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GERMYLENES AS MONOMERS FOR POLYMER SYNTHESIS

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ABSTRACT

Germylenes have been utilized as monomers for polymer synthesis for the first time. The construction of a repeating unit of O—Ge—O, O—Ge—Ge—O, O—Ge—C, and C—Ge—C as well as the formation of polygermane have been achieved on the basis of new concepts of "oxidation-reduction copolymerization" and "ligand substitution polymerization." The former involves a redox process between a germylene (reductant monomer, M_{red}) and an oxidant monomer (M_{OX}). The M_{OX} employed are *p*-benzoquinone derivatives, cyclic α,β-unsaturated ketones, and substituted acetylenes. During the copolymerization, the germylene (M_{red}) is oxidized and the M_{OX} is reduced ("oxidation-reduction copolymerization"). The reaction mechanism between germylenes and *p*-benzoquinone derivatives has been elucidated as copolymerization proceeding via a biradical propagating species involving a germyl radical and/or a semiquinone radical. This is, to our best knowledge, the first clear-cut evidence for a biradical mechanism in polymerization chemistry. A new type of polymerization for the synthesis of polygermanes has been established by the reaction of germanium dichloride and various alkyllithium compounds ("ligand substitution polymerization").

INTRODUCTION

Progress in polymer science strongly depends on the creation of new polymeric materials having a heteroatom in the repeating unit as one of main factors which will determine their physical and chemical properties. Organometallic polymers having a metal atom in the main chain have attracted the interest of many polymer chemists, because the nature of the metal atom governs the properties of the organometallic polymers. Recently, germanium-containing polymers have become very important substances due to their unique characteristics in materials science [1–3]. For instance, from the electrochemical viewpoint, some germanium-containing polymers show semiconductive properties [3]. To date, all of these polymers have been synthesized by the condensation reaction of a tetravalent germanium dihalide with bifunctional alcohol or carboxylic acid, giving rise to polymers, normally, of very low molecular weight. This fact indicates that the use of tetravalent germanium compounds is not suitable for the production of new polymer materials of higher molecular weight. On the other hand, divalent germanium compounds, germylenes, are very interesting chemical species from the viewpoint of their reactivity toward a variety of oxidants because they have a strong reducing ability owing to the lone pair on the germanium atom [4]. They also have a vacant 4*p* orbital, showing the characteristic feature similar to a Lewis acid. See Fig. 1.

It had been well known that divalent germanium species cannot be isolated as stable compounds having a monomeric structure [5]. It is only recently that germylenes having a bulky electron-donating group were found to exist as a stable monomeric divalent species [6]. This article deals with the result of newly developed polymerization reactions using stable germylenes as monomers. The resulting germanium-containing polymers have a unique structure from which new chemical and physical properties can be expected.

1:1 ALTERNATING COPOLYMERIZATION WITH *p*-BENZOQUINONE DERIVATIVES

Divalent germanium compounds, germylenes, are very reactive as a reductant monomer (M_{red}) in combination with *p*-benzoquinone derivatives as an oxidant monomer (M_{OX}) ("oxidation–reduction copolymerization") [7]. A germylene 1 and

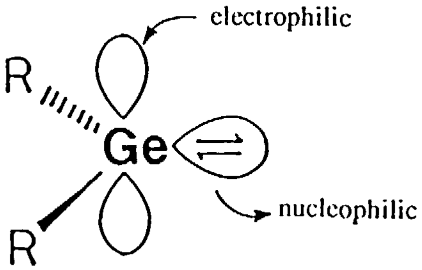


FIG. 1. Structure of germylene indicating the lone pair (nucleophilic center) and the 4*p* vacant orbital (electrophilic center).

