NOTE

Alternating copolymerization of cyclic germylenes with *N*-phenyl-*p*-quinoneimine via oxidation-reduction process

Hiroshi Takano¹, Masafumi Hiraishi¹, Shigeru Yaguchi¹, Satoru Iwata¹, Shin-ichiro Shoda¹ and Shiro Kobayashi^{1,2}

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INTRODUCTION

Divalent germanium species (germylenes) continue to attract a great deal of interest as a heavy carbene analogue in the organometallic chemistry^{1–4} and polymerization chemistry fields.^{5,6} As part of a series reporting our investigations on polymer synthesis via low valent 14th group elements, we reported new polymerization reactions using a germylene as a monomer (*oxidation-reduction copolymerization*): copolymerization of germylenes with *p*-benzoquinones,^{5–9} α,β -unsaturated ketones,^{10–12} thiethane,¹³ and thiiranes.¹⁴ The germylene and acetylene monomer copolymerize, at room temperature, in the presence of a Rh catalyst.¹⁵ Similar copolymerization reactions were observed not only with germylenes but also with stannylenes.^{16,17} There are recent reports of the synthesis of Ge-containing polymers of the germylene-ethynylene type, and the optical properties of the copolymer were measured.¹⁸

As a result of the study of the copolymerization between germylenes and *p*-benzoquinones, we proposed the new biradical copolymerization mechanism based on detailed NMR, electron spin resonance (ESR), and UV-VIS spectroscopic investigations.⁸ We also found that the periodicity of the resulting copolymer strongly depends on the structure of germylenes; the use of an acyclic germylene gave 1:1 alternating copolymers,^{7,8} whereas five- and six-membered cyclic germylenes produced 2:1 periodic copolymers.⁹

Very recently, we reported a new copolymerization between an acyclic germylene and *N*-phenyl-*p*-quinoneimine, producing a 1:1 alternating copolymer of high molecular weight, in high yields.¹⁹ Here, we report a new 1:1 oxidation-reduction alternating copolymerization of cyclic germylenes (**1a–1c**) with *N*-phenyl-*p*-quinoneimine (**2**), which is an extension of our previous study.¹⁹ **1a** is a five-membered, **1b** is a six-membered, and **1c** is a seven-membered cyclic germylene, and they all have a Me₃Si-N group. **1** served as a reductant monomer whereas **2** as an oxidant monomer to give copolymers (**3**) (Scheme 1). In contrast to the previous observation, where the use of cyclic germylenes lead to the formation of 2:1 periodic copolymers,⁹

the present copolymerization using monomer **2** produces all 1:1 alternating copolymers (**3a–3c**).

EXPERIMENTAL PROCEDURE

Materials

Preparation of **1a** and **1b** was previously reported.⁹ **1c** was prepared under argon by the reaction of GeCl₂1,4-dioxane complex with the corresponding lithium amide as previously described,⁸ boiling point; 76 °C/0.10 mmHg, ¹H NMR (C₆D₆) δ 0.23 (s, SiCH₃, 18H), 1.58 (s, NCH₂CH₂, 4H), 3.36 (s, NCH₂, 4H); ¹³C NMR(C₆D₆) δ 1.2 (SiCH₃), 30.6 (NCH₂CH₂), 46.1 (NCH₂). **2** was obtained before.¹⁹ Tetrahydrofuran (THF) was distilled before use. Other solvents were commercial reagents and used as obtained.

Copolymerization

Typically, the copolymerization of **1c** with **2** was carried out as follows: To a THF solution of **1c** (0.13 g, 0.43 mmol in 2.2 mL of THF) was added a 2.1 mL solution of THF containing **2** (0.079 g, 0.43 mmol) at –78 °C, with stirring, under argon. After stirring at –78 °C for 30 min, the reaction mixture was poured into 50 mL of acetonitrile, with stirring. A white precipitate was obtained, collected by filtration, and dried in vacuo to yield 0.11 g (51%) of copolymer **3c**: ¹H NMR (CDCl₃) δ –0.08 (s, SiCH₃, 18H), 1.59 (s, NCH₂CH₂, 4H), 3.02 (s, NCH₂, 4H), 6.60–7.10 (m, Ar-H, 9H); ¹³C NMR (CDCl₃) δ –0.9 (SiCH₃), 32.5 (NCH₂CH₂), 45.4 (NCH₂) 120.6, 123.3, 128.4, 128.8 (CH of Ar), 140.4 (C-NPh), 150.4 (C-N), 153.7 (C-O).

