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Novel 2:1 Periodic Copolymers from Cyclic Germylenes and *p*-Benzoquinone Derivatives

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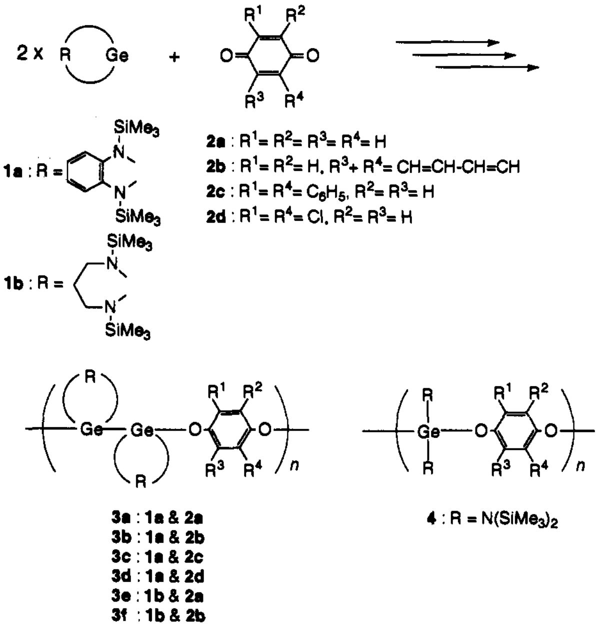
Organometallic polymers and non carbon backbone polymers such as silicon,[1] germanium,[2] and tin[3] have attracted much attention because of their importance in both science and industrial applications. Among them, organogermanium polymers have shown photoactivity and bleaching behavior,[4] strong thermochromic properties,[5] and semiconductive behavior.[6] These polymers are generally synthesized by a polycondensation and an alkali metal coupling reaction.[2,4–6] Recently, we introduced divalent germanium species (germylenes)[2,7] as monomer into polymer synthesis and explored new 1:1 alternating copolymerizations of germylenes with *p*-benzoquinone derivatives[8] and with α,β-unsaturated cyclic ketones.[9] The former produced a thermally stable poly(germanium oxide) derivative[8] with a molecular weight higher than 10^6, and the latter gave a high molecular weight ($M_w > 10^5$) poly(germanium enolate), the first example of a poly(metal enolate) which was unexpectedly stable.[9]

The present communication discloses a synthesis of novel germanium-containing polymers (**3**) by copolymerization of a cyclic germylene (**1**) with a *p*-benzoquinone derivative (**2**). The resulting copolymer **3** has 2:1 periodic germanium(IV) and *p*-hydroquinone units in the main chain. The 2:1 periodically sequence-regulated structure **3** is strikingly different from the 1:1 alternating structure (**4**) derived from an acyclic germylene and **2**.[8] All the copolymers **3** are of relatively high molecular weight and are soluble in common organic solvents. During the copolymerization, germylene **1** was oxidized while *p*-benzoquinone derivative **2** was reduced ("oxidation–reduction copolymerization").[8]

Table 1. Periodic Copolymerization of Germylene **1a** with *p*-Benzoquinone **2a**. Effect of Monomer Feed Ratio[a]

entry	feed ratio **1a**:**2a**	copolymer **3a**		
		yield,[b] %	$M_w \times 10^{-4}$ [c]	M_w/M_n [c]
1	1.0:1.0	86	6.50[d]	2.88
2	2.0:1.0	91	28.7	2.14
3	4.0:1.0	~100	6.99	1.99

[a] The copolymerization was carried out by using **1a** + **2a** = 2.4 mmol in 15 mL of toluene at −78 °C for 1 h under argon. [b] Isolated yield; the yield percent was calculated from monomer **1a** mass for entry 1 and monomer **2a** mass for entry 3, on the assumption that the stoichiometry was 2:1. [c] Determined by gel permeation chromatography (GPC): eluent, $CHCl_3$; flow rate, 1.0 mL/min; column, TSK-GEL G5000H; polystyrene standards. [d] $M_n = 1.52 \times 10^4$ determined by vapor pressure osmometry (VPO) in benzene at 40 °C.



The copolymerization of the five-membered germylene, 1,3-bis(trimethylsilyl)-1,3-diaza-2-germaindan (**1a**)[10] with *p*-benzoquinone (**2a**) took place at −78 °C in toluene without added catalyst to afford 2:1 periodic copolymer **3a** in high yields, regardless of the different monomer feed ratio used (Table 1). Under these reaction conditions, the copolymerization was actually completed within 10 min. The stoichiometry of **1a** and **2a** was 2:1, and the excess monomer remained unchanged after completion of the reaction.

The structure of copolymer **3a** was determined by ^1H and ^{13}C NMR spectroscopies as well as elemental analysis.[11] The ^{13}C NMR spectrum of copolymer **3a** showed six peaks at δ 0.2, 114.5, 118.2, 119.1, 140.3, and 150.8 ppm assignable to the carbon atoms denoted as a–f, respectively, for the 2:1 periodic structure in Figure 1.

A variety of 2:1 periodic copolymers can be synthesized by combining germylene **1a** with the other three *p*-benzoquinone derivatives (**2b-d**) or by combining the six-membered germylene, 1,3-bis(trimethylsilyl)-1,3-diaza-2-germacyclohexane (**1b**)[12] with two *p*-benzoquinone derivatives (**2a** and **2b**). These copolymer-

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(11) Copolymer **3a**: ^1H NMR ($CDCl_3$) δ −0.04 (s, $SiCH_3$, 18H), 0.32 (s, $SiCH_3$, 18H), 6.35 (s, OC_6H_4O, 4H), 6.70 (s, *m*-H of NC_6H_4N, 4H), 6.87 (s, *o*-H of NC_6H_4N, 4H). Elemental analysis data found for **3a** ($(C_{30}H_{48}Ge_2N_4O_2Si_4)_n$): C, 48.09; H, 6.42; N, 6.80. Calcd: C, 47.77; H, 6.41; N, 7.43.