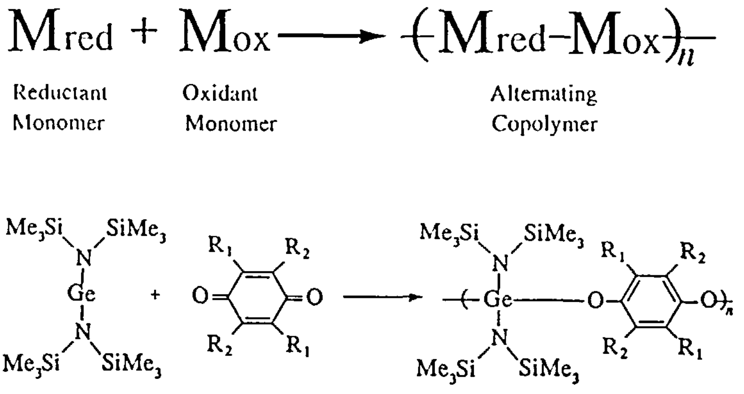
a *p*-benzoquinone derivative **2** reacted without any catalyst at −78°C, and the copolymerization was completed within 1 hour to give an alternating copolymer **3** with high molecular weight, e.g., MW > 10^6, in almost quantitative yield (Scheme 1). It is to be noted that most of the resulting copolymers are soluble in common organic solvents. The new copolymerization involving the redox process enables us to prepare polymers of very high molecular weight, which is very difficult to achieve by using the conventional condensation polymerization of tetravalent germanium compounds. The physical properties of the resulting copolymers, including thermal stability and degradability by γ-rays [8], have been investigated.

The copolymerization mechanism has been definitely proven to be a biradical mechanism based on the results of several experiments: ESR spectroscopy of the reaction mixture, a model reaction, and a trapping reaction of a germyl biradical [9]. One of these experiments involved the end-capping reaction of the germyl biradical **4** by use of dibenzyldisulfide, giving rise to the oligomer **5** as shown in Scheme 2.

A new germanium-containing copolymer having a benzylmercapto group at both polymer ends has been isolated, clearly indicating that a germyl biradical species is a reactive intermediate responsible for copolymerization. This is the first example of polymerization which proceeds via a biradical mechanism.

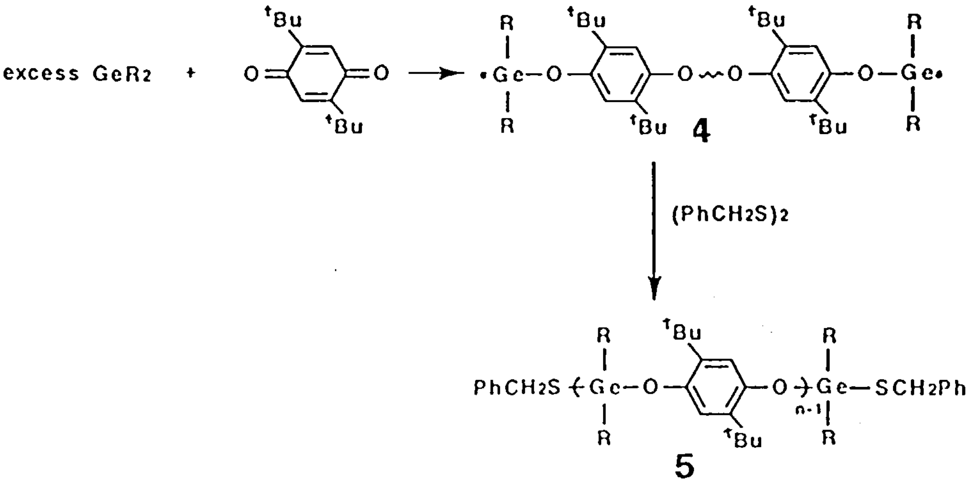
2:1 PERIODIC COPOLYMERIZATION WITH *p*-BENZOQUINONE DERIVATIVES

The reaction of a germylene with *p*-benzoquinone derivatives depends on the structure of the germylene used. Five- and six-membered cyclic germylenes **6** reacted with a *p*-benzoquinone derivative under similar reaction conditions as those for the 1:1 copolymerization described above, giving rise to the copolymer **7** which has a 2:1 periodic structure and a molecular weight higher than 10^5 [10] (Scheme 3). The 2:1 periodic structure was strictly controlled under a variety of reaction conditions.



1 **2** **3**

SCHEME 1.

