A Novel Redox Process for the Construction of Germanium-Containing Polymers by Utilizing Germylenes and *p*-Benzoquinone Derivatives: First Clear-Cut Evidence for a Biradical Propagation Mechanism in Polymerization Chemistry

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Abstract: Germylenes bearing bulky amide groups have been copolymerized with various *p*-benzoquinone derivatives without any added catalyst to give a novel class of germanium-containing polymers having a tetravalent germanium unit and a *p*-hydroquinone unit alternatingly in the main chain. During the copolymerization, the germylene (reductant monomer) is oxidized and the *p*-benzoquinone derivative (oxidant monomer) is reduced ("oxidation—reduction copolymerization"). The resulting copolymers have high molecular weight (M_w; from 2.0×10^4 up to 1.4×10^6) and most of them are soluble in common organic solvents. ESR studies of the copolymerization system and of the model reactions including the structural elucidation of the products gave the first clear-cut evidence for a *biradical mechanism* involving a germyl radical and a semiquinone radical. Trapping experiments using a disulfide, tetramethylpiperidinyloxy (TEMPO) radical, and a sterically hindered *p*-benzoquinone derivative further supported the biradical structure of the propagating polymer ends.

Introduction

The role of polymers containing 14 group elements has become very important in material sciences due to their unique chemical or physical properties derived from the organometallic unit structures.[1] Organogermane polymers are photoactive and show bleaching behaviors,[2] strong thermochromic properties,[3] and semiconductivity.[4] Preparation of these polymers, however, utilizes the classical methodologies like sodium coupling of a germanium dihalide[2,3] or polycondensation between a germanium dihydroxide and a dihalide or a bifunctional organic compound such as a diol or dicarboxylic acid.[4] These polycondensation processes require an acid scavenger or coupling reagent to promote the reaction effectively, and the molecular weight of the resulting polymer is normally low.

On the other hand, much attention has been paid to ger-mylenes and stannylenes, heavy carbene analogues, as metastable species in organic chemistry.[5] Germylenes and stannylenes have lone pair electrons as well as a vacant orbital, which implies that they can act both as a nucleophile and an electrophile. These species are, therefore, potentially useful for polymer synthesis because they can form two new bonds on the germanium or tin atom via α,α-addition by changing their valency from two to four. In spite of their potential, very little attention was paid to germylenes and stannylenes in polymer chemistry. Only a few studies concerning reactions of halogermylenes with aldehydes and imines have been reported so far.[6]

Organogermylenes and organostannylenes having substituents such as methyl, ethyl, and phenyl groups are not able to exist as monomers because they polymerize spontaneously to give the corresponding polygermanes and polystannanes, respectively. The pioneering works for the synthesis of thermally stable, monomeric germylenes and stannylenes have been reported by Lappert and his co-workers,[7] showing that a very bulky substituent on the germanium or tin atom prevents the self-oligomerization and/or polymerization. In addition, very recently a stable silylene with a bulky, unsaturated cyclic ligand has been reported for the first time.[8]

Recently, in a series of a new class of polymerizations which involve a redox process by utilizing a low-valent chemical

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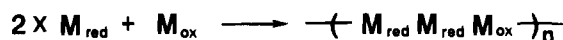
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Scheme 1

$$\mathbf{M}_{red} + \mathbf{M}_{ox} \longrightarrow \mathbf{+M}_{red}\mathbf{M}_{ox}\mathbf{+}_{n}$$

Scheme 2

$$2 \times \mathbf{M}_{red} + \mathbf{M}_{ox} \longrightarrow \mathbf{+M}_{red}\mathbf{M}_{red}\mathbf{M}_{ox}\mathbf{+}_{n}$$

species,[9] we have reported a new copolymerization reaction between a germylene, bis[bis(trimethylsilyl)amido]germanium (1), and p-benzoquinone derivatives at a lower temperature without any catalyst, giving rise to high molecular weight copolymers having a tetravalent germanium unit and a p-hydroquinone unit alternatingly in the main chain.[10a] The reaction was designed on the basis of a new concept of "oxidation—reduction alternating copolymerization" where a germylene acts as a reductant monomer (M_{red}) and a p-benzoquinone derivative behaves as an oxidant monomer (M_{ox}) (Scheme 1). In contrast to the acyclic germylene 1, a cyclic germylene copolymerized with a p-benzoquinone derivative under similar reaction conditions to produce a 2:1 periodic copolymer of high molecular weight in high yields (Scheme 2).[10b]

The present paper describes the details of the alternating copolymerization (Scheme 3) and provides the first clear-cut evidence of the copolymerization via a biradical mechanism in polymerization chemistry.

Results and Discussion

Alternating Copolymerization and Product Copolymers. 1. Copolymerization of Germylenes with p-Benzoquinone Derivatives. The germylene 1 reacted with p-benzoquinone (3a) smoothly at −78 °C in toluene to give the corresponding alternating copolymer 4a in good yield. The copolymerization was initiated simply by mixing toluene solutions of 1 and of 3a without using any catalyst. The resulting copolymer was purified by precipitation from acetonitrile under argon. The reaction proceeded very rapidly and actually completed within 10 min. A prolonged reaction time did not affect the yield. Table 1 shows the effect of temperature and solvent on the copolymerization of 1 with 3a. Various solvents were found usable for affording copolymers having high molecular weight ($M_w > 5.1 \times 10^4$) in high yields at a wide range of reaction temperatures from −78 to 50 °C. The molecular weight of 4a, however, decreased slightly with the increase of reaction temperature when tetrahydrofuran (THF) was used as the solvent (entry 7).[11] Dichloromethane and chloroform were found unsuitable as solvent, probably because oxidative addition of the germylene toward the carbon—chlorine bond occurred.[12] The use of n-hexane also gave a copolymer having a 1:1 monomer composition although the reaction system was heterogeneous during the copolymerization because of the poor solubility of 3a (entry 5).

Furthermore, the copolymerization in all cases resulted in the copolymer having a 1:1 alternating structure with high molecular weight regardless of the monomer feed ratio of reductant and oxidant monomers (Table 2). The excess amount of the reductant or oxidant monomer was found to remain unchanged after the completion of the reaction. Thus, the 1:1 alternating structure is controlled very strictly under a wide variety of copolymerization conditions.

Various p-benzoquinone derivatives (3b−i) have successfully been copolymerized with 1 (Table 3). Even sterically hindered p-benzoquinone derivatives, 2,5-di-tert-butyl-p-benzoquinone (3b), 2,5-di-tert-amyl-p-benzoquinone (3c), and 2,5-diphenyl-p-benzoquinone (3e) smoothly reacted with 1 to give the corresponding alternating copolymers in good yields (entries 1−4 and 6), indicating the high reactivity of 1 toward compounds having a carbon—oxygen double bond.[13] Copolymer 4c with higher molecular weight was produced in n-hexane solvent (entries 3 and 4). 2,5-Dichloro-p-benzoquinone (3d) also gave the corresponding alternating copolymer 4d quantitatively (entry 5). This result shows no insertion reaction of the germylene into the carbon—chlorine bond, probably due to its inertness toward a carbon(sp²)—chlorine bond.
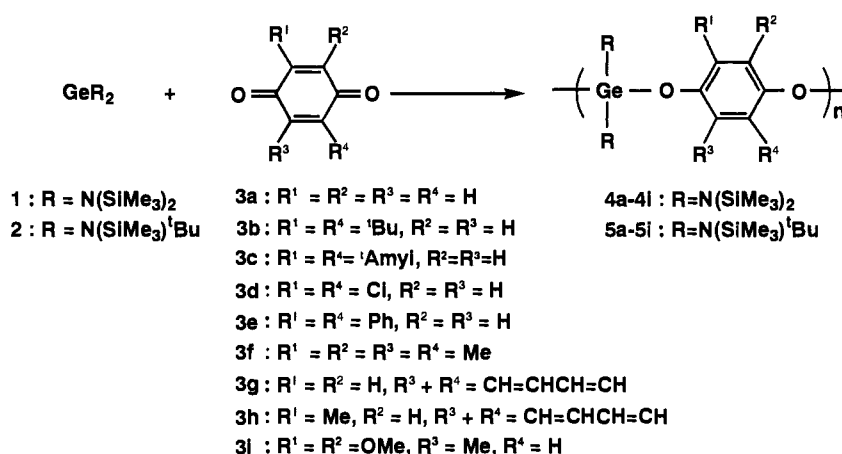
Trisubstituted quinones, 2-methyl-1,4-naphthoquinone (3h) and 2,3-dimethoxy-5-methyl-p-benzoquinone (3i), also afforded the corresponding copolymers soluble in organic solvents (entries 10 and 11) whereas the copolymer prepared from duroquinone (3f) was insoluble in any organic solvents (entry 7). All the resulting copolymers have moderately high molecular weight ($M_w > 2.9 \times 10^4$). Among them, the copolymer 4g prepared from 1 and 1,4-naphthoquinone (3g) at −78 °C for 5 min showed an extremely high molecular weight ($M_w = 1.4 \times 10^6$) and gave a transparent film by the casting method from chloroform (entry 8).

Table 4 summarizes the results of copolymerizations using bis[(tert-butyl-trimethylsilyl)amido]germanium (2) as reductant monomer. The reaction with various p-benzoquinone derivatives (3a−i) proceeded smoothly in THF at −78 °C to give the corresponding alternating copolymers (5a−i) in good yields. Remarkable increase of molecular weight in producing copolymer 5c was observed by replacing the solvent from THF to n-hexane (entries 3 and 4). All the above copolymers except for 4f and 5f are soluble in organic solvents such as benzene, chloroform, and THF.

2. Characterization of the Copolymers. The structure of the resulting copolymers was determined by ¹H and ¹³C NMR and IR spectra as well as by elemental analysis. A typical case of copolymer 4g is described as follows. The ¹H NMR spectrum of 4g (entry 8 in Table 3) exhibited signals at δ 0.30 ascribable to the methyl protons of the trimethylsilyl group and at δ 7.12, 7.39, and 8.16 due to the aromatic protons of the ether form of 1,4-dihydroxynaphthalene. The ratio of peak areas of the trimethylsilyl protons and the aromatic protons clearly showed that the copolymer consists of a 1:1 unit derived from 1 and 3g, which was also supported by elemental analysis. The ¹³C NMR spectrum of 4g indicated the signal pattern of an aromatic ring system in addition to a strong singlet peak due to the trimethylsilyl group (Figure 1). The signals at 112.6 and 146.2 ppm are ascribable to the C(2,3) and C(1,4) carbon atoms, respectively, which are very similar to those of 1,4-dihydroxynaphthalene bis(trimethylsilyl ether), a model compound of the copolymer unit structure. The signals due to the carbonyl carbons in the monomer 3g completely disappeared. These

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Scheme 3

1 : R = N(SiMe$_3$)$_2$
2 : R = N(SiMe$_3$)^{t}Bu

3a : R^1 = R^2 = R^3 = R^4 = H
3b : R^1 = R^4 = ^{t}Bu, R^2 = R^3 = H
3c : R^1 = R^4= ^{t}Amyl, R^2=R^3=H
3d : R^1 = R^4 = Cl, R^2 = R^3 = H
3e : R^1 = R^4 = Ph, R^2 = R^3 = H
3f : R^1 = R^2 = R^3 = R^4 = Me
3g : R^1 = R^2 = H, R^3 + R^4 = CH=CHCH=CH
3h : R^1 = Me, R^2 = H, R^3 + R^4 = CH=CHCH=CH
3i : R^1 = R^2 =OMe, R^3 = Me, R^4 = H

4a-4l : R=N(SiMe$_3$)$_2$
5a-5l : R=N(SiMe$_3$)^{t}Bu

Table 1. Copolymerization of Germylene **1** with *p*-Benzoquinone(**3a**): Effect of Solvent and Reaction Temperature[a]

			copolymer **4a**		
entry	solvent	temp (°C)	yield (%)[b]	M_w[c]	M_w/M_n[c]
1	toluene	−78	quant	1.9×10^5	2.72
2	toluene	0	quant	1.4×10^5	2.32
3	toluene	50	quant	1.2×10^5	2.18
4	benzene	25	quant	1.6×10^5	2.73
5	*n*-hexane	0	99	1.8×10^5	2.92
6	THF	−78	94	1.4×10^{5} ^{d}	2.63
7	THF	50	93	5.1×10^4	3.97
8	diethyl ether	0	99	1.0×10^5	2.64
9	chlorobenzene	0	96	1.3×10^5	3.31

[a] Copolymerization was carried out with 1:1 feed molar ratio of **1** and **3a** for 1 h under argon. [b] Isolated yield. [c] Determined by GPC. [d] M_n = 4.0 × 10^4 (determined by vapor pressure osmometry (VPO) in benzene at 40 °C).

Table 2. Copolymerization of Germylene **1** with *p*-Benzoquinone (**3a**): Effect of the Feed Molar Ratio of Monomers[a]

	feed molar ratio	copolymer **4a**		
entry	1:3a	yield (%)[b]	M_w	M_w/M_n[c]
1	0.25:1.0	84	1.9×10^5	1.90
2	0.50:1.0	82	2.9×10^5	2.02
3	1.0:1.0	quant	1.2×10^5	1.77
4	2.0:1.0	quant	1.2×10^5	1.89
5	4.0:1.0	quant	1.1×10^5	2.13

[a] Copolymerization was carried out in toluene at −78 °C for 0.5 h under argon. [b] Isolated yield; the yield percent was calculated from monomer **1** mass for entries 1 and 2 and monomer **2a** mass for entries 4 and 5, on the assumption that the stoichiometry was 1:1. [c] Determined by GPC.