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Table 2. 2:1 Periodic Copolymerization of Germylenes **1** with *p*-Benzoquinone Derivatives **2** under Various Reaction Conditions

	copolymerization[a]				copolymer 3			
	monomers[b]							
entry	1	2	solvent	time, h	structure	yield,[c] %	$M_w \times 10^{-4}$ [d]	M_w/M_n[d]
1	**1a**	**2a**	THF	1	**3a**	96	28.4	1.94
2	**1a**	**2b**	toluene	1	**3b**	93	24.3	2.23
3	**1a**	**2c**	toluene	1	**3c**	84	48.3	1.94
4	**1a**	**2d**	toluene	1	**3d**	93	2.38	3.06
5	**1b**	**2a**	THF	0.5	**3e**	86	39.0	1.67
6	**1b**	**2b**	THF	0.5	**3f**	87	63.9	1.38

[a] Temperature -78 °C. [b] Monomer feed molar ratio, **1**:**2** = 2.0:1.0. [c] Isolated yield. [d] Determined by GPC under analysis conditions similar to those in Table 1.

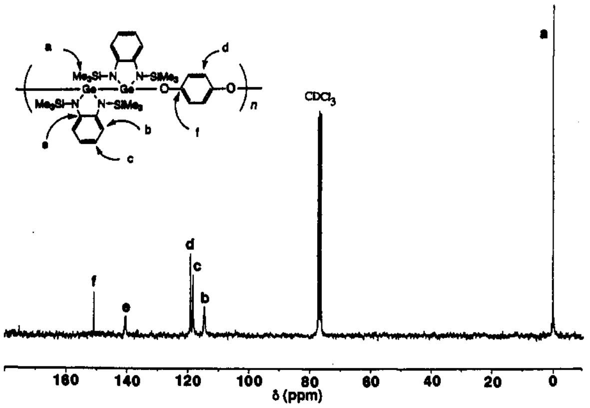
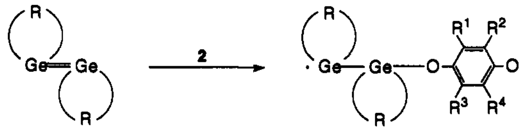


Figure 1. ^{13}C NMR spectrum of copolymer **3a** (entry 1 of Table 1) in $CDCl_3$.

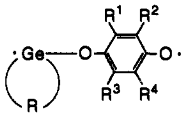
izations similarly occurred without catalyst at -78 °C in toluene or tetrahydrofuran (THF) within 1 h, producing the corresponding 2:1 periodic copolymers (**3a-f**)[13] of relatively high molecular weight in high yields (Table 2).

All these copolymers **3** are fine white powders soluble in common organic solvents like toluene, *n*-hexane, THF, and chloroform and insoluble in acetonitrile and water. Differential scanning calorimetric (DSC) analysis showed that copolymers **3a** and **3b** decomposed at 151.6 and 173.1 °C, respectively, before melting.[14] Copolymers **3a-c** gave transparent films when cast from chloroform.

At present, the copolymerization mechanism of this precise architecture of the 2:1 periodic alignment is not yet clear, but is conceived to proceed via one of the following radical pathways.[15] First, a dimer form of **1**, digermene **5**, may exist in equilibrium with **1**,[16] and a hypothetical monomer **5** reacts with **2** giving rise to a genetic (newly formed) 2:1 biradical intermediate **6**. Successive radical coupling reactions lead to copolymer **3**. Second, a 2:1 periodic propagation proceeds involving a 1:1 biradical intermediate **7**[17] followed by the addition of **1** to give the similar 2:1 intermediate **6**. Third, a genetic 2:1 biradical intermediate **8** formed by the reaction of **7** with **1** leads to **3** via coupling of **8**.



5 **6**



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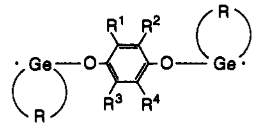

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Further studies on the physical and chemical properties of these polymers having a specific 2:1 periodic structure and the mechanism of the copolymerization are now under way.

Supplementary Material Available: NMR and analytical data for **3b-f** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(12) **1b** is a new compound: pale yellowish liquid (bp 55-62 °C/0.2 Torr); ^{1}H NMR (C_6D_6) δ 0.41 (s, $SiCH_3$, 18H), 1.87 (m, NCH_2CH_2, 2H), 3.25 (m, NCH_2, 4H); ^{13}C NMR (C_6D_6) δ 3.66 ($SiCH_3$), 37.56 (NCH_2CH_2), 47.79 (NCH_2). Anal. Calcd for $C_9H_{24}GeN_2Si_2$: C, 37.39; H, 8.37; N, 9.69. Found: C, 36.98; H, 8.56; N, 9.58.

(13) All data of ^{1}H and ^{13}C NMR spectra as well as elemental analysis satisfactorily supported the structure of copolymers **3b-f**.

(14) The thermal behavior was compared with copolymers **4**. The melt transition temperatures (T_m) of **4** obtained from **2a** and **2b** were 234.7 and 234.9 °C, respectively. The difference in the T_m between **3** and **4** is due to the presence of the Ge-Ge bond in the main chain of **3**.

(15) A biradical mechanism has been established for the 1:1 alternating copolymerization to produce copolymers **4**.[8b] A comprehensive paper (Kobayashi, S.; Iwata, S.; Abe, M.; Shoda, S.) is in preparation.

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