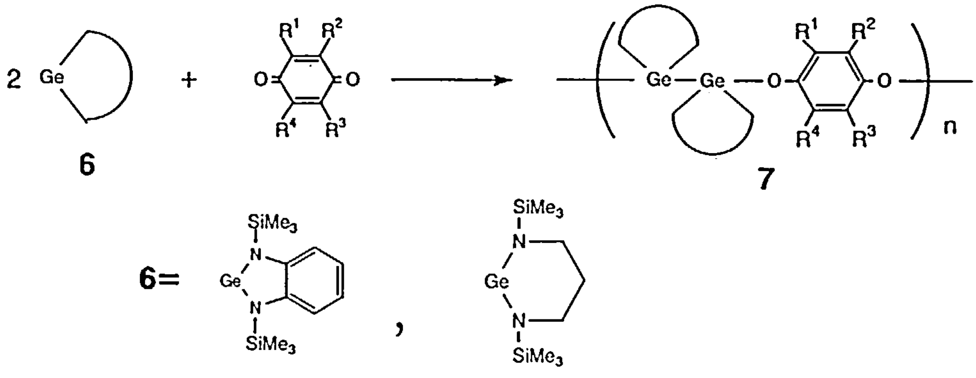


SCHEME 2.

The resulting copolymers have lower decomposition temperatures than 1:1 alternating copolymers, which may be explained by the existence of a Ge—Ge bond in the main chain.

1:1 ALTERNATING COPOLYMERIZATION WITH CYCLIC α,β-UNSATURATED KETONES

Poly(metal enolate)s, polymers having a metal enolate structure in the main chain, are interesting substances from the viewpoint of both basic organometallic chemistry and material science. In organic synthesis, with no exceptions, a metal enolate has been utilized as an reactive intermediate for alkylations or aldol condensations. There has been no report of the isolation of a polymeric form of metal



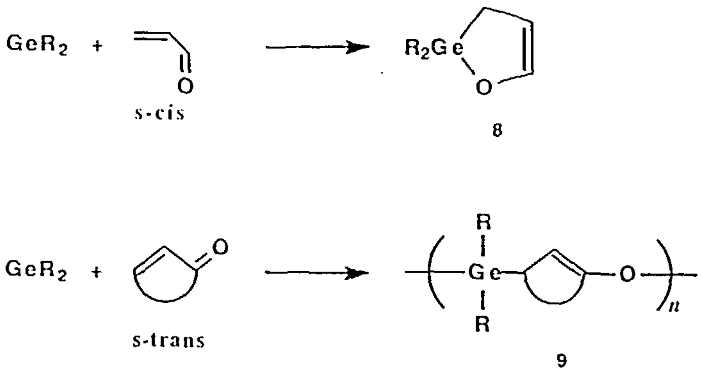
SCHEME 3.

enolate derivatives in the field of material science. In our studies for the development of a new polymerization using germylenes, a poly(germanium enolate) has been synthesized and isolated for the first time [11]. The discovery involves the formation of a cyclic germanium enolate (8) by the reaction of a germylene and various α,β-unsaturated carbonyl compounds [12].

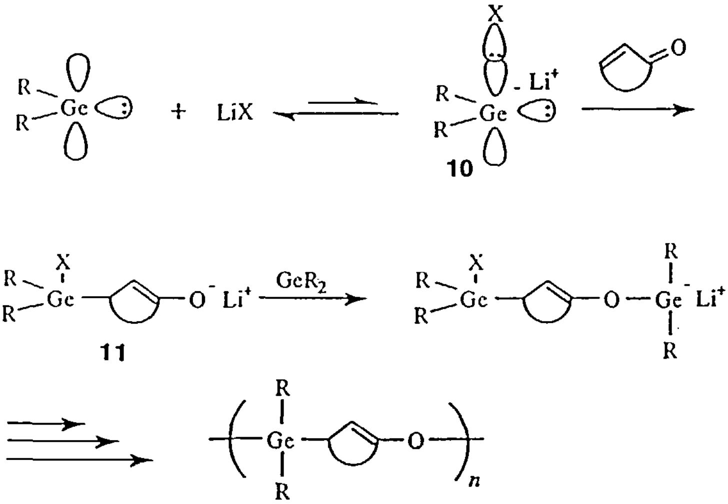
The cyclic enolate formation is explained by a Michael-type addition of the germylene to the carbonyl compound whose preferable conformation is *s-cis,* followed by a intramolecular cyclization of a germyl anion species (Scheme 4). It was therefore postulated that the use of a carbonyl compound having an *s-trans* conformation would lead to polymer formation because ring closure of the resulted germyl anion is impossible. After screening various reaction conditions such as reaction temperature, solvent, and additive, we found that the copolymerization requires a catalyst such as a lithium compound.