Table 3. Copolymerization of Germylene **1** with Various *p*-Benzoquinone Derivatives **3b**−i[a]

		copolymer **4**			
entry	quinone	yield (%)[b]	structure	M_w[c]	M_w/M_n[c]
1	3b	94	4b	5.8×10^4	2.51
2[d]	3b	96	4b	4.3×10^5	2.04
3	3c	92	4c	2.9×10^4	1.98
4[d]	3c	95	4c	5.7×10^5	3.02
5	3d	quant	4d	2.9×10^4	1.98
6	3e	89	4e	8.6×10^4	2.72
7	3f	92	4f	*e*	*e*
8[f]	3g	96	4g	1.4×10^6	2.44
9[g]	3g	93	4g	2.0×10^{5} ^{h}	2.69
10	3h	95	4h	3.9×10^4	2.75
11	3i	90	4l	2.6×10^5	3.57

[a] Copolymerization was carried out with 1:1 feed molar ratio of **1** and **3** in toluene at −78 °C for 1 h under argon. [b] Isolated yield. [c] Determined by GPC. [d] In *n*-hexane for 5 min. [e] Insoluble in organic solvents. [f] Reaction time: 5 min. [g] In THF. [h] M_n = 7.9 × 10^4 (determined by VPO in benzene at 40 °C).

Table 4. Copolymerization of Germylene **2** with Various *p*-Benzoquinone Derivatives **3a**−i[a]

		copolymer **5**			
entry	quinone	yield (%)[b]	structure	M_w[c]	M_w/M_n[c]
1	3a	94	5a	5.5×10^4	2.44
2	3b	95	5b	3.9×10^4	1.96
3	3c	84	5c	2.0×10^4	2.24
4[d]	3c	94	5c	9.7×10^5	3.53
5	3d	quant	5d	1.4×10^5	2.63
6	3e	88	5e	4.5×10^4	2.05
7[e]	3f	89	5f	*f*	*f*
8	3g	93	5g	1.6×10^5	2.09
9	3h	quant	5h	2.4×10^5	1.80
10	3i	quant	5l	5.9×10^4	2.74

[a] Copolymerization was carried out with 1:1 feed molar ratio of **2** and **3** in THF at −78 °C for 1 h under argon. [b] Isolated yield. [c] Determined by GPC. [d] In *n*-hexane for 5 min. [e] At room temperature for 12 h. [f] Insoluble in organic solvents.

results clearly indicate that the 1,4-naphthoquinone moiety has been reduced to the corresponding *p*-hydroquinone form; no substitution on a carbon atom of the quinoid ring occurred to give a polymer having a carbonyl group. The selective formation of **4g** was also supported by the IR spectrum; no absorption due to the carbonyl carbon formed by such a side reaction was detected and the absorptions derived from the aromatic ring were observed at 1614 and 1588 cm^{-1}.

The structures of insoluble copolymers **4f** and **5f** were determined by cross-polarization magic angle spinning (CP/MAS) solid ^{13}C NMR spectra, IR spectra, and elemental analyses. The CP/MAS ^{13}C NMR spectrum of **4f** (entry 7 in Table 3) showed four peaks at 7.1, 16.2, 125.6, and 147.9 ppm, ascribable to the carbon atoms denoted by a, b, c, and d, respectively (Figure 2). The CP/MAS ^{13}C NMR spectrum of **5f** also showed the signals at 125.4 and 148.2 ppm, ascribable to the aromatic carbon atoms. Elemental analyses of the

copolymers were in good agreement with the expected ratio of 1:1 for the products. The IR spectra of **4f** and **5f** showed no absorption at 1629 cm^{-1} due to the carbonyl carbon of the monomer **3f**, indicating that complete reduction of **3f** took place.

All the copolymers obtained using other *p*-benzoquinone derivatives also indicated the 1:1 composition of a tetravalent germanium unit and a *p*-hydroquinone unit. A homopolymerized unit of the germylenes or *p*-benzoquinone derivative was not detected. The selective formation of the 1:1 alternating structure is explained by the steric hindrance of the bulky substituent on the germylenes to prevent the Ge−Ge bond
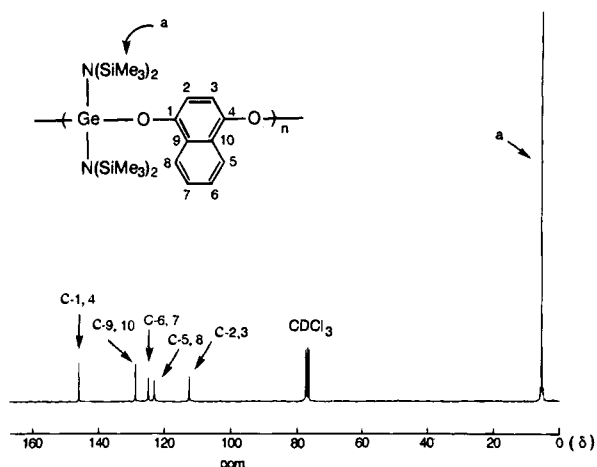
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Figure 1. ^{13}C NMR spectrum of copolymer **4g** in CDCl$_3$.

Figure 2. Solid CP/MAS ^{13}C NMR spectrum of copolymer **4f**.

Figure 3. Molecular weight (M_n) change of copolymers **4b** (●) and **4g** (■) in THF−water solution determined by GPC; (O) M_w/M_n change of copolymer **4g** determined by GPC.

the molecular weight distribution increased (open circle in Figure 3), indicating that the naphthalene ring is not bulky enough compared with the *tert*-butyl group to prevent the hydrolytic cleavage.

Copolymerization Mechanism. 1. Model System. A model reaction using the germylenes (**1** and **2**) and 2,6-di-*tert*-butyl-*p*-benzoquinone (**6**) was designed, in which **6** does not undergo the copolymerization because of the steric hindrance of two *tert*-butyl groups but does react with the germylene (Scheme 4). When germylene **1** was treated with 2 equiv of **6** in *n*-hexane at 0 °C, a cyclohexadienone dimer derivative (**7a**) was isolated as white solids in 62% yield. The 1:2 adduct formation is explained by assuming the existence of a semi-quinone biradical derivative (**8a**) which undergoes an intramolecular coupling reaction at the less sterically hindered ring carbon atom, giving rise to **7a**.[15]

It has been found that the product **7a** is in equilibrium with a biradical species (**8a**) in *n*-hexane solution. Actually, the ESR spectrum of the product **7a** in *n*-hexane showed a 1:2:1 triplet signal due to the semiquinone biradical **8a** (g = 2.0046). The concentration of **8a** was determined to be 7.1% at 20 °C by using 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) radical as external standard. The hyperfine coupling constant (hfc) derived from two hydrogens on the aromatic ring of **8a** indicated a normal value (A_H = 1.06 G). Germylene **2** also reacted with 2 equiv of **6** to give the corresponding cyclohexadienone dimer derivative **7b** in 82% yield. The ESR spectrum of the product in *n*-hexane showed a 1:2:1 triplet signal due to the semiquinone radical **8b** (g = 2.0047, A_H = 1.10 G). The concentration of **8b** was found to be 0.2% at 20 °C (determined by using TEMPO radical as external standard), indicating that the equilibrium shifted greatly toward **7b** in *n*-hexane.[16]

The ^{1}H NMR spectrum of **7a** in CDCl$_3$ showed a signal at δ 0.39 and 1.20 due to the trimethylsilyl group and the *tert*-butyl group, respectively (Figure 4a). The ratio of these peaks clearly

formation and the poor homopolymerizability of the *p*-benzoquinone derivatives.

3. Stability of the Copolymers. The copolymers were thermally stable and melted without decomposition. The glass transition and melt transition temperatures of **4a** (entry 1 in Table 1) and **4g** (entry 9 in Table 3) determined by differential scanning calorimetry (DSC) were T_g = 75.6 °C, T_m = 234.7 °C and T_g = 46.1 °C, T_m = 234.9 °C, respectively. All of the resulting copolymers are stable at room temperature. No decrease of molecular weight has been observed even after exposing them to air for several months.

In order to examine the stability toward moisture more precisely, the following hydrolysis experiment has been carried out. A THF−water solution of **4b** or **4g** was stirred at room temperature, and molecular weight change was monitored by gel permeation chromatography (GPC). The GPC analysis showed no decrease of the molecular weight for **4b** after the solution was stirred for 24 h (black circle in Figure 3). The IR spectrum indicated no absorptions due to the NH moiety which would be detected if the hydrolytic cleavage of the amide substituent occurred. It has been well known that Si−N, Ge−N, and Ge−O bonds are easily cleaved by the attack of nucleophiles such as an alcohol or water.[14] In the case of **4b**, however, the steric hindrance of the *tert*-butyl group of a 2,5-di-*tert*-butylhydroquinone unit may prevent a water molecule from attacking the silicon or germanium atom. The copolymer **4g** was gradually hydrolyzed (black square in Figure 3) and

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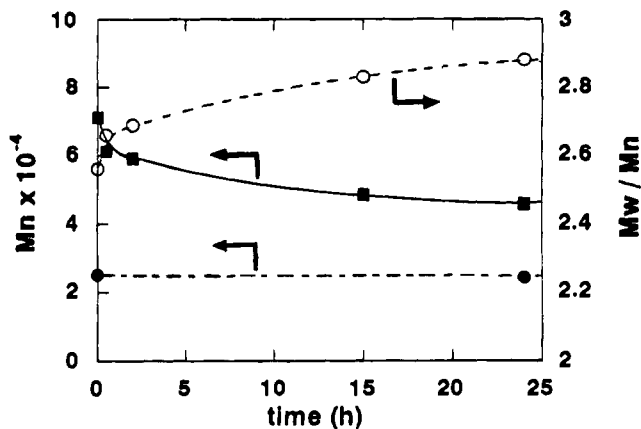
(15) Relevant to the present reaction, an *o*-semiquinone radical derivative has been reported to cause a hydrogen abstraction from the *tert*-butyl group at the ortho position to generate isobutene. Rivière-Baudet, M.; Morere, A.; Khallaayoun, A. *J. Organomet. Chem.* **1993**, *443*, 43.

(16) Generally, signals in the ESR spectrum of a biradical are affected by each other through a spin−spin interaction. The biradical species **8a** and **8b**, however, showed no pair of spin−triplet features in THF solution at 20 °C or in a frozen THF solution at 77 K. Chandross and Kreilick reported that bis-phenoxyl radical obtained by oxidation of 2,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)propane does not show a pair of spin−triplet features because the equilibrium is shifted toward the direction of intramolecular bond formation almost completely. Chandross, E. A.; Kreilick, R. *J. Am. Chem. Soc.* (a) **1963**, *85*, 2530; (b) **1964**, *86*, 117.
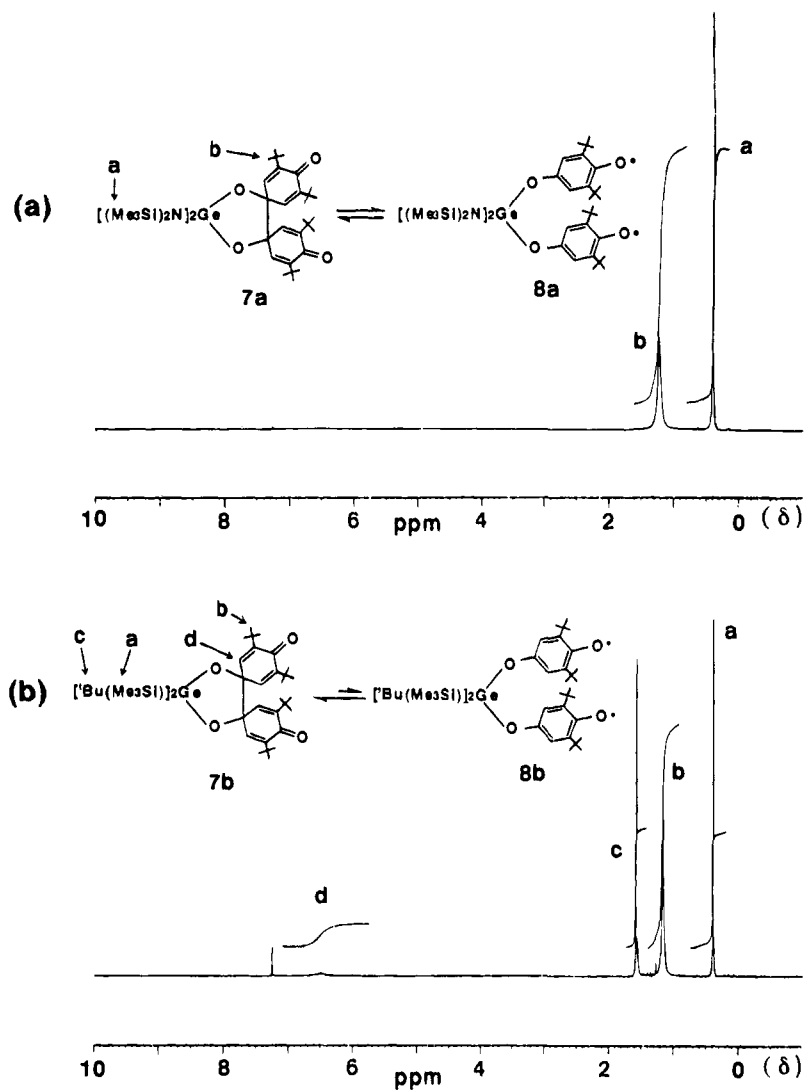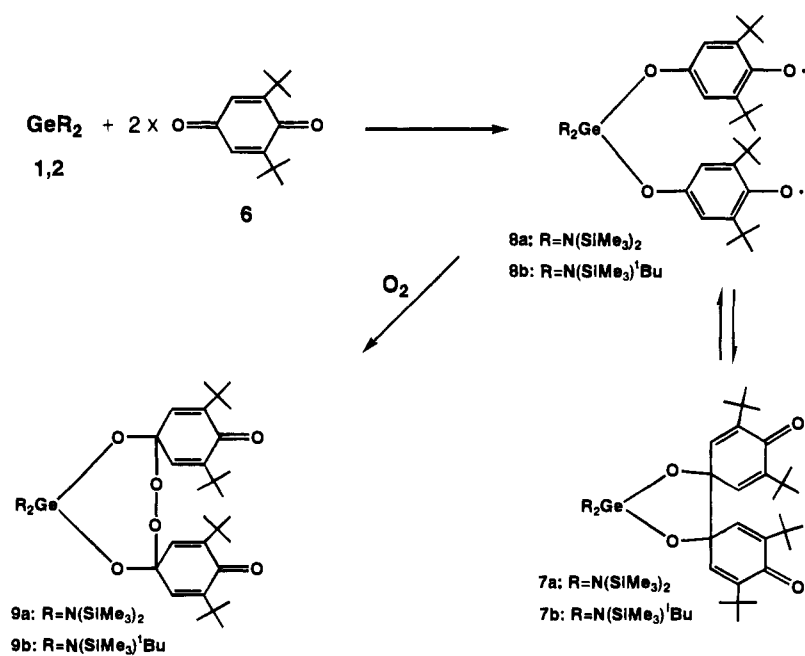
Figure 4. ¹H NMR spectra of the equilibrium mixture of (a) **7a** and **8a** and (b) **7b** and **8b**, both in CDCl₃.