Copolymerizations of **1a** and **1b** with **2** were similarly performed and ¹H and ¹³C NMR data for the copolymers are as follows: **3a**: ¹H NMR (CDCl₃) δ –0.06 (br. s, SiMe₃, 18H), 6.38–7.06 (br. m, Ar-H, 13H); ¹³C NMR (CDCl₃) δ –0.1 (SiCH₃) 114.4, 118.5, 119.3, 121.8, 123.5, 128.7 (CH of Ar), 138.3 (C-N-*o*-phenylene), 140.1 (C-N-phenyl), 149.1 (C-N-*p*-phenylene), 152.8 (C-O-*p*-phenylene). **3b**: ¹H NMR (CDCl₃) δ –0.09 (br. s, SiCH₃, 18H), 1.64 (s, NCH₂CH₂, 2H), 3.15 (s, NCH₂, 4H), 6.65–7.18 (m, Ar-H, 9H); ¹³C NMR (CDCl₃)

¹Department of Materials Chemistry, Graduate School of Engineering, Tohoku University, Aoba-ku, Sendai, Japan and ²Center for Fiber & Textile Science, Kyoto Institute of Technology, Matsugasaki, Kyoto, Japan

Correspondence: Professor S Kobayashi, Center for Fiber & Textile Science, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan.

E-mail: kobayash@kit.ac.jp

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Scheme 1 Alternating copolymerization of cyclic germylene (1) with *N*-phenyl-*p*-quinoneimine (2) to produce an alternating copolymer (3).

Table 1 Alternating copolymerization of cyclic germylene (1) with *N*-phenyl-*p*-quinoneimine (2) under various reaction conditions

Code	Germylene	Copolymerization ^a		Copolymer (3)			
		Monomer feed molar ratio		Yield ^b (%)	$M_w \times 10^{-4c}$	M_w/M_n^c	Structure
		1 : 2	Time (min)				
1	1a	1.0 : 1.0	30	57	3.31	2.59	3a
2	1a	1.0 : 2.0	30	70	5.69	2.43	3a
3	1b	1.0 : 1.0	30	66	11.7	3.39	3b
4	1b	1.0 : 1.0	60	78	20.2	1.77	3b
5	1b	2.0 : 1.0	60	~100	18.6	1.51	3b
6	1c	1.0 : 1.0	30	51	17.2	1.4	3c

^aCopolymerization was carried out in THF at -78 °C under argon.

^bIsolated yields, based on the 1.0 : 1.0 molar stoichiometry of the copolymer structure.

^cDetermined by GPC.

δ -0.5 (SiCH₃), 31.6 (NCH₂CH₂), 46.2 (NCH₂) 120.3, 120.4, 123.5, 128.3 (CH of Ar), 140.6 (C-NPh), 150.7 (C-N), 153.6 (C-O).

Analytical methods

¹H and ¹³C NMR measurements were conducted on a Bruker AC-250 T spectrometer (Yokohama, Japan). Gel permeation chromatographic (GPC) analysis was carried out by using chloroform as eluent, employing polystyrene as standard.

RESULTS AND DISCUSSION

Copolymerization reaction

The copolymerization is shown by Scheme 1. Germynes are so air-sensitive that the copolymerization was carried out under argon atmosphere. Germylene monomers (1a–1c) reacted very rapidly at -78 °C in THF with monomer 2, giving rise to alternating copolymer (3) within 60 min. The copolymerization results are given in Table 1.