A germylene was copolymerized with cyclic α,β-unsaturated ketones at 0°C with LiCl, LiBr, $LiNR_2$, LiR, NaOR, etc. as the catalyst, giving rise to a 1:1 alternating copolymer (9) with a molecular weight higher than 10^5. The cyclic ketones used were five-, six-, and seven-membered compounds. It is to be noted that a neutral salt like LiCl is able to catalyze the copolymerization. The resulting copolymer was found to have considerable stability toward moisture. An aqueous THF solution of the resulting copolymer was stirred at room temperature for 24 hours, and the copolymer was recovered. The gel permeation chromatography (GPC) chart of the recovered copolymer shows little molecular weight change. It is worth emphasizing that the resulting copolymer is unusually stable for its chemical structure involving a metal enolate in the main chain, and it has potential utility as a new material [13].

The reaction mechanism of the copolymerization can be explained by assuming the initial formation of a germyl anion species (10) by the coordination of the lithium catalyst with the vacant orbital of the germylene (Scheme 5). The second step consists of a nucleophilic attack of the resulting germyl anion on the β-carbon atom of the cyclic ketone, which leads to a lithium enolate (11). This lithium enolate further coordinates with the germylene, regenerating the germyl anion. By repeating the above processes, alternating copolymerization proceeds, avoiding homo unit formation of the Ge—Ge bond, probably due to the large steric hindrance of the



SCHEME 4.



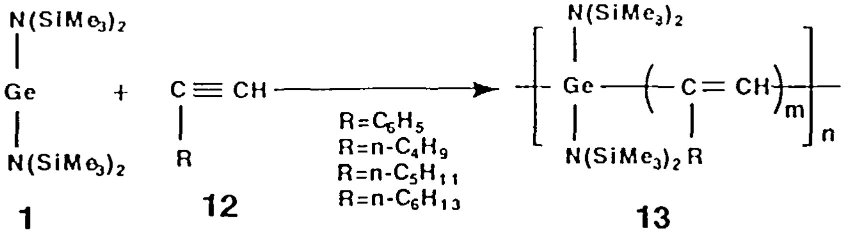
SCHEME 5.

amide group on the germanium atom. The extremely poor homopolymerizability of the cyclic α,β-unsaturated ketone also excludes its homo sequence. These factors cause the alternating propagation which leads to the copolymer.

COPOLYMERIZATION WITH ACETYLENE MONOMERS

A germylene, bis[bis(trimethylsilyl)amido] germanium (1), was copolymerized with acetylene monomers 12 with a rhodium compound as the catalyst to give copolymers 13 with a structure having an excess of acetylene units [14] (Scheme 6). The structure of the product was analyzed by ^{13}C-, ^{1}H-NMR, and IR spectroscopies, and the molecular weight was determined by GPC. The results of the copolymerization of 1 with various acetylene derivatives are summarized in Table 1.

The rhodium complex of norbornadiene [15] was active for the copolymerization of 1 with phenylacetylene (12a), 1-hexyne (12b), 1-heptyne (12c), and 1-octyne (12d). In the combination of 1 with 12a, this catalyst causes the homopropagation



SCHEME 6.