Scheme 4

indicates that the product is a 1:2 adduct of **1** and **6**. Interestingly, no signal due to the vinylic protons of **7a** and aromatic

protons of **8a** could be detected. The disappearance of the signals can be explained by a rapid interconversion between

7a and **8a** as well as by a spin relaxation. The moderate broadening of the peak due to the *tert*-butyl group is also caused by a spin—spin relaxation. On the other hand, the ¹H NMR spectrum of **7b** showed a broad peak at δ 6.5 ascribable to the vinylic protons of the cyclohexadienone ring (Figure 4b). The appearance of these peaks indicates that the rate of the interconversion between **7b** and **8b** is slow and the equilibrium shifts greatly toward the former. The ¹³C NMR spectra of **7a** and **7b** in CDCl₃ showed no signal due to the cyclohexadienone ring carbon atoms. Furthermore, ¹³C signals of the *tert*-butyl group on the ring of **7a** could not be detected, whereas those of **7b** were observed as a broad signal. These NMR behaviors indicate that the delocalization of the unpaired electrons into p orbitals of the aromatic ring greatly takes place in the case of **7a** due to the larger concentration of species **8a** (7.1%), whereas it takes place to a lesser extent in the case of **7b** due to the smaller concentration of species **8b** (0.2%).

The UV—vis spectrum of **7a** in *n*-hexane showed an absorption at 405 nm due to **8a**, characteristic to semiquinone radicals; however, **7b** did not give the corresponding absorption due to the very low concentration of **8b** as observed by ESR spectroscopy.

Clear evidence for the structure of **7a** was obtained by means of CP/MAS solid ¹³C NMR spectrum. The two peaks at 140 and 145 ppm are ascribable to the vinyl carbons of the cyclohexadienone ring. The absorption at 186 ppm is due to the carbonyl carbon. The presence of the peak at 80 ppm assignable to the quaternary carbon strongly supports the spirocyclic structure of **7a** as a result of the coupling of the semiquinone radicals. The spectrum of **7b** showed a similar pattern, supporting a spirocyclohexadienone structure. Thus, there was no indication of the presence of **8a** or **8b** in the solid state. The IR spectrum of **7a** in the solid state showed two absorptions at 1659 and 1636 cm⁻¹, characteristic of a cyclohexadienone ring.[17] The absence of the absorption at around 1570 cm⁻¹ due to semiquinone radical indicated that the equilibrium shifted virtually toward **7a** in the solid state.

The structures of biradicals **8a** and **8b** were confirmed further by converting them to seven-membered cyclic peroxide derivatives **9a** and **9b**, respectively, by air-oxidation. When **7a** was first prepared from **1** and **6** in *n*-hexane and then exposed to air for 12 h, a cyclic peroxide (**9a**) was obtained as yellow crystals (69% isolated yield). This result indicates that biradical **8a** was effectively trapped by an oxygen molecule.[18] The molecular structure of the peroxide derivative **9a** was definitely determined by X-ray crystallographic analysis (Figure 5).

The bond lengths and bond angles of **9a** are summarized in Table 5. The cyclic peroxide **9a** possesses a 2-fold rotation axis through a germanium atom. The bond distances C(13)—C(14) (1.309(15) Å) and C(16)—C(17) (1.323(15) Å) showed values close to the standard C=C double bond. The average bond angle, Ge—N—Si and Si—N—Si, is 119.7(4)°, indicating that the geometry on the nitrogen atoms is almost planar. The O(18)—O(18)′ bond distance is a normal one. The relatively higher decomposition point (dp = 189 °C) of **9a** is probably due to very slight ring strain of the seven-membered ring. The structure of **9a** was also supported by the IR spectrum which showed a doublet absorption at 1665 and 1642 cm⁻¹ characteristic of a cyclohexadienone ring.

All these data clearly indicate that germylenes produce biradical species in the reaction with *p*-benzoquinone derivatives.

(17) Mueller, E.; Ley, K. *Chem. Ber.* **1954**, *87*, 922.

(18) It is to be noted that the isolated species **7a** and **7b** produced cyclic peroxide adducts **9a** and **9b**, respectively, via oxidation with air in chloroform. The oxidation of **7a** was observed to be faster than that of **7b** by monitoring the reaction system by ¹H NMR spectroscopy at room temperature.
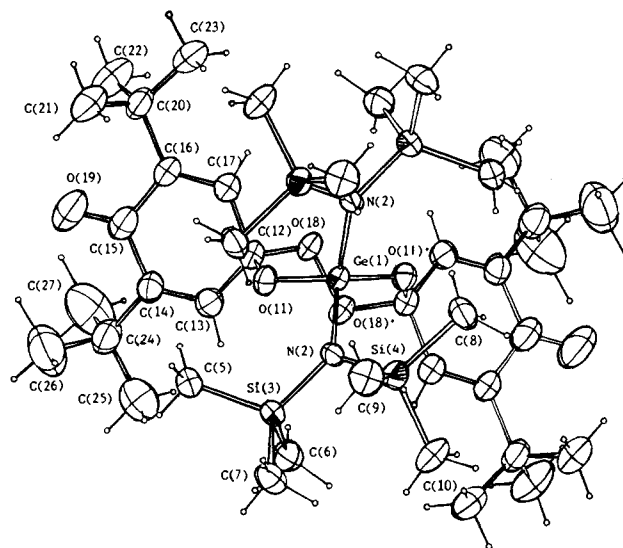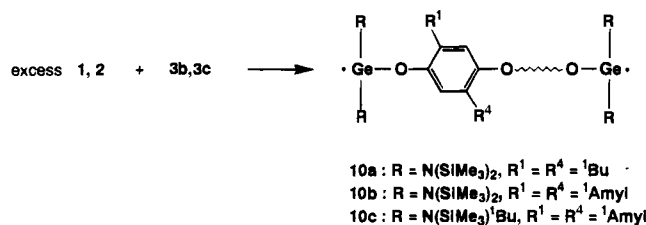

Figure 5. Molecular structure of [(Me₃Si)₂N]₂GeO₂[OC₆H₂ᵗBu₂]₂ (**9a**).

Table 5. Selective Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for **9a**

Ge(1)—N(2)	1.846(7)	Ge(1)—O(11)	1.801(6)
Si(3)—N(2)	1.779(7)	Si(4)—N(2)	1.749(7)
O(11)—C(12)	1.408(10)	O(18)—C(12)	1.450(12)
O(18)—O(18)′	1.485(8)	C(12)—C(13)	1.484(13)
C(12)—C(17)	1.494(13)	C(13)—C(14)	1.309(15)
C(14)—C(15)	1.472(18)	C(16)—C(15)	1.502(18)
C(15)—O(19)	1.187(23)	C(16)—C(17)	1.323(15)
N(2)—Ge(1)—O(11)	101.6(3)	N(2)—Ge(1)—N(2)′	118.3(3)
O(11)—Ge(1)—O(11)′	109.0(3)	Ge(1)—N(2)—Si(3)	119.9(4)
Ge(1)—N(2)—Si(4)	118.9(4)	Si(4)—N(2)—Si(3)	120.4(4)
Ge(1)—O(11)—C(12)	128.5(5)	C(12)—O(18)—O(18)′	107.2(6)
O(11)—C(12)—O(18)	111.1(7)	O(11)—C(12)—C(13)	107.9(7)
O(11)—C(12)—C(17)	110.1(7)	O(18)—C(12)—C(13)	110.2(7)
O(18)—C(12)—C(17)	102.9(7)	C(17)—C(16)—C(15)	118.9(10)
C(15)—C(16)—C(20)	116.9(10)	C(17)—C(16)—C(20)	124.2(10)
C(12)—C(17)—C(16)	123.5(9)		

Scheme 5

excess **1, 2** + **3b,3c** ⟶

10a : R = N(SiMe₃)₂, R¹ = R⁴ = ᵗBu
10b : R = N(SiMe₃)₂, R¹ = R⁴ = ᵗAmyl
10c : R = N(SiMe₃)ᵗBu, R¹ = R⁴ = ᵗAmyl

2. Copolymerization System. ESR study of the copolymerization system using an excess amount of the germylene **1** or **2** with *p*-benzoquinone derivative **3b** or **3c** has been carried out for the detection of germyl radicals (Scheme 5).

The spectrum of a mixture of **1** and **3b** (50 mol % for **1**) showed a quintet signal with a ratio of 1:2:3:2:1, ascribable to a germyl radical (**10a**) located at both polymer ends (Figure 6). The coupling observed (10.06 G) is due to the two nitrogen atoms (I = 1) on the germanium. Ten satellite peaks due to ⁷³Ge (I = ⁹/₂) were also observed.[19] The smaller g value of **10a** (g = 1.9986) compared with Me₃Ge• (g = 2.010)[20] and Ph₃Ge• (g = 2.0054)[21] clearly indicates that the geometry of **10a** is different from that of the germyl radicals bound to three

(19) Since the natural abundance of ⁷³Ge is 7.6%, the intensity of the satellites is much lower than that of the main signal.

(20) Bennett, S. W.; Eaborn, C.; Hudson, A.; Hussain, H. A.; Jackson, R. A. *J. Organomet. Chem.* **1969**, *16*, P36.

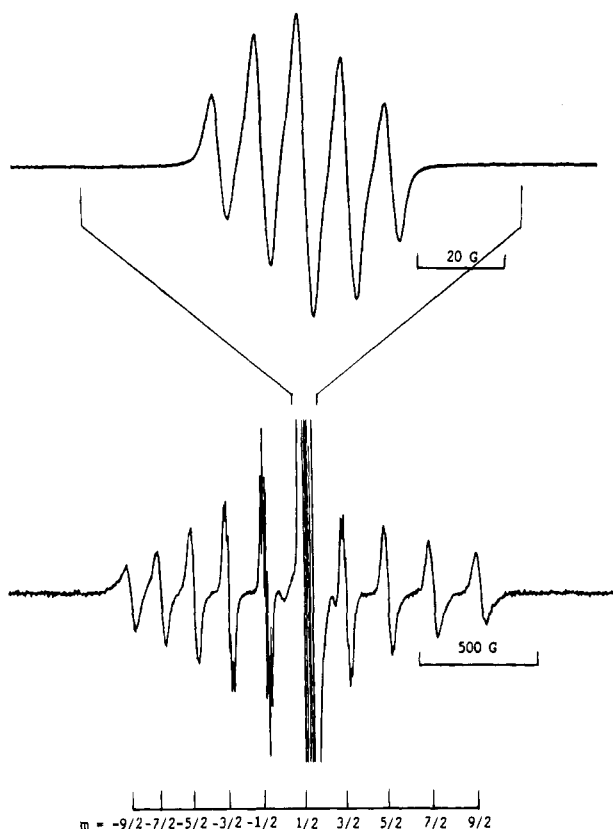(21) Hudson, A. *Electron Spin Reson.* **1976**, *3*, 248.

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Figure 6. ESR spectrum of a reaction mixture of 1 with 50 mol % of 3b.

Table 6. ESR Parameters for Germyl Radicals[a]

germylene	quinone	germyl radical	hfc values (A_N and A_{Ge})/G	g
1	3b	10a	10.06 (N) 166 (^{73}Ge)	1.9986
1	3c	10b	10.03 (N) 167 (^{73}Ge)	1.9985
2	3c	10c	10.97 (N) 159 (^{73}Ge)	1.9991
		•Ge[N(SiMe₃)₂]₃	10.6 (N)[b] 171 (^{73}Ge)	1.9991[b]
		•Ge[N(SiMe₃)ᵗBu]₃	12.9 (N)[b] 173 (^{73}Ge)	1.9998[b]

[a] ESR measurement was carried out at 20 °C in *n*-hexane. [b] The values were taken from the literature.[24]

carbon atoms and hence is of a structure rather close to a pyramidal shape due to the electronegative oxygen atoms bound to the germanium atom.[22] The similarity in *g* values between 10a and triaminogermyl radicals, •Ge[N(SiMe₃)₂]₃ and •Ge[N(SiMe₃)ᵗBu]₃[23] generated by photolysis of 1 and 2, respectively, indicates that they have a similar geometry on the germanium atom.

