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Synthesis of Germanium Enolate Polymers from Germylene Monomers

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Abstract: A novel germanium containing polymer, poly(germanium enolate), has been synthesized by the reaction of a divalent germanium compound, germylene, with a cyclic α,β-unsaturated ketone in the presence of a catalytic amount of a lithium compound. The germylene was also copolymerized with a cyclic α,β-unsaturated lactone, affording an unstable polymer having a ketene acetal structure in the main chain. The resulting polymers are the first example having a metal enolate structure as repeating unit.

Introduction

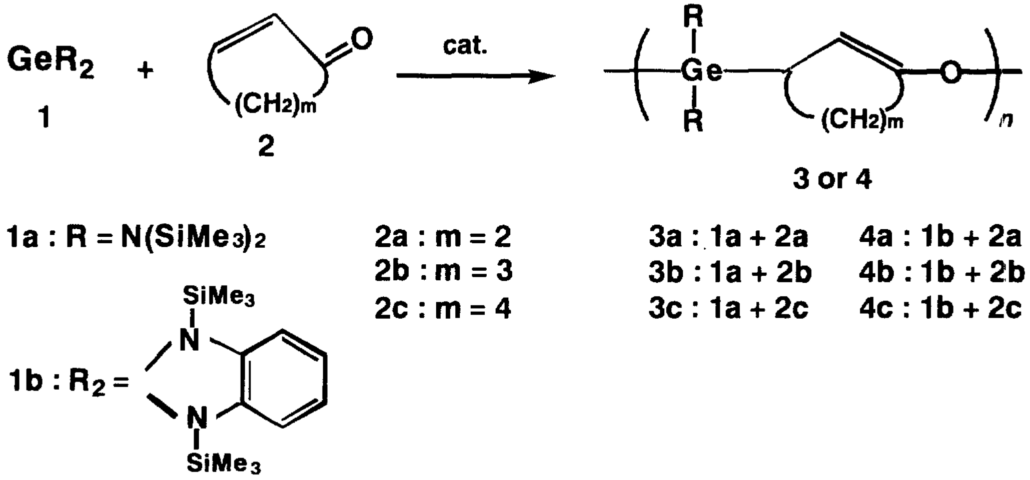
The modern synthetic organic chemistry has greatly owed its rapid progress to the development of metal enolates. Due to their high reactivities toward electrophiles, metal enolates have been utilized as intermediates for various synthetic reactions, such as alkylation of carbonyl compounds and aldol condensation.[1] In polymer science, in spite of the growing interest in organometallic polymers,[2] no report on the formation of polymeric metal enolates leading to new materials has been appeared for the following reasons. First, metal enolate formation is accomplished by the reaction of a carbonyl compound and a reagent that has an electrophilic metallic center and a nucleophilic center where these two reactive centers must be separated as a result of the formation of an enolate structure.[3] Consequently, all known enolates produced have monomeric structures; the preparation of a polymeric enolate cannot be achieved based on the normal principle of metal enolate generation. Secondly, metal enolates have long been considered very unstable because the metal-oxygen bond cleavage occurs easily by a nucleophilic attack of water molecule on the metal atom.

Poly(germanium enolate)s are organometallic polymers having a structure composed of carbon-carbon double bond, oxygen, and germanium in the main chain. Such polymers are very interesting substances from the viewpoint of material science because of their unusual structures of germanium enolate units. In organic chemistry, the generation of a germanium enolate has so far been achieved by the metal exchange reaction of the corresponding lithium enolate by a tetravalent germanium compound;[4] few reports on the germanium enolate formation starting from a divalent germanium compound (germylene) has been made.[5]

Germylenes are potentially useful reagents for the construction of polymeric germanium enolate since they have both a nucleophilic center, due to the lone pair electrons, and an electrophilic center, due to the 4p vacant orbital, on the same germanium atom.[6] Consequently, germylenes are able to reduce various oxidants by changing their valency state from two to four. By using the reducing ability of germylenes, novel copolymerization reactions with *p*-benzoquinone derivatives,[7] acetylenic compounds,[8] and cyclic sulfides[9] have been developed. Generally, divalent germanium species, germylenes, can not exist as monomeric compounds and immediately polymerize or dimerize spontaneously. Germylenes are fairly stable and can be purified by distillation or recrystallization provided that an appropriate ligand is attached to the germanium atom. The pioneering work for the synthesis of stable germylenes was performed by Lappert and co-workers.[10] They showed that a bulky substituent on the center germanium atom prevents self-polymerization or dimerization.

In the course of our investigation aimed at developing new polymer materials based on the concept of "oxidation-reduction copolymerization",[7a] we have found that the reaction of a germylene with cyclic α,β-unsaturated ketones having an *s*-trans structure gives alternating copolymers having a germanium enolate structure in the main chain (Scheme 1)[11]. This alternating copolymerization using a germylene was applied to a cyclic α,β-unsaturated lactone to form an unstable germanium containing polymer having a ketene acetal structure. This paper summarizes the results of the poly(germanium enolate) syntheses via these new methodologies which involve a redox process utilizing germylenes and cyclic α,β-unsaturated carbonyl compounds.

