with **2** is described as a radical process, more likely a biradical process, in the following manner (Scheme 3). The first step is the formation of the biradical **6** via an oxidation-reduction process. This biradical possesses two unpaired electrons: one located on the germanium atom and the other delocalized on the *N*-aromatic rings. The Ge-O bond formation is more favorable because the imino group of **2** is sterically restricted due to the phenyl substituent. Additionally, the radical $\bullet\text{N}-\text{C}_6\text{H}_5$ is more stable due to the delocalization of unpaired electrons on the phenyl ring(s). Then, **1** attacks **6** to produce the germyl diradicals **7**, whereas **2** attacks **6** to give the anilino biradicals **8**. Successive reactions among monomers (**1** or **2**), **6**, **7** and **8** produce copolymer **9** with two germyl radicals, copolymer **10** with two anilino radicals and copolymer **11** with a germyl radical and an anilino radical at the polymer end. The radical coupling reactions between the germyl radical part and the anilino radical part of biradicals **6–11**, as well as these radicals-monomer (**1** or **2**) reactions,

eventually occur, resulting in the alternating copolymer **3**. When excess **1** is used, an equimolar amount of **1** and **2** is consumed to yield copolymer biradicals such as **11**. The remaining **1** reacts with the anilino radical to give the germyl diradicals, such as **9**, as a relatively stable species. Among the biradicals, **6–11** (except **9**) are most likely short-lived species and are thus difficult to directly observe.

It is assumed that among all of the reaction steps in Scheme 3, the formation of **6** from **1** and **2** via the oxidation-reduction process is most likely the most rapid. This assumption explains the production of a high molecular weight alternating copolymer **3** ($M_w = 7.05 \times 10^4$), even with the feed ratio of **1a**:**2** = 100:90, as shown by Code 3 (Table 1). The behaviors of this copolymerization do not resemble the polycondensation of two bifunctional monomers but instead resemble the rapid initiation type polymerization as already noted,¹⁰ where the initiation is the reaction of **1** and **2** to form **6**. Then, **6** most likely behaves as a propagating monomer, giving rise to the alternating copolymer **3**. In this sense, 10% excess of comonomer **1** did not disturb the production of a high molecular weight copolymer, which differs from the normally observed results in polycondensation reactions.

CONCLUSION

An oxidation-reduction, alternating copolymerization of a germylene (**1a** or **1b**) with a quinoneimine (**2**) has been reported, where **1** was used as a reductant monomer and **2** was employed as a new oxidant monomer. The reaction took place smoothly at 0°C without added catalyst or initiator to produce alternating copolymers (**3a** and **3b**) that have high molecular weights in high yields. The copolymers were soluble in an organic solvent and tolerant of hydrolysis. ESR studies of the reaction revealed that the copolymerization proceeded most plausibly via a biradical mechanism.

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