The similar ESR signal could be observed until 98 mol % of 3b was added to the solution of 1. When an equimolar amount of 3b to 1 was added, the signal completely disappeared. Similarly, other germyl radicals 10b,c were observed. The ESR parameters of these germyl radicals are summarized in Table 6.

The hyperfine constant (hfc) values due to the nitrogen atom (A_N) were found to be smaller than those of the corresponding triaminogermyl radicals. This result can be explained by assuming the decrease of the electron density at the nitrogen atom, which is caused by delocalization of the electron into the hydroquinone unit. The larger A_{Ge} values for 10a—c compared with •GeMe₃ (A_{Ge} = 83 G) indicate a more pyramidalized geometry of the germanium atom but less than that of •GeCl₃ which is almost tetrahedral (A_{Ge} = 220 G).[25] The coupling of the unpaired electron with ^{73}Ge should give satellites with equal intensity. However, the intensities of the outer satellite signals of 10a are lower than those of the inner satellites, and coupling due to the nitrogen is not observed for outer satellites. Since

the rotation of the germyl radical is reduced because of its polymeric structure, the anisotropy of the hyperfine interaction may not be completely averaged.

Generally, the dimerization and disproportionation of radicals on a group 14 element proceed very fast under the condition of diffusion control.[26] However, all of the germyl radicals obtained from the germylenes with 3b and 3c showed remarkable persistency. For example, a half-life time ($t_{1/2}$) of 10a (5.5 × 10⁻³ M) was 14.5 h in *n*-hexane at 20 °C. The Ge—Ge bond formation by the coupling of two germyl radicals is completely prohibited due to the bulkiness of the substituents on the germanium atom. The hydrogen abstraction by the germyl radical from *n*-hexane is not favorable because of the lower bond energy of Ge—H compared to that of C—H for alkanes.[24] In THF the stability of 10a was found to be lower than that in *n*-hexane, and the ESR signal of 10a completely disappeared after 0.5 h. The result may be due to a hydrogen abstraction by the germyl radical from the α-methylene of THF.

In the copolymerization of 1 with 3c, the germyl radical determined by ESR spectroscopy maintained the concentration of approximately 10⁻³ M until the added amount of 3c reached 94 mol % for 1. The ESR signal abruptly decreased when both comonomers became close to equimolar and finally disappeared when the added amount of 3c became exactly equimolar to 1. Concurrently, the viscosity of the reaction mixture increased very rapidly at the final stage. These results imply that the coupling reaction between oligomer radicals took place, leading to the production of higher molecular weight copolymers.

A UV—vis spectrum of a reaction mixture of 1 and 60 mol % of 3c in *n*-hexane showed no absorptions derived from the monomer 3c at 306 and 459 nm, apparently indicating the complete consumption of 3c (Figure 7). The absorptions at 365 nm (peak A) and the broad shoulder (peak B) in the visible region are due to the excess of 1 and the germyl radicals bonded to the polymer chain, respectively.

3. Quenching of the Germyl Radical. The germyl radical 10a was quenched with benzyl disulfide (11) to confirm the biradical structure. When the polymerization was carried out in the presence of 11 at −78 °C, a copolymer (13) having a benzylmercapto group at both polymer ends was obtained along with 12, the addition product of the disulfide to 1 (Scheme 6). The VPO analysis of the resulting copolymer 13 showed the molecular weight (M_n) of 3200 (M_w/M_n = 1.11). Degree of polymerization (DP) value calculated from the ¹H NMR peak areas due to the methylene protons ($δ$ 3.95) of benzyl sulfide and the aromatic protons ($δ$ 7.2—7.4) in 2,5-di-*tert*-butyl-hydroquinone units was 5.43, which is in good agreement with the DP value of 5.17 obtained by VPO. Elemental analysis

(22) (a) Pauling, L. *J. Chem. Phys.* **1969**, *51*, 2767. (b) Gynane, M. J. S.; Lappert, M. F.; Riley, P. I.; Rivière, P.; Rivière-Baudet, M. *J. Organomet. Chem.* **1980**, *202*, 5.

(23) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.

(24) (a) Lappert, M. F.; Lednor, P. W. *Adv. Organomet. Chem.* **1976**, *14*, 345. (b) Rivière, P.; Rivière-Baudet, M.; Satgé, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, pp 399—518.

(25) Roncin, J.; Debuyst, R. *J. Chem. Phys.* **1969**, *51*, 577.

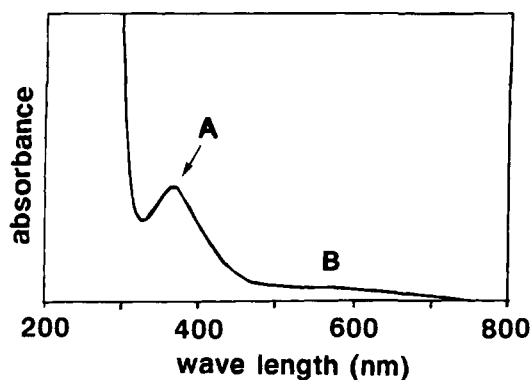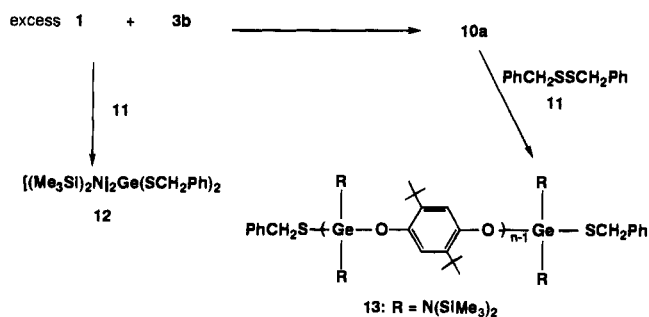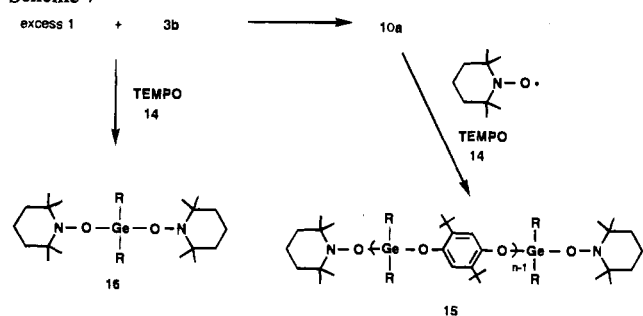(26) Ingold, K. U. In *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York.

Figure 7. UV−vis spectrum of a reaction mixture of 1 and 60% of 3c in *n*-hexane.

Scheme 6

Scheme 7

supported the fact that the product **13** has two sulfur atoms per polymer chain. These results clearly indicate the initial formation of a germyl biradical **10a** by the reaction of **1** and **3b**.

The biradical **10a** was further trapped by TEMPO radical (**14**) to afford a TEMPO group-terminated copolymer (**15**) quantitatively as well as a 2:1 adduct (**16**)[27] from **14** and **1** (Scheme 7). The presence of two TEMPO groups in **15** was confirmed by means of VPO and ^{1}H NMR measurements as well as elemental analysis.

4. Spin Trapping of Germyl Radicals. Spin trapping of the germyl radical **10** has been carried out by using 2,6-di-*tert*-butyl-*p*-benzoquinone (**6**) or 2,4,6-tri-*tert*-butylnitrosobenzene (**17**) as trapping reagent (Scheme 8). For example, when **6** was added to a *n*-hexane solution of **10b** at room temperature, the color of the solution changed from dark brown to red, indicating that the germyl biradical **10b** was converted completely to a semiquinone biradical (**18b**). Reprecipitation of the product into a mixture of acetonitrile and ethyl ether gave a red-colored copolymer (**18b**), quantitatively.

The ESR spectrum of **18b** in *n*-hexane showed a 1:2:1 triplet signal due to the terminal semiquinone radical (A_H = 1.08 G, g = 2.0046, spin concentration = 3.96 × 10^{19} spins/g, Figure

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(27) The formation of the 2:1 adduct **16** shows that the germylene can react with a radical species, indicating the biradical feature of the germylene. The X-ray structural analysis of **16** will be reported elsewhere.
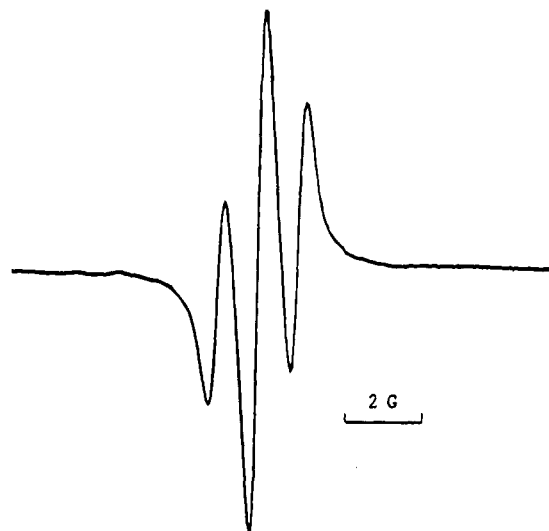

Figure 8. ESR spectrum of an *n*-hexane solution of **18b** at 20 °C.

8). The number of semiquinone radicals per one polymer chain (*N*) was determined by the spin concentration and molecular weight values as *N* = 2.15, which is very close to the theoretical value of 2.00.

The other germyl radicals **10a** and **10c** have also successfully been trapped by **6** to give the corresponding copolymer biradicals **18a** and **18c**, respectively (Table 7).[28] All these *N* values lie in the range of 1.36−2.15, which can be taken as close to the theoretical value within experimental error, and hence, definitely support the biradical structure **10**. The ESR parameters and the absorptions in IR and UV spectroscopies of the spin-trapped copolymers are summarized in Table 8.

The spin trapping of **10a** and **10b** using **17** also took place smoothly to give the corresponding copolymers **19a** and **19b** having two anilino radicals. The ESR spectrum of the *n*-hexane solution of **19b** showed a triple triplet signal due to the terminal anilino radical. No signal due to nitroxide radical was observed. Steric effect and a relatively strong Ge−O bond demand the selective formation of anilino radicals. The coupling constants due to the nitrogen atom and two aromatic protons at the meta position are A_N = 8.44 G and A_H = 2.80 G, respectively. The smaller A_N value compared with that of the anilino radical obtained by the spin trapping of triethylsilyl radical with **17** (A_N = 10.33, A_H = 1.96 G)[29] indicates that the electrons are delocalized in the aromatic ring. The copolymer showed red color both in solution and as a solid. UV−vis spectrum of **19b** in *n*-hexane showed the broad absorption at 479 nm due to the anilino radical[30] which is responsible for the red color of the copolymer. The number of anilino radicals per polymer chain of **19a** and **19b** was 1.69 and 1.91, respectively (Table 7). These results are in good agreement with those of the spin trapping with **6**.

It is known that semiquinone radicals are easily oxidized in air to give the corresponding peroxide.[30] However, the spin adducts **18a**, **18b**, and **18c** are quite stable both in solid state

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(28) Slight decrease of the number of semiquinone radicals (*N* in Table 7) for **18a** indicates that the *tert*-butyl group of the hydroquinone unit is less effective in stabilizing the germyl radical than the *tert*-amyl group. A smaller *N* value for the copolymer **18c** obtained by spin trapping of **10c** indicates that N(SiM₃)₂ group is a better substituent to stabilize the germyl radical than the *tert*-butyl group. The increase of delocalization of the electron into the empty 3d orbital of the silicon atom by replacing the *tert*-butyl group with SiM₃ probably brings about the more persistent nature of the germyl radicals having an N(SiMe₃)₂ group.

(29) Terabe, S.; Konaka, R. *J. Chem. Soc., Perkin Trans. 11* **1973**, 369.

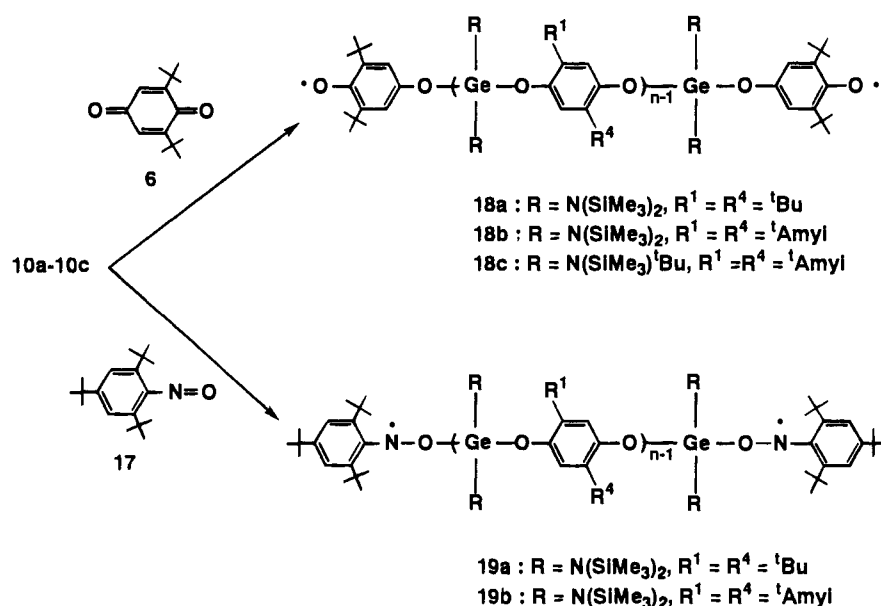(30) Land, E. J.; Porter, G.; Strachan, E. *Trans. Faraday Soc.* **1963**, *59*, 1885.