TABLE 1. Copolymerization of **1** with **12** by a Rhodium Catalyst under Various Conditions[a]

	Copolymerization					Copolymer			
Entry	**1**, mmol	**12**	[Rh],[b] mmol	Solvent, mL	Time, h	Yield of **13**, %[c]	$M_n \times 10^3$ [d]	M_w/M_n	**1**:**12** Molar ratio[e]
1	1.10	**12a**	0	Toluene (4.0)	48	0			
2	0.84	**12a**	0.012	NEt_3 (6.0)	5 min	30	21.6	2.1	1:8.3
3	1.11	**12a**	0.017	Toluene (4.0)	1	36	16.7	6.6	1:5.0
4	1.10	**12a**	0.017[f]	NEt_3 (4.0)	21	10	10.2	1.5	1:1.5
5	0.49	**12b**	0.0054	Toluene (3.0)	13	35	4.9	2.3	1:2.6
6	1.22	**12c**	0.021	NEt_3 (4.0)	5	31	4.4	2.1	1:2.9
7	0.97	**12d**	0.021	NEt_3 (4.0)	5	30	3.9	1.8	1:2.5

[a] With the equimolar feed ratio of **1** and **12** carried out at room temperature under argon.

[b] $[Rh(norbornadiene)Cl]_2$ except for Entry 4.

[c] Methanol insoluble part.

[d] Determined by GPC.

[e] Calculated from ^1H NMR.

[f] $[Rh(C_2H_4)_2Cl]_2$ as catalyst.

of **12a**, resulting in a smaller germylene unit content in the copolymer, probably due to the high activity of the catalyst (Entries 2 and 3 in Table 1) compared with the copolymerization of **1** with other 1-alkynes (**12b–d**). A less active catalyst for the homopolymerization of phenylacetylene, $[Rh(C_2H_4)_2Cl]_2$ [16], gave copolymer **13a** with a much higher germylene unit content (Entry 4 in Table 1).

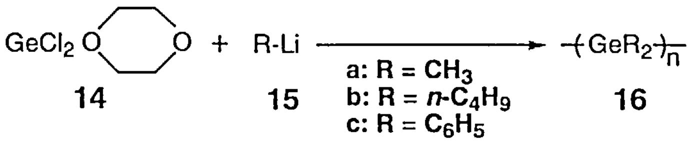
The lower content of germylene units in copolymer **13** in almost all cases may be explained by the relatively high homopropagation tendency of acetylene monomers, while the germylene monomer cannot homopropagate because of its bulky ligand. The relatively lower copolymer yield may be due to the smaller copolymerizability of the germylene monomer.

Besides the catalysts used above, several other transition metal compounds were examined for the copolymerization of **1** with **12a**. Compounds like $Pd[PPh_3]_4$ and $RhCl[PPh_3]_3$, which were not effective for the homopolymerization of **12a**, also showed no catalytic activity. It is well known that molybdenum and tungsten compounds are very effective for the homopolymerization of acetylene monomers [17, 18]. When $MoCl_5$ and WCl_6 were used, their catalytic activity was not high and the copolymer yield was very low. In the case of disubstituted acetylenes such as 2-hexyne and 1-phenyl-1-propyne, their homopolymerizations and copolymerizations with **1** were difficult with the rhodium norbornadiene complex as catalyst.

LIGAND SUBSTITUTION POLYMERIZATION TO POLYGERMANES

High molecular weight polygermanes **16** were synthesized by ligand substitution of the 1,4-dioxane complex of germanium dichloride **14** with organolithium compounds **15** at a lower reaction temperature ("ligand substitution polymerization") [19] (Scheme 7). The polymerization gives rise to much higher yields of polygermanes than those using the conventional Wurtz-type coupling reaction. The results for ligand substitution polymerization are summarized in Table 2.

In a typical experiment (Entry 4 in Table 2), 2.43 mmol **14** was suspended in 20 mL diethyl ether under argon, and the resulting suspension was cooled to −78°C. To this suspension was slowly added 4.86 mmol *n*-butyllithium over 15 minutes. After stirring for 1 hour at −78°C, the reaction mixture was condensed under reduced pressure and extracted by 40 mL toluene. Very viscous materials with a pale yellow color were obtained (98% yield). The product was analyzed by NMR, IR, and UV spectroscopies. Polymerization involving the ligand substitution was completed within 2 hours even at a lower reaction temperature (−78°C). The product polymers showed two molecular weight distributions when the reaction was carried out at −78°C (Entries 1 and 4). This bimodal molecular weight distribution is similar to the polygermanes formed by the Wurtz-type coupling reaction. The



SCHEME 7.