Three cyclic germynes (1a–1c) in combination with 2 gave alternating copolymers (3a–3c) with high molecular weight in all reactions. It is to be noted that cyclic germylene 1c (seven-membered) has been studied for the first time here in the oxidation-reduction copolymerizations.^{7–9,19} As a typical example (Code 6), the reaction of germylene 1c with 2 in a 1.0:1.0 molar ratio produced copolymer 3c in 51% yield, having a M_w value of 1.72×10^5 . The ¹H NMR spectrum of 3c is shown in Figure 1. The peak assignments are given in the figure, and the detailed chemical shift data are found in the above experimental section. The peak integral ratio of SiCH₃ and the total

aromatic protons is 18:9, which definitely shows the 1:1 composition structure and confirms the alternating structure. Figure 2 shows the ¹³C NMR spectrum of copolymer 3c, supporting again the alternating structure. The peak assignments are given in the figure, with the detailed chemical shift data found in the experimental section. All these data clearly prove the 1:1 alternating structure of copolymer 3c.

In a similar way, the copolymer structures of 3a and 3b were determined using ¹H and ¹³C NMR spectroscopic methods, and the detailed signal assignment data are given in the experimental section. These data confirm the 1:1 alternating copolymer structure in all cases (Codes 1–5), as indicated in Table 1. With the different monomer ratios, Codes 1 and 2 for 1a and Codes 4 and 5 for 1b, respectively, the copolymers still showed the 1:1 alternating structure, and the alternating structure regulation was well kept, regardless of the monomer ratio. All of the copolymers were white powdery materials that were stable under air for more than a few months. They were not readily degraded due to the moisture in air.

For the mechanism of the copolymerization, monomers 1 and 2 first form biradical 4 via a highly reactive oxidation-reduction process, which is considered a key intermediate in producing the 1:1 alternating copolymer (Scheme 2). Once the intermediate 4 is formed, the following steps, involving a biradical method (fully discussed by ESR spectroscopic studies in previous reports), results in the formation of the alternating copolymer.¹⁹ The formation of a biradical (4) having a germyl radical and a nitrogen radical from 1 and 2 seems to be much preferable to the formation of a biradical having germyl and oxygen radicals. This is due to the higher stability of the nitrogen radical,

Figure 1 ^1H NMR spectrum of copolymer **3c** (CDCl_3).

Figure 2 ^{13}C NMR spectrum of copolymer **3c** (CDCl_3).

Scheme 2 Formation of a key-intermediate of biradical **4**.

which is stabilized by the phenyl group, compared to the stability of the oxygen radical. In addition, the oxygen radical formation is less favored due to the steric repulsion between the *N*-phenyl substituent and the trimethylsilylated substituents on the germylene.¹⁹

The copolymerization of cyclic germynes **1** with a quinoneimine **2** gave 1:1 alternating copolymers **3**, regardless of the germylene structure. These results are quite different from those of the copolymerization of **1** with *p*-benzoquinones, which gave different type of copolymers depending upon the germylene structure, i.e., producing 1:1 alternating copolymers from acyclic germynes^{7,8} and 2:1 periodic copolymers from cyclic germynes such as **1a** and **1b**.⁹ The difference arises from the structural differences between the bond angles and the bond lengths of C-O in the *p*-benzoquinones and C-NPh, which causes steric and reactivity differences in the intermediate radical species and leads to differential monomer reactivity; the nitrogen radical of **4** does not react with **1** but does react with the germynyl radical. It is not possible, at this point, to completely exclude the Ge-Ge bond formation because such bond formation was previously noted.⁹ A more precise explanation requires further detailed studies.

CONCLUSION

Cyclic germynes with five- (**1a**), six- (**1b**), and seven- (**1c**) membered rings, underwent the copolymerization with *N*-phenyl-*p*-quinoneimine (**2**) smoothly at -78 °C to give copolymers (**3a**, **3b** and **3c**, respectively) having a tetravalent germanium unit and a *p*-aminophenol unit, alternately. These results are in striking contrast compared to those of the copolymerization of cyclic germynes (**1a** and **1b**) with a *p*-benzoquinone, which gave 2:1 periodic copolymers.

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