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Scheme 8

18a : R = N(SiMe₃)₂, R¹ = R⁴ = ᵗBu
18b : R = N(SiMe₃)₂, R¹ = R⁴ = ᵗAmyl
18c : R = N(SiMe₃)ᵗBu, R¹ =R⁴ = ᵗAmyl

19a : R = N(SiMe₃)₂, R¹ = R⁴ = ᵗBu
19b : R = N(SiMe₃)₂, R¹ = R⁴ = ᵗAmyl

Table 7. Results of Spin Trapping of the Germyl Radicals

germyl radical[a]	adduct	M_n^b	M_w/M_n^c	spin conc[d] (spins/g)	N^e
10a	18a	2.73×10^4	1.67	3.52×10^{19}	1.60
10b	18b	3.28×10^4	1.58	3.96×10^{19}	2.15
10c	18c	3.80×10^4	1.33	2.15×10^{19}	1.36
10a	19a	4.60×10^4	1.95	2.22×10^{19}	1.69
10b	19b	2.94×10^4	1.75	3.90×10^{19}	1.91

[a] Germyl radicals were produced by the reaction of a p-benzoquinone derivative with a slight excess of germylene ([quinone]/[germylene] = 0.94) in n-hexane at −78 °C. Yield of the copolymer was quantitative in all cases. [b] Determined by VPO in benzene at 40 °C. [c] Determined by GPC. [d] Spin concentration was measured before isolation of the copolymer. [e] Number of radicals introduced per polymer chain.

Table 8. Spectral Data of the Spin Adducts

spin adduct	ESR parameters[a]	IR (cm⁻¹)	UV (nm)[a]
18a	$g = 2.0047$ $A_H = 1.09$ G	1571	405
18b	$g = 2.0046$ $A_H = 2.0046$	1569	404
18c	$g = 2.0045$ $A_H = 1.08$ G	1574	405
19a	$g = 2.0035$ $A_N = 8.55$ G $A_H = 2.74$ G	b	477
19b	$g = 2.0035$ $A_N = 8.44$ G $A_H = 2.80$ G	b	479

[a] In n-hexane at 20 °C. [b] Not measured.

and in solution. The intensity of the absorption at 404 nm due to the semiquinone radicals did not decrease after an n-hexane solution of **18b** was exposed to air for 24 h. Thus, the semiquinone radicals at the polymer ends are very stable owing to bulky groups on the germanium atom, and hence do not undergo a coupling reaction to give products such as **9** via a peroxide intermediate.

The IR spectrum of **18b** in the solid state showed a weak absorption at 1569 cm⁻¹ due to the terminal semiquinone radicals.[30] The absence of a doublet peak around 1650 cm⁻¹, which is characteristic of the cyclohexadienone ring, indicates no coupling reaction of the semiquinone radicals.
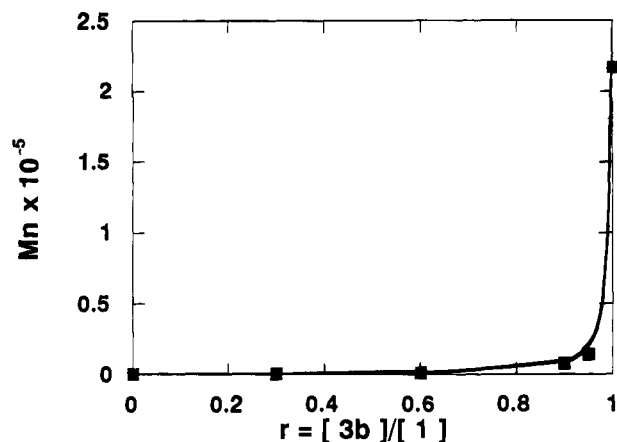
When the copolymerization of **1** and **3b** was carried out in the presence of **6** (feed molar ratio **1:3b:6** = 100:24:3) in

n-hexane, the germyl radical coexisted with the semiquinone radical. The ESR spectrum of the reaction mixture indicated that the concentration ratio of the germyl radical and the semiquinone radical was 76:24. The intensity of the signal did not change for a few minutes, indicating no bond formation between the germyl radical and the semiquinone radical due to steric hindrance. When the feed ratio was changed to **1:3b:6** = 100:52:6.5, the semiquinone radical was formed predominantly (germyl radical:semiquinone radical = 42:58). Furthermore, when quinone **3b** was added up to the equimolar amount for **1**, then the signal of the germyl radical completely disappeared and the signal due to the semiquinone radical remained. The final product is probably the copolymer **18b**, having two semiquinone radicals at the polymer ends.

5. Relationship between Monomer Feed Ratio and Molecular Weight. The copolymerization behavior depends on the combination of the two monomers. In many cases the molecular weight of the product copolymers was very high regardless of the monomer feed ratio. In the case of the reaction between **1** and **3b**, however, a clear relationship between the monomer feed ratio and the number-average molecular weight of the copolymer was observed. The copolymerization was carried out by addition of **3b** to an excess of **1** in n-hexane at −78 °C. The reaction mixture was allowed to warm up to room temperature, and the resulting germyl radical and unreacted **1** were quenched with TEMPO radical **14** giving rise to alternating copolymer **15** having a TEMPO group at both chain ends along with **16**.

The relationship between the feed ratio $r = [3b]/[1]$ and molecular weight (M_n) of the mixture of **15** and **16** is shown in Figure 9. The M_n value ($M_n = 800$) is quite low at $r = 0.3$, which is due to the formation of a mixture of **15** (M_n of the isolated sample = 1070) and a large amount of **16**. The M_n value moderately increases with an increase of r until $r = 0.9$. At $r = 0.9$, the value became 7700. A drastic increase of the M_n value was observed above $r = 0.9$; at $r = 0.95$, M_n was 14,200. At the equivalent point ($r = 1.0$), M_n reaches 2.1×10^5.

These behaviors are identical with those observed in polycondensation between two bifunctional monomers such as a glycol and a dicarboxylic acid diester to produce a polyester. It is therefore possible to treat the copolymerization of **1** and **3b** as a typical polycondensation type of two bifunctional mono-

Figure 9. Relationship between the feed ratio and M_n in the copolymerization of **1** and **3b** in *n*-hexane at −78 °C for 5 min. The solid line was obtained according to $P_n = (1 + r)/(1 − r)$.

Figure 10. Relationship between the feed ratio and M_n in the copolymerization of **1** and **3g** in toluene at −78 °C for 5 min: (●) M_n of the copolymer obtained from **1** and **3g**; (■) average M_n of the mixture of copolymer **15** and the adduct of germylene and TEMPO radical **16**.

mers. The average degree of polymerization (P_n) is expressed with the feed ratio (r) and the extent of reaction (p) for **3b** by the following equation.[31]

$$P_n = (1 + r)/(2r(1 − p) + (1 − r))$$

Since an excess of germylene was used for **3b** ($p = 1$), the equation can be described with a more simple form.

$$P_n = (1 + r)/(1 − r)$$

The calculated M_n value by using this equation is given by the solid line in Figure 9. The experimental data (black squares in Figure 9) are almost on the calculated line. These results imply that both **1** and **3b** behave like a biradical monomer: the reactivities of **1** and its radical species and of **3b** and its radical species are very similar and the polymerization proceeds via biradical propagating ends. This result strongly supports the view that the copolymerization of **1** with **3b** proceeds via a biradical mechanism.

For the polycondensation of two bifunctional monomers, polydispersity at $r = 1$ is described using the extent of reaction p as follows.

$$M_w/M_n = 1 + p$$

The observed polydispersity (M_w/M_n) of the copolymer **4b** was found to be 2.04, which is in good agreement with the calculated value of 2 ($p = 1$).

The relationship between the feed ratio of the two monomers and the molecular weight of the copolymer greatly depends on the combination of the germylene and the *p*-benzoquinone derivative employed. Figure 10 shows the relationship between the feed ratio $r = $ [**3g**]/[**1**] and the molecular weight of the products. The molecular weight (M_n) reached 1.8×10^5 at $r = 0.3$. The copolymer **4g** having high molecular weight was obtained even at such a smaller r value, and a drastic increase of the molecular weight around the equivalent point could not be observed, implying that the rate of propagation is much faster than that of initiation. It was very difficult to detect a germyl radical in the copolymerization of **1** with **3g** because the concentration of the propagating ends is probably too low.

The molecular weight of copolymer **4g** could be controlled by addition of TEMPO radical **14** to the copolymerization system as a monofunctional monomer. The sucessive addition
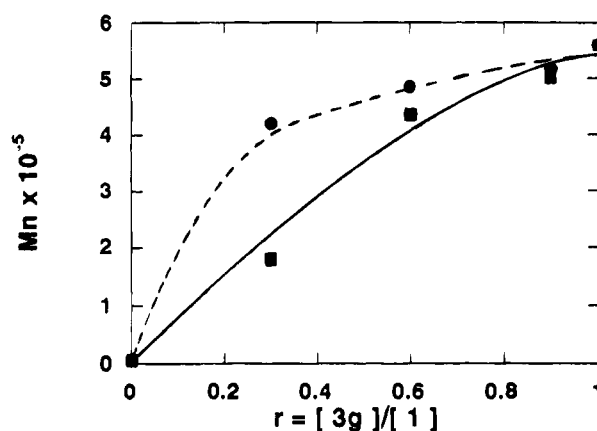
of **14** did not have any effect on the molecular weight, probably because the reaction of **1** and **3g** took place very rapidly. However, control has successfully been achieved by addition of a mixture of **3g** and **14** into **1** (Figure 10). With an increase in the amount of **14**, the molecular weight of the resulting copolymer decreased and its polydispersity increased. The GPC profile of the resulting copolymer showed two peaks, and the intensity of the peak in lower molecular weight region increased with an increase of **14**. These results may be explained by assuming that **14** is involved in generation of a monoradical (**20**) as an initiator and less involved in quenching the propagating radicals (Scheme 9).

6. Reaction Mechanism. In the present copolymerization, the following four elementary reactions are operative: a monomer−monomer reaction (eq 1), monomer−radical reactions (eqs 2 and 3), and a radical−radical coupling reaction (eq 4), respectively (as a representative of *p*-benzoquinone derivatives, *p*-benzoquinone is given here as **3**) (Scheme 10).

Reaction 1 is an initiation reaction to generate a biradical species, which involves the oxidation of the germylene and reduction of the quinone. Reactions 2 and 3 correspond to a propagation, producing an alternating unit. Reaction 4 is a radical coupling reaction to cause an increase and/or jump of the molecular weight. Other conceivable reactions forming homo units of Ge−Ge and **3**−**3**, respectively, are ruled out due to the steric hindrance caused by a bulky R group in R_2Ge and the thermodynamically very unstable O−O bond formation, respectively.

On the basis of the experimental findings and of the above brief survey of the elementary reactions, the following mechanism has been proposed for the copolymerization (Scheme 11). The first step is the formation of a genetic biradical species (**21**), a short-lived intermediate with two unpaired electrons, one delocalized on the semiquinone ring and the other on the germanium atom.[32] Since a germylene has a singlet ground state,[33] direct formation of **21** from **1** and **3** is inconceivable. There are two possible pathways leading to **21**, involving an ion pair intermediate of a germyl cation radical and a semiquinone anion radical via a single electron transfer from **1** to **3**

(31) *Macromolecules, An Introduction to Polymer Science*; Bovey, F. A., Winslow, F. H., Eds.; Academic Press: New York, 1979; pp 180−185.

(32) A similar biradical is proposed for the reaction of tin dichloride with 3,5-di-*tert*-butyl-*o*-quinone. Annan, T. A.; McGarvey, B. R.; Ozarowski, A.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, 439.
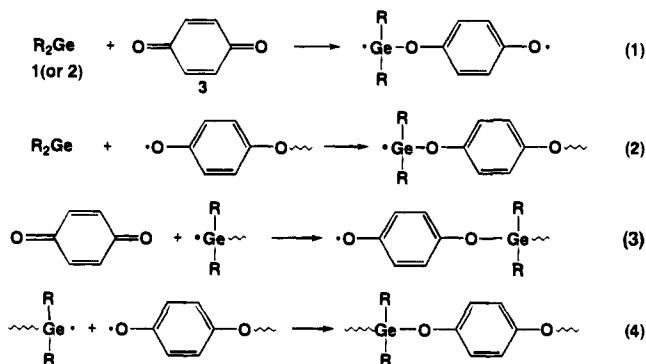
(33) Barthelat, J.-C.; Roch, B. S.; Trinquier, G.; Satgé, J. *J. Am. Chem. Soc.* **1980**, *102*, 4080.
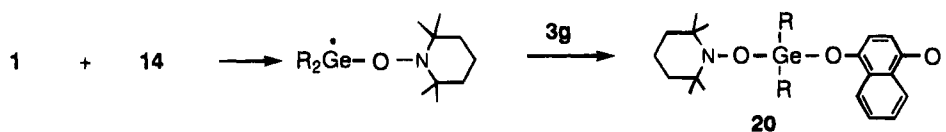
Scheme 9

Scheme 10

and involving a 1-oxa-2-germacyclopropane derivative (oxa-germirane) intermediate.[34]

The resulting biradical **21** further reacts with **1** or **3** to give the corresponding germyl biradical **22** or a semiquinone biradical (**23**). The successive addition of **1** and **3** in an alternating fashion gives a copolymer (**24**) having two germyl radicals at the polymer ends, a copolymer (**25**) having two semiquinone radicals, and/or a copolymer (**26**) having a germyl radical and a semiquinone radical. The coupling between these biradicals takes place concurrently to the addition of monomers to propagating ends.