TABLE 2. Synthesis of Polygermanes by Ligand Substitution Polymerization of **14**

Reaction[a]					Polymers				
Entry	**14**, mmol	**15**	T, °C	Time, h	Structure	Yield,[b] %	$M_w \times 10^3$ [c]	M_w/M_n [c]	Composition, %[d]
1	1.74	**15a**	−78	2	**16a**	45	31.0	7.76	47
							1.3	1.31	53
2	2.62	**15b**	0	2	**16b**	95	1.3	1.09	
3	2.78	**15b**	0	2	**16b**	39	1.5	1.31	
4	2.43	**15b**	−78	1	**16b**	98	17.9	2.88	39
							1.4	1.12	61
5	1.81	**15c**	0	1	**16c**	83	0.7	1.17	
6	1.72	**15c**	−78	3	**16c**	58	1.0	1.21	

[a] The feed molar ratio **15**/**14** = 2.0 in 20.0 mL of diethyl ether.

[b] The yields for Entries 1, 3, and 6 were isolated by precipitation from methanol, and the yields for Entries 2, 4, and 5 were isolated by extraction using toluene.

[c] Determined by GPC.

[d] Based on GPC trace profile.

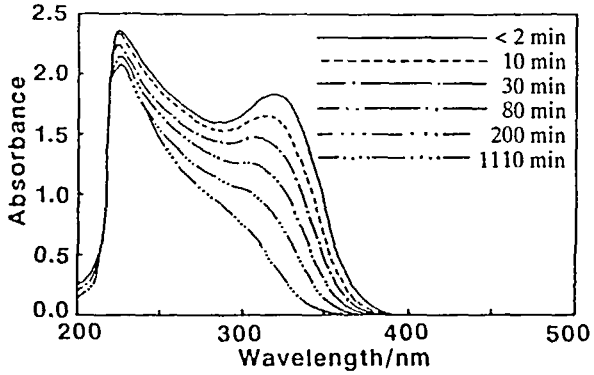


FIG. 2. UV absorption change of product **16b** in THF under exposure to daylight.

higher portion was not formed when the reaction was carried out at 0°C with both phenyllithium (Entry 5) and *n*-butyllithium (Entries 2 and 3) or even at −78°C with phenyllithium (Entry 6). It is reasonable to assume that cyclic oligomers were formed as the lower molecular weight portion in competition with linear polymer formation. The broad molecular weight distribution of the higher portion was probably due to photoinduced degradation. Product **16a** is a white powder, slightly soluble in chloroform. The higher molecular weight poly(di-*n*-butylgermane) (**16b**, Entry 4) is a very viscous material with a pale yellow color. It is soluble in such common organic solvents as chloroform, toluene, and tetrahydrofuran (THF).

All of the products showed very strong UV absorption owing to the Ge—Ge σ-bond conjugation. The absorption maxima in THF at room temperature for product **16b** was observed at 218 nm (Entry 2) and 324 nm (Entry 4). This proves that an increase of molecular weight leads to longer Ge—Ge σ-bond conjugation. The higher molecular weight products were very photosensitive, especially in solution form. Figure 2 shows the UV absorption change of product **16b** (Entry 4) in THF in a UV cell under exposure to daylight at room temperature. The longer the exposure time, the smaller the molecular weight and the shorter the UV absorption maximum. After storage in THF for 2 hours under exposure to daylight, all of the higher molecular weight portion disappeared according to GPC analysis. Polymer chain scission behavior was also found in the solid form, but not as pronounced as in the solution form.

CONCLUSION

Novel germanium-containing polymers obtained by newly developed polymerizations have potential utility as functional polymers based on the characteristic features derived from the unique unit structure of the germanium atom. From the viewpoint of polymer synthesis, there are many possibilities for utilization of various oxidants as M_{OX} copolymerizable with M_{red} of germylenes. The structure modification of a germylene also makes it possible to expand the scope of "oxidation-reduction copolymerization." The "ligand substitution polymerization," which consists of a ligand exchange reaction between a germanium dihalide and an alkyl metal compound, was found to be a very useful method for the construction of a polygermane moiety having various alkyl side chains on the germanium atom.

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