Depending on the combination of **1** (or **2**) with **3**, the rate of the elementary reactions changes greatly and affects the copolymerization features. In one case, the observations of the monomer feed ratio vs molecular weight (Figure 9) and the molecular weight distribution in the copolymerization of **1** with **3b** indicated that the rates of the initiation reaction 1, the propagation reactions 2 and 3, and the coupling reaction 4 were comparable. In the copolymerization of **1** with **3g**, however, the propagation reactions 2 and 3, and probably the coupling reaction 4 also proceeded much faster than the initiation reaction 1 as observed in Figure 10.

In the present copolymerization, all chemical species involved in the propagating process have biradical structures; the copolymerization proceeds via a *biradical propagation mechanism*.

Conclusion

The syntheses of novel germanium-containing polymers have been achieved by the copolymerization of germylenes and *p*-benzoquinone derivatives. The copolymerization took place without an added initiator at a low temperature to give 1:1 alternating copolymers with high molecular weight in high yields. The present methodology which involves the combination of a reductant monomer and an oxidant monomer (oxidation—reduction copolymerization) would be applicable to the preparation of various organometallic polymers of other group 14 elements. The results of the extensive studies clearly show that the copolymerization proceeds via biradical propagating species. In the polymerization chemistry, a biradical mechanism has often been discussed, particularly for the thermal polymerization of styrene. In 1937, Flory proposed a biradical

intermediate ("Flory's biradical").[35] Later, Tobolsky ruled out the biradical mechanism.[36] Mayo extensively carried out kinetic studies and found that the rate of polymerization is proportional to [styrene]$^{2.5}$ suggesting a bimolecular reaction involving a Diels—Alder dimer and/or a charge-transfer complex. However, the polymerization was found to be a monoradical system.[37] In the thermal, spontaneous, and photoinduced alternating copolymerizations, a biradical intermediate was considered but the mechanism was not well clarified.[38] Consequently, the biradical polymerization reaction has not been established yet. The present copolymerization, therefore, is the first example with clear-cut evidence of a "biradical polymerization mechanism".

Experimental Section

Measurements. NMR spectra (^{1}H, ^{13}C) were recorded on a Bruker AM-250T spectrometer. CP/MAS ^{13}C NMR spectra were recorded on a Bruker MSL400 spectrometer using the carbonyl carbon of glycine (176.03 ppm) as external standard. IR spectra were taken on a Shimazdu IR-460 spectrometer. UV—vis spectra were obtained on a Shimazdu UV-160 spectrophotometer by using a 10 mm quartz cell. Gel permeation chromatographic (GPC) analysis was carried out by using TSK-GEL G5000H or Hitachi gelpack A-130 or A-150 GPC columns (chloroform eluent, polystyrene standard). The molecular weight data were obtained by a Corona 117 vapor pressure osmometer (VPO) in benzene at 40 °C. Mass spectra were taken on a JEOL JMS-D300 mass spectrometer. ESR spectra were taken on a Bruker ESP300 spectrometer. The spin concentrations of the radicals were determined by comparison of the ESR signal of a *n*-hexane solution of 2,2,6,6-tetramethylpiperidinyloxyl [TEMPO, Aldrich). The X-ray crystallographic analysis data were collected on a Rigaku Denki AFC-5PR diffractometer and corrected for Lorentz polarization effects. All calculations were performed by the ACOS2000 computer at Tohoku University using the applied liberty program UNICSIII System and Rantan 81 direct method program with some modification.

Materials. Germylenes were prepared by the reaction of GeCl$_2$ 1,4-dioxane complex and appropriate lithium amides according to the literature.[39] The *p*-benzoquinone derivative **3c** was obtained by the oxidation of 2,5-di-*tert*-amylhydroquinone with nitric acid and was purified by recrystallization and sublimation. Other *p*-benzoquinone derivatives were commercially available. Benzyl disulfide was purified by recrystallization from ethanol. TEMPO radical **14** and nitroso compound **17** were used without purification. Benzene, toluene, *n*-hexane, diethyl ether, and THF were distilled from sodium—benzophenone. Acetonitrile and chlorobenzene were distilled from calcium hydride. Polymerization was performed in a glass reaction flask under argon.

Copolymerization of Germylene 1 with *p*-Benzoquinone (3a). To a toluene solution (6 mL) of germylene **1** (0.328 g, 0.83 mmol) was added a toluene solution (2 mL) of *p*-benzoquinone (**3a**) (88 mg, 0.81 mmol) at −78 °C with stirring. After being stirred for 1 h, the viscous reaction mixture was poured into 130 mL of acetonitrile under argon. The white precipitates were collected by filtration and dried in vacuo

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(34) The definite evidence for 1,2-addition of a germylene to a carbonyl group has not been reported. However, an oxagermirane derivative is postulated as intermediate for the oligomerization of a halogermylene with an aldehyde.[6]

(35) Flory, P. J. *J. Am. Chem. Soc.* **1937**, *59*, 241.
(36) Johnson, D. H.; Tobolsky, A. V. *J. Am. Chem. Soc.* **1952**, *74*, 938.
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(38) (a) Kokubo, T.; Iwatsuki, S.: Yamashita, Y. *Makromol. Chem.* **1969**, *123*, 256. (b) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 440. (c) Brandt, M. W.; Mulvaney, J. E.; Hall, H. K., Jr. *Macromolecules* **1988**, *21*, 1553. (d) Hall, H. K., Jr.; Itoh, T.; Iwatsuki, S.; Padias, A. B.; Nulvaney, J. E. *Macromolecules* **1990**, *23*, 913. (e) Li, T.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1990**, *23*, 3899. (f) Li, T.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1990**, *23*, 3904.
(39) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Lappert, M. F.; Thorne, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1551.

Scheme 11
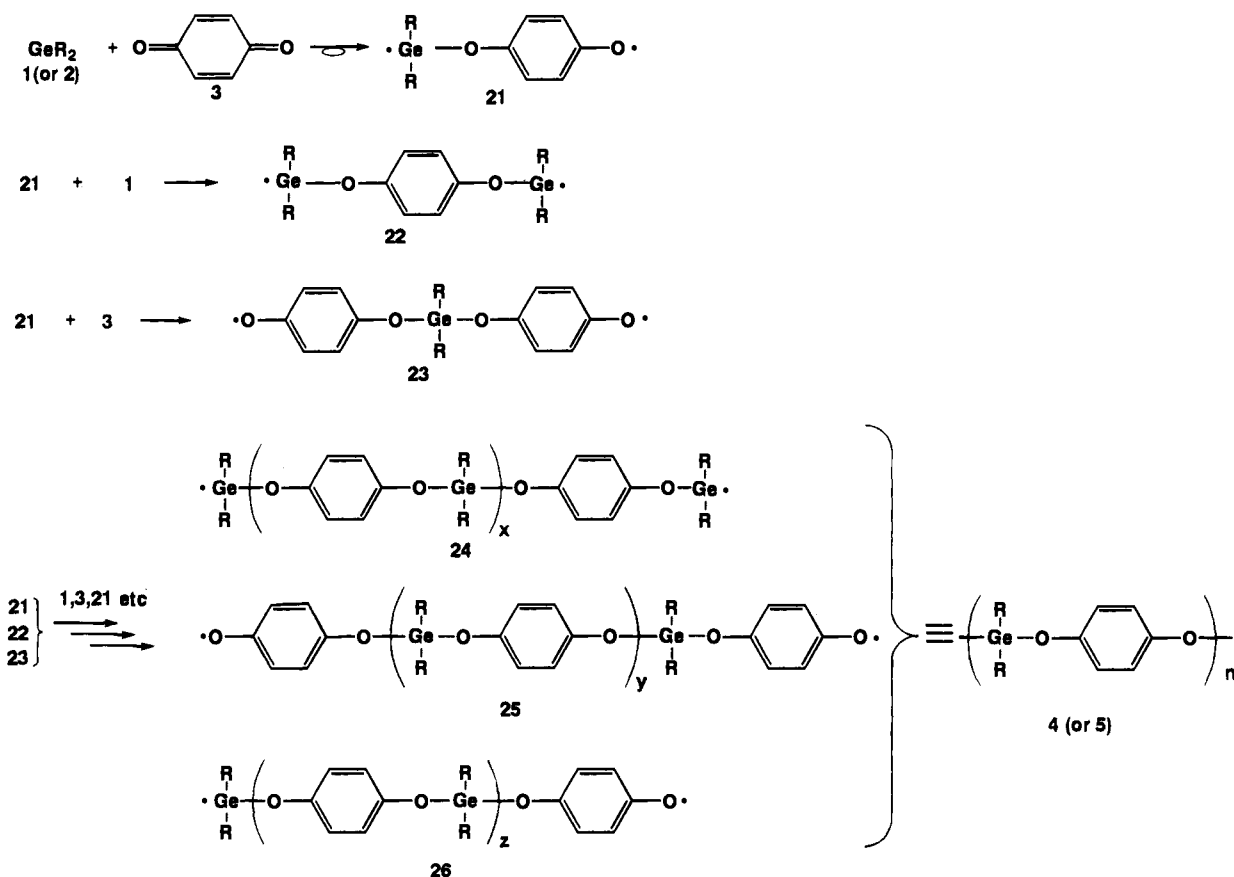
to give 0.408 g of copolymer **4a** (100% yield): ^{1}H NMR (CDCl$_3$) δ 0.25 (s, SiMe$_3$, 36H), 6.92 (s, Ar, 4H); ^{13}C NMR (CDCl$_3$) δ 5.54 (SiMe$_3$), 120.9 (CH or Ar), 150.1 (C—O); IR 2950, 1501, 1251, 1205, 842, 761, 673 cm^{-1}. Anal. Calcd for (C$_{18}$H$_{40}$GeN$_2$O$_2$Si$_4$)$_n$: C, 43.11; H, 8.04; N, 5.59. Found: C, 43.58; H, 8.24; N, 5.53.

Copolymerizations using other *p*-benzoquinone derivatives and germylenes were carried out in a similar manner.

Copolymer 4b: ^{1}H NMR (CDCl$_3$) δ 0.29 (s, SiMe$_3$, 36H), 0.94 (br, Bu, 9H), 1.52 (br, Bu, 9H), 6.78 (br, Ar, 2H); ^{13}C NMR (CDCl$_3$) δ 6.85 (SiMe$_3$), 31.6 (*Me$_3$*C), 34.8 (Me$_3$*C*), 121.7 (CH of Ar), 136.2 (*C*-Bu), 150.8 (C—O); IR 2950, 1480, 1357, 1255, 1115, 1101, 849, 751, 671 cm^{-1}. Anal. Calcd for (C$_{26}$H$_{56}$GeN$_2$O$_2$Si$_4$)$_n$: C, 50.88; H, 9.20; N, 4.56. Found: C, 50.29; H, 9.14; N, 4.75.

Copolymer 4c: ^{1}H NMR (CDCl$_3$) δ 0.18−0.37 (br, SiMe$_3$, *Me*CH$_2$, 42H), 1.33−2.77 (br, *Me$_2$*C, MeC*H$_2$*, 16H), 6.78 (br, Ar, 2H); ^{13}C NMR (CDCl$_3$) δ 7.1 (SiMe$_3$), 9.4 (*Me*CH$_2$), 27.5−29.0 (*Me$_2$*C), 33.5 (CH$_2$), 37.2−38.6 (Me$_2$*C*), 120.7−125.7 (CH of Ar), 135.5 (*C*-amyl), 149.4 (C—O); IR 1474, 1350, 1251, 1170, 1109, 843, 671 cm^{-1}. Anal. Calcd for (C$_{28}$H$_{60}$GeN$_2$O$_2$Si$_4$)$_n$: C, 52.41; H, 9.42; N, 4.37. Found: C, 51.81; H, 9.33; N, 4.08.

Copolymer 4d: ^{1}H NMR (CDCl$_3$) δ 0.29 (s, SiMe$_3$, 36H), 7.59 (s, Ar, 2H); ^{13}C NMR (CDCl$_3$) δ 5.2 (SiMe$_3$), 121.8 (CH or Ar), 122.1 (C—Cl), 145.8 (C—O); IR 1464, 1356, 1249, 1194, 1077, 849, 759 cm^{-1}. Anal. Calcd for (C$_{18}$H$_{38}$Cl$_2$GeN$_2$O$_2$Si$_4$)$_n$: C, 37.89; H, 6.71; N, 4.91; Cl, 12.45. Found: C, 37.08; H, 6.51; N, 4.67; Cl, 12.66.

Copolymer 4e: ^{1}H NMR (CDCl$_3$) δ −0.02 (s, SiMe$_3$, 36H), 7.10 (br, Ar, 12H); ^{13}C NMR (CDCl$_3$) δ 5.2 (SiMe$_3$), 123.7, 126.4, 127.4, 130.1, 131.4 (Ar), 138.9 (*C*—Ph), 146.4 (C—O). IR: 1502, 1469, 1371, 1248, 1179, 849, 753 cm^{-1}. Anal. Calcd for (C$_{30}$H$_{48}$GeN$_2$O$_2$Si$_4$)$_n$: C, 55.12; H, 7.40; N, 4.29. Found: C, 54.18; H, 7.66; N, 4.41.

Copolymerization of 1 with 3f. A toluene solution (7.5 mL) of **3f** (0.419 g, 2.55 mmol) was added to a toluene solution (5 mL) of **1** (1.004 g, 2.55 mmol) at −78 °C with stirring under argon. The reaction mixture was stirred for 1 h, and the resulting precipitates were collected by filtration, washed with toluene (10 mL × 2), and dried in vacuo to give 1.310 g of **4f** (92%): ^{13}C NMR (solid) δ 7.1 (SiMe$_3$), 16.2 (Me), 125.6 (*C*—Me), 147.9 (C—O); IR: 2945, 1454, 1249, 1071, 876, 850,

757, 670 cm^{-1}. Anal. Calcd for (C$_{22}$H$_{48}$GeN$_2$O$_2$Si$_4$)$_n$: C, 47.39; H, 8.68; N, 5.03. Found: C, 47.04; H, 8.89; N, 5.67.

Copolymer 4g: ^{1}H NMR (CDCl$_3$) δ 0.30 (s, SiMe$_3$, 36H), 7.12 (br, Ar, 2H), 7.39 (br, Ar, 2H), 8.16 (br, Ar, 2H); ^{13}C NMR: (CDCl$_3$) δ 5.7 (SiMe$_3$), 112.6 (C-2,3), 123.2 (C-5,8), 124.9 (C-6,7), 128.7 (C-9,10), 146.2 (C—O); IR 1614, 1588, 1504, 1448, 1373, 1256, 1223, 1063, 907, 869, 834 cm^{-1}. Anal. Calcd for (C$_{22}$H$_{42}$GeN$_2$O$_2$Si$_4$)$_n$: C, 47.91; H, 7.68; N, 5.08. Found: C, 48.20; H, 7.17; N, 5.41.

Copolymer 4h: ^{1}H NMR (CDCl$_3$) δ 0.26 (s, SiMe$_3$, 36H), 2.21 (br, Me, 3H), 7.06 (br, Ar, 2H), 7.38 (br, Ar, 1H), 7.89 (br, Ar, 1H); 8.07 (br, Ar, 1H); ^{13}C NMR (CDCl$_3$) δ 5.9 (SiMe$_3$), 18.6 (Me), 115.1 (C-3), 123.0, 123.1, 124.3 (C-2,5,6,7,8), 126.7, 129.2 (C9,10), 143.0 (C-1), 146.9 (C-4); IR 2945, 1592, 1349, 1253, 1081, 839, 760 cm^{-1}. Anal. Calcd for (C$_{23}$H$_{44}$GeN$_2$O$_2$Si$_4$)$_n$: C, 48.85; H, 7.84; N, 4.95. Found: C, 48.11; H, 7.82; N, 4.79.

Copolymer 4i: ^{1}H NMR (CDCl$_3$) δ 0.26 (s, SiMe$_3$, 36H), 1.97 (br, *Me*-Ar, 3H), 3.62 (br, OMe, 3H), 3.72 (br, OMe, 3H), 6.97 (br, Ar, 1H); ^{13}C NMR (CDCl$_3$) δ 5.57 (SiMe$_3$), 18.0 (*Me*−Ar), 59.8, 60.5 (OMe), 116.0 (CH or Ar), 124.8 (*C*−Me), 140.5, 142.0, 144.1, 146.8 (C—O); IR 2945, 1478, 1249, 1219, 1076, 1011, 955, 870, 756 cm^{-1}. Anal. Calcd for (C$_{21}$H$_{46}$GeN$_2$O$_4$Si$_4$)$_n$: C, 43.83; H, 8.06; N, 4.87. Found: C, 43.10; H, 8.49; N, 4.59.

Copolymer 5a: ^{1}H NMR (CDCl$_3$) δ 0.27 (s, SiMe$_3$, 18H), 1.43 (s, Bu, 18H), 6.94 (s, Ar, 4H); ^{13}C NMR (CDCl$_3$) δ 7.4 (SiMe$_3$), 34.7 (*Me$_3$*C), 55.6 (Me$_3$*C*—N), 121.0 (CH of Ar), 149.9 (C—O); IR 2950, 1494, 1286, 1248, 1180, 1093, 1034, 953, 846, 782, 663 cm^{-1}. Anal. Calcd for (C$_{20}$H$_{40}$GeN$_2$O$_2$Si$_2$)$_n$: C, 51.18; H, 8.59; N, 5.97. Found: C, 51.18; H, 8.59; N, 5.97.

Copolymer 5b: ^{1}H NMR (CDCl$_3$) δ 0.38−0.52 (br, SiMe$_3$, 18H), 0.98 (br, *Bu*−Ar, 9H), 1.46 (br, Bu−N, 18H), 1.61 (br, *Bu*−Ar, 9H), 6.90−7.02 (br, Ar, 2H); ^{13}C NMR (CDCl$_3$) δ 8.5 (SiMe$_3$), 31.5 (*Me$_3$*C−Ar), 36.0 (Me$_3$*C*−Ar, *Me$_3$*C−N), 56.9−58.3 (Me$_3$*C*−N), 122.0 (CH of Ar), 136.6 (*C*−Bu), 148.9 (C—O); IR 2945, 1481, 1352, 1180, 1115, 1030, 852, 755 cm^{-1}. Anal. Calcd for (C$_{28}$H$_{56}$GeN$_2$O$_2$Si$_2$)$_n$: C, 57.83; H, 9.71; N, 4.82. Found: C, 57.68; H, 10.13; N, 4.70.

Copolymer 5c: ^{1}H NMR (CDCl$_3$) δ 0.34 (br, SiMe$_3$, *Me*CH$_2$, 24H), 1.64 (br, Bu−N, MeC*H$_2$*, 34H), 6.90 (br, Ar, 2H); ^{13}C NMR (CDCl$_3$)

8.6 (SiMe₃), 9.8 (*Me*CH₂), 28.1 (*Me₂*C), 34.9 (Me*CH₂*), 36.0 (*Me₃*C—N), 38.7 (Me₂*C*), 56.9–58.4 (C—N), 119.4–124.1 (CH of Ar), 132.8–134.0 (*C*-amyl), 148.9–151.0 (C—O); IR 2955, 1481, 1351, 1253, 1171, 1113, 1031, 847, 732 cm⁻¹. Anal. Calcd for (C₃₀H₆₀GeN₂O₂Si₂)ₙ: C, 59.11; H, 9.92; N, 4.60. Found: C, 58.93; H, 10.00; N, 4.33.

Copolymer 5d: ¹H NMR (CDCl₃) δ 0.35 (s, SiMe₃, 18H), 1.46 (s, Bu, 18H), 7.59 (s, Ar, 2H); ¹³C NMR (CDCl₃) 7.1 (SiMe₃), 34.6 (*Me₃*C), 57.2 (Me₃*C*), 122.1 (CH of Ar), 122.4 (C—Cl), 145.8 (C—O); IR 2955, 1463, 1359, 1248, 1196, 1077, 858, 779, 754 cm⁻¹. Anal. Calcd for (C₂₀H₃₈Cl₂GeN₂O₂Si₂)ₙ: C, 44.63; H, 7.12; N, 5.20; Cl, 13.17. Found: C, 44.42, H, 7.21; N, 5.08; Cl, 13.18.

Copolymer 5e: ¹H NMR (CDCl₃) δ 0.03 (s, SiMe₃, 18H), 1.26 (s, Bu, 18H), 7.13 (br, Ar, 12H); ¹³C NMR (CDCl₃) δ 7.1 (SiMe₃), 34.3 (*Me₃*C), 57.4 (Me₃*C*), 123.8, 126.0, 127.3, 130.1, 131.4 (Ar), 139.3(*C*—Ph), 146.6 (C—O); IR 2955, 1503, 1469, 1371, 1251, 1178, 854, 753, cm⁻¹. Anal. Calcd for (C₃₂H₄₈GeN₂O₂Si₂)ₙ: C, 61.81; H, 9.28; N, 4.51. Found: C, 61.95; H, 8.00; N, 4.41.

Copolymer 5f. The copolymerization was carried out in a similar manner as the reaction of **1** with **3f. 5f:** ¹³C NMR (solid) δ 9.4 (SiMe₃), 17.4 (*Me*—Ar), 35.3 (*Me₃*C), 56.8 (Me₃*C*), 125.4 (*C*—Me), 148.2 (C—O); IR (KBr) 2940, 1455, 1397, 1248, 1180, 1070, 856, 779, 666 cm⁻¹. Anal. Calcd for (C₂₄H₄₈GeN₂O₂Si₂)ₙ: C, 54.81; H, 9.21; N, 5.33. Found: C, 55.12; H, 9.33; N, 4.98.

Copolymer 5g: ¹H NMR (CDCl₃) δ 0.32 (s, SiMe₃, 18H), 1.51 (s, Bu, 18H), 7.15 (br, Ar, 2H), 7.50 (br, Ar, 2H), 8.22 (br, Ar, 2H); ¹³C NMR (CDCl₃) δ 7.4 (SiMe₃), 34.7 (*Me₃*C), 57.2 (Me₃*C*), 112.8 (C-2,3), 123.3, 124.4 (C-5,6,7,8), 128.9 (C-9,10), 146.0 (C—O); IR 2950, 1611, 1584, 1448, 1373, 1248, 1222, 1177, 1148, 1068, 931, 832, 755, 663 cm⁻¹. Anal. Calcd for (C₂₄H₄₂GeN₂O₂Si₂)ₙ: C, 55.50; H, 8.15; N, 5.39. Found: C, 55.10; H, 8.18; N, 5.33.

Copolymer 5h: ¹H NMR (CDCl₃) δ 0.33 (s, SiMe₃, 18H), 1.41 (s, Bu, 18H), 2.17 (s, *Me*—Ar, 3H), 7.16 (br, Ar, 2H), 7.49 (br, Ar, 1H), 8.17 (br, Ar, 2H); ¹³C NMR (CDCl₃) δ 8.0 (SiMe₃), 19.0 (*Me*—Ar), 34.4 (*Me₃*C), 57.3 (Me₃*C*), 116.6 (C-3), 123.0, 123.6, 124.1 (C-2,5,6,7,8), 126.9, 129.4 (C-9,10), 143.2 (C-1), 146.6 (C-4); IR 2950, 1619, 1597, 1459, 1377, 1350, 1254, 1213, 1164, 1080, 1035, 915, 865, 837, 753, 697, 665, 540, 475 cm⁻¹. Anal. Calcd for (C₂₅H₄₄GeN₂O₂Si₂)ₙ: C, 56.29; H, 8.31; N, 5.25. Found: C, 55.62; H, 8.43; N, 5.09.

Copolymer 5i: ¹H NMR (CDCl₃) δ 0.35 (s, SiMe₃, 18H), 1.43 (s, Bu, 18H), 1.99 (br, *Me*—Ar, 3H), 3.66 (br, OMe, 3H), 3.75 (br, OMe, 3H), 7.06 (br, Ar, 1H); ¹³C NMR (CDCl₃) δ 7.4 (SiMe₃), 18.6 (*Me*—Ar), 34.4 (*Me₃*C), 57.0 (Me₃*C*), 60,0, 60.5 (OMe), 117.3 (CH of Ar), 124.7 (*Me*—Ar), 140.6, 142.0, 143.7, 146.3 (C—O); IR 2950, 1482, 1424, 1402, 1353, 1248, 1219, 1180, 1114, 1075, 857, 987, 858, 758, 667 cm⁻¹. Anal. Calcd for (C₂₃H₄₆GeN₂O₄Si₂)ₙ: C, 50.84; H, 8.53; N, 5.16. Found: C, 50.09; H, 8.58; N, 5.07.

Stability of Copolymer. To a THF solution (7 mL) of **4b** (55 mg) was added 0.4 mL of water, and the mixture was stirred for 24 h at room temperature. The GPC analysis of recovered copolymer indicated no decrease of molecular weight. The IR and ¹H NMR spectra of the revcovered copolymer were identical with those of the starting copolymer. Stability of the copolymer **4g** toward moisture was examined in a similar manner as described above.

Production and Characterization of 7a. A solution of 2,6-di-*tert*-butyl-*p*-benzoquinone (**6**) (1.120 g, 5.08 mmol) in *n*-hexane (10 mL) was slowly added to a solution of the germylene **1** (1.005 g, 2.56 mmol) in *n*-hexane (4 mL) at 0 °C with stirring under argon, and the mixture was stirred for 10 min. The color of the solution changed to red, and white precipitates were formed in the course of the addition. The reaction mixture was cooled to −78 °C. The white precipitates were collected with filtration, washed with cold *n*-hexane (6 mL), and dried in vacuo (1.306 g, 62%): ¹H NMR (CDCl₃) δ 0.39 (s, SiMe₃, 36H), 1.20 (br, Bu, 36H); ¹³C NMR (CDCl₃) δ 5.9 (SiMe₃); ¹³C NMR (solid) 5.7 (SiMe₃), 30.1 (*Me₃*C), 35.1 (Me₃*C*), 80.9 (C—O), 140.0 (CH=), 145.6 (*C*—Bu), 185.5 (C=O); IR (KBr) 2940, 1663, 1637, 1471, 1384, 1355, 1320, 1252, 1197, 1153, 1102, 1042, 1007, 955, 877, 755, 722, 670 cm⁻¹. Anal. Calcd for C₄₀H₇₆GeN₂O₄Si₄: C, 57.61; H, 9.18; N, 3.36. Found: C, 57.29; H, 9.25; N, 3.28.

Production and Characterization of 7b. A solution of **6** (0.700 g, 3.18 mmol) in *n*-heaxne (6 mL) was added to a solution of the germylene **2** (0.578 g, 1.60 mmol) in *n*-hexane (3 mL) at 0 °C under

argon atmosphere, and the reaction mixture was stirred for 10 min. After removal of half the volume of the solvent, the mixture was cooled to −78 °C. The white crystals were collected and washed with cold *n*-hexane (2 mL × 2) and then dried in vacuo (1.053 g, 82%): ¹H NMR (CDCl₃) δ 0.39 (s, SiMe₃, 18H), 1.16 (br, *Bu*C=, 36H), 1.57 (s, Bu—N, 18H), 6.50 (very br, CH=, 2H); ¹³C NMR (CDCl₃) δ 7.5 (SiMe₃), 29.6 (*Me₃*CC=), 35.0 (*Me₃*C—N), 56.5 (Me₃*C*—N); ¹³C NMR (solid) 8.6 (SiMe₃), 29.9 (*Me₃*CC=), 35.3 (*Me₃*C—N, Me₃CC=), 56.6 (Me₃*C*—N), 81.2 (C—O), 140.3 (CH=), 145.1, 145.6 (*C*—Bu), 185.9 (C=O); IR (KBr) 2950, 1659, 1636, 1472, 1356, 1251, 1179, 1039, 1002, 954, 925, 865, 780, 759 cm⁻¹. Anal. Calcd for C₄₂H₇₆GeN₂O₄Si₂: C, 62.91; H, 9.55; N, 3.49. Found: C, 62.97; H, 9.67; N, 3.42.

Synthesis of 9a. A solution of **6** (0.704 g, 3.19 mmol) in *n*-hexane (8 mL) was added to a solution of **1** (0.626 g, 1.59 mmol) in *n*-hexane (4 mL) at 0 °C with stirring under argon. The color of the solution changed to red, and the white precipitates were gradually formed. After the mixture was stirred for 1 h, 15 mL of *n*-hexane was added to dissolve the precipitates. The exposure of the solution to air for 12 h at room temperature gave **9a** in the form of yellow crystals (0.950 g, 69%): dp = 189 °C; ¹H NMR (CDCl₃) δ 0.33 (s, SiMe₃, 36H), 1.20 (s, Bu, 18H), 1.25 (s, Bu, 18H), 6.46 (d, CH=, 2H, J = 3.1 Hz), 6.81 (d, CH=, 2H, J = 3.1 Hz); ¹³C NMR (CDCl₃) δ 5.7 (SiMe₃), 29.1, 29.4 (*Me₃*C), 34.7, 35.4 (Me₃*C*), 98.3 (C—O), 132.9, 135.9 (CH=), 145.3, 149.9 (*C*—Bu), 186.2 (C=O); IR (KBr), 2950, 1665, 1642, 1355, 1324, 1250, 1066, 1018, 944, 872, 757 cm⁻¹. Anal. Calcd for C₄₀H₇₆GeN₂O₆Si₄: C, 55.47; H, 8.85; N, 3.23. Found: C, 55.23; H, 9.24; N, 3.30.

Synthesis of 9b. A solution of **6** (0.917 g, 4.16 mmol) in *n*-hexane (6 mL) was added to a solution of **2** (0.752 g, 2.08 mmol) in *n*-hexane (4 mL) at 0 °C with stirring under argon, and the reaction mixture was stirred for 1 h. *n*-Hexane (50 mL) was added to the mixture, and the mixture was exposed to air for 2 weeks. The yellow crystals **9b** were collected and dried in vacuo (0.834 g, 50%): dp = 193−194 °C; ¹H NMR (CDCl₃) δ 0.38 (s, SiMe₃, 18H), 1.20 (s, *Bu*C=, 18H), 1.25 (s, *Bu*C=, 18H) 1.52 (s, Bu—N, 18H), 6.58 (d, CH=, 2H, J = 2.9 Hz), 6.84 (d, CH=, 2H, J = 2.9 Hz); ¹³C NMR (CDCl₃) δ 7.3 (SiMe₃), 29.3, 29.5 (*Me₃*C—C), 34.8 (Me₃*C*—C, *Me₃*C—N)), 35.6 (Me₃*C*—C), 55.9 (Me₃*C*—N), 98.3 (C—O), 133.5, 136.37 (CH=), 145.1, 149.9 (*C*—Bu), 186.8 (C=O); IR (KBr) 2950, 1665, 1641, 1472, 1360, 1326, 1133, 1063, 1025, 960, 930, 854, 760 cm⁻¹. Anal. Calcd for C₄₂H₇₆GeN₂O₆Si₂: C, 60.50; H, 9.19; N, 3.36. Found: C, 60.40; H, 9.24; N, 3.38.

Detection of the Germyl Radical by ESR Spectroscopy. In a U-type reaction vessel connected to an ESR tube, toluene solutions of **1** and **3b** were set separately. The whole reaction system was degassed by 4 freeze—thaw cycles and sealed under a reduced pressure at liquid nitrogen temperature. The solution of **3b** was introduced to the solution of **1** at 20 °C by controlling the rate of addition with a two-way stopcock. The resulting reaction mixture was directrly subjected to the ESR measurement at 20 °C.

Quenching of Germyl Biradical 10a with Benzyl Disulfide (11). A mixture of 2,5-di-*tert*-butyl-*p*-bezoquinone (**3b**) (0.226 g, 1.03 mmol) and **11** (0.252 g, 1.02 mmol) in toluene (3 mL) was added to a solution of **1** (0.804 g, 2.04 mmol) in toluene (2 mL) at −78 °C with stirring under argon. The color of the solution changed from yellow to dark brown. Then the reaction mixture was allowed to warm to room temperature, stirred for 1 h, and poured into 50 mL of acetonitrile. The resulting white powdery product was reprecipitated two times from acetonitrile (0.675 g, 85% yield based on **3b**). The ¹H NMR spectrum of the product showed the structure of the alternating copolymer **13**, having the benzylmercapto group at both chain ends: Mₙ = 3200 (n = 5.17) (determined by VPO); ¹H NMR (CDCl₃) δ 0.03−0.40 (br, SiMe₃), 0.78−1.05 (br, Bu), 1.51 (br, Bu), 3.95 (br, CH₂), 6.44−6.82 (br, Ar), 7.16−7.37 (br, Ar); IR 2950, 1487, 1356, 1254, 1181, 1117, 853, 761, 675 cm⁻¹. Anal. Calcd for n = 5.17: C, 50.47; H, 8.93; N, 4.53; S, 2.00. Found: C, 49.56; H, 9.18; N, 4.38; S, 2.34.

The acetonitrile-soluble part was condensed, and the residue was recrystallized from 15 mL of *n*-hexane at −78 °C to give **12** (0.378 g, 58% yield based on **11**, mp 157−158 °C): ¹H NMR (CDCl₃) δ 0.39 (s, SiMe₃, 36H), 3.95 (s, CH₂, 4H), 7.26−7.38 (m, Ar, 10H); ¹³C NMR (CDCl₃) δ 6.3 (SiMe₃), 34.4 (CH₂), 127.0, 128.5, 128.9, 139.0 (Ar); IR 2940, 1484, 1442, 1245, 967, 760, 696 cm⁻¹; MS (70 eV) *m/e* (rel intensity) 625 (10, M⁺ − Me), 517 (100), 411 (15). Anal. Calcd for

$C_{26}H_{50}GeN_2S_2Si_4$: C, 48.81; H, 7.88; N, 4.38; S, 10.02. Found: C, 48.95; H, 8.02; N, 4.48; S, 9.26.

Quenching of the Germyl Radical with TEMPO Radical 14 in Toluene. A solution of **3b** (0.294 g, 1.33 mmol) in toluene (5.4 mL) was added to a solution of **1** (1.058 g, 2.69 mmol) at −78 °C with stirring under argon. Then a toluene solution (2.7 mL) of **14** (0.400 g, 2.56 mmol) was added, and the mixture was stirred for 1 h. The reaction mixture was allowed to warm to room temperature during a period of 0.5 h and stirred for 1 h. Reprecipitation three times from 60 mL of acetonitrile was necessary to separate the polymeric reaction product **15** of **1** with **14** free from the 1:2 adduct **16**. The white precipitates **15** were dried in vacuo (0.823 g, 84% yield based on **3b**): $M_n = 4190$ ($n = 6.68$, determined by VPO); ^1H NMR (CDCl$_3$) δ 0.11−0.47 (br, SiMe$_3$), 0.98−1.54 (br, Bu, Me, CH$_2$), 6.75 (br, Ar); ^{13}C NMR (CDCl$_3$) δ 6.5−8.8 (SiMe$_3$), 16.6−17.0 (CH$_2$), 22.0−22.4 (Me), 30.8−31.9 (*Me*$_3$C), 34.1−34.9 (Me$_3$*C*), 41.3−41.4 (CH$_2$), 60.4−61.8 (C−N), 119.2−120.9 (CH of Ar), 133.6−137.0 (*C*−Bu), 149.3−150.9 (C−O); IR 2945, 1478, 1351, 1248, 1178, 1113, 847 cm^{-1}. Anal. Calcd for $n = 6.68$: C, 50.92; H, 9.38; N, 5.13. Found: C, 49.94; H, 9.19; N, 5.07.

The acetonitrile-soluble part was concentrated, and recrystallization from acetonitrile−ethyl ether (10:1) gave **16** as colorless crystals (0.034 g, 4% yield based on **14**): dp = 147 °C; ^1H NMR (CDCl$_3$) δ 0.41 (s, SiMe$_3$, 36H), 1.21 (br, Me, 24H), 1.34 (br, CH$_2$, 4H), 1.52 (br, CH$_2$, 8H); IR 2915, 1454, 1361, 1250, 1176, 1125, 844, 774, 665 cm^{-1}. Anal. Calcd for $C_{30}H_{72}GeN_4O_2Si_4$: C, 51.05; H, 10.28; N, 7.94. Found: C, 50.57; H, 10.54; N, 7.70.

Spin Trapping of the Germyl Radical by 2,6-Di-*tert*-butyl-*p*-benzoquinone (6). An *n*-hexane solution (23 mL) of **3c** (0.367 g, 1.48 mmol) was added to a solution of **1** (0.619 g, 1.57 mmol) in *n*-hexane (3 mL) at −78 °C with stirring under argon, and the reaction mixture was stirred for 5 min at −78 °C. The dark brown solution was allowed to warm to room temperature, and a solution of **6** (23 mg, 0.10 mmol) in *n*-hexane (3 mL) was added. The red-colored solution was stirred for 1 h, and the solvent was evaporated to dryness. The resulting red product was dissolved in 20 mL of THF and reprecipitated from a mixture of acetonitrile (50 mL)/ethyl ether (25 mL). The precipitate was collected by filtration and dried in vacuo, giving rise to alternating copolymer **18b** quantitatively. The spin trapping experiments using other germyl radicals (**10a**, **10c**) with **6**, and (**10a**, **10b**) with **17** have been carried out in a similar manner.

Relationship between M_n of 4b and the Feed Ratio. An *n*-hexane solution (20 mL) of **3b** (0.631 g, 2.86 mmol) was added to an *n*-hexane solution (6 mL) of **1** (1.192 g, 3.03 mmol) at −78 °C with stirring under argon. After 5 min of stirring, the dark brown colored reaction mixture was allowed to warm to room temperature. Then an n-hexane

solution (4 mL) of **14** (0.047 g, 0.30 mmol) was added. The resulting colorless reaction mixture was condensed and dried in vacuo. The product was dissolved in 40 mL of THF, and the solution was poured into 100 mL of acetonitrile. The precipitates were collected by filtration and dried in vacuo (yield, 1.825 g). Quenching of the germyl radical generated by the other feed ratio was carried out in a similar manner as the above.

Relationship between M_n of 4g and the Feed Ratio. A solution of **3g** (0.307 g, 1.94 mmol) in toluene (25 mL) was added to a solution of **1** (0.849 g, 2.16 mmol) in toluene (4.2 mL) at −78 °C with stirring under argon, and the mixture was stirred for 5 min. The reaction mixture was allowed to warm to room temperature, and a toluene solution (2 mL) of **14** (0.067 g, 0.43 mmol) was added. After the solution was condensed, GPC analysis was carried out by using the crude mixture.

Copolymerization of 1 with 3g in the Presence of 14. A mixture of **3g** (0.453 g, 2.87 mmol) and **14** (0.032g, 0.20 mmol) in benzene (7.2 mL) was added to a benzene solution (4.8 mL) of **1** (1.134 g, 2.88 mmol) at 20 °C with stirring under argon. After being stirred for 1 h, the reaction mixture was poured into 100 mL of acetonitrile and the white precipitates were collected by filtration and dried in vacuo (1.242 g). Experiments for other mixing ratios of **3g** and **14** were carried out in a similar manner as described above.

Supplementary Material Available: Data from the X-ray crystallographic analysis of the cyclic peroxide derivative **9a** of the germylene/*p*-benzoquinone biradical including crystal data, bond lengths, bond angles, atomic parameters, and anisotropic temperature factors (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.