Scheme 1



1a : R = N(SiMe$_3$)$_2$

1b : R$_2$ =

2a : m = 2
2b : m = 3
2c : m = 4

3a : 1a + 2a
3b : 1a + 2b
3c : 1a + 2c

4a : 1b + 2a
4b : 1b + 2b
4c : 1b + 2c

Results and Discussion

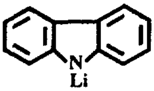
Copolymerization of germylenes and cyclic α,β-unsaturated ketones: Bis[bis(trimethylsilyl)amino] germanium(II) (**1a**) was copolymerized with 2-cyclopenten-1-one (**2a**), giving rise to a novel germanium containing polymer **3**, poly(germanium enolate), in good yields. The resulting copolymer was purified by precipitation from acetonitrile. The copolymerization took place smoothly at 0 °C in tetrahydrofuran (THF) in the presence of a catalytic amount of various lithium compounds (Table 1). Various lithium salts such as *n*-butyllithium, lithium alkoxides, and amidolithium compounds were found effective to promote the copolymerization (entries 2-7). In the absence of catalyst, no polymeric product was obtained (entry 1). Neutral salts (lithium chloride, lithium bromide, and lithium iodide) are also active as catalyst, which allows one to carry out the copolymerization under essentially neutral conditions (entries 9-11). Lithium fluoride did not catalyzed the coplymerization probably due to its low solubility in THF (entry 8). Other metal salts such as sodium chloride, potassium chloride, potassium chloride/18-crown-6, and tetrabutylammonium chloride did not produce copolymers (entries 12-15). Radical initiators like tetramethylpiperidinyloxyl (TEMPO) and 2,2'-azobisisobutyronitrile (AIBN) did not initiate the copolymerization (entries 16 and 17).

Six and seven membered cyclic α,β-unsaturated ketones, 2-cyclohexen-1-one (**2b**) and 2-cyclohepten-1-one (**2c**), were also copolymerized with the germylene to afford poly(germanium enolate)s with high molecular weights in good yields (Table 2). These reactions also require a catalytic amount of the lithium compounds as an initiatior. *n*-Butyllithium, an amidolithium, and a neutral lithium salt can initiate the copolymerization effectively. However, for the copolymerization of **1a** and **2c** by using carbazolyl lithium, lithium chloride, lithium bromide, or lithium iodide as catalyst, the addition of 10 mol % was necessary in order to initiate the copolymerization; when the reaction was carried out in the presence of 1 mol % of the catalyst, polymeric products could not be obtained. All the copolymerization reactions were completed within 3 h, indicating the high nucleophilic character of **1** toward the carbon-carbon double bonds in α,β-unsaturated carbonyl compounds. The effect of reaction temperature and the concentration of catalyst on the yield of copolymerization of **1a** and **2a**, **2b** or **2c** was investigated. When the reaction was carried out at lower temperature (-42 °C) the copolymerization did not take place. At room temperature, the molecular weight decreased. The yield and molecular weight greatly decreased in case of high reaction temperature (50 °C). These results suggest that a reactive anionic intermediate lithium or germanium species cannot be generated or is too unstable to exist as a propagating center for the polymerization at 50 °C.

The copolymerization of 1,3-bis(trimethylsilyl)-1,3-diaza-2-germa(II)indan (**1b**), a germylene having a cyclic structure, with the comonomer **2** was then examined. When the five and six membered α,β-unsaturated ketones, **2a** and **2b**, were reacted with **1b** in the presene of a catalytic amount of *n*-butyllithium or $Li(SiMe_3)_2$, the corresponding alternating copolymers were obtained in modest yields (Table 3). However, lithium chloride was found ineffective for the initiation of copolymerization. The copolymer could not be obtained from the seven membered α,β-unsaturated ketone **2c**. The lower yields of the products compared with the copolymerization using **1a** and difference of the copolymerizability between **1a** and **1b** towards the comonomers **2a**, **2b** and **2c** may be explained by assuming the difference of nucleophilicity of the lone pair electrons on the germanium atom of **1b**. The nucleophilicity of the lone pair electrons of **1b** is estimated to be lower than that of **1a** because of both the existence of the benzene ring and the smaller bond angle of N-Ge-N in **1b**.

Structure Determination and Physical Properties of Poly(germanium enolate): The ^{1}H-NMR spectrum of the copolymer **3b** obtained from **1a** and 2-cyclohexen-1-one (**2b**) exhibits signals which are

Table 1. Copolymerization of Germylene 1a with 2a[a]

entry	cat.	cat.(mol%)	yield(%)[b]	M_w[c]	M_w/M_n[c]
1	none	0.0	0		
2	*n*-BuLi	1.0	89	5.2x10^4	2.65
3	EtOLi	8.8	99	4.5x10^4	2.56
4	^{t}BuOLi	1.0	92	6.6x10^4	1.49
5	Ph$_3$COLi	1.0	89	5.0x10^4	2.17
6	LiN(SiMe$_3$)$_2$	0.9	90	4.8x10^5	4.74
7		1.0	40	3.5x10^4	2.91
8	LiF	1.0	0		
9	LiCl	1.0	85	1.1x10^5	2.63
10	LiBr	1.0	83	5.4x10^4	1.31
11	LiI	1.0	99	9.7x10^4	1.69
12	NaCl	1.0	0		
13	KCl	1.0	0		
14	KCl+18-Crown-6	1.0	0		
15	*n*-Bu$_4$NCl	1.0	0		
16	TEMPO	1.0	0		
17	AIBN[d]	1.0	0		

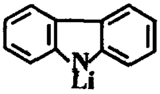
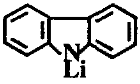
a) Copolymerization was carried out in THF at 0 °C for 3h.

b) Isolated yield.

c) Determined by GPC.

d) 80 °C.

Table 2. Copolymerization of Germylene 1a with 2b or 2c [a]

comonomer	cat.	cat.(mol%)	yield(%)[b]	M_w[c]	M_w/M_n[c]
2b	none	0.0	0		
2b	*n*-BuLi	1.0	90	$7.6\mathrm{x}10^{4}$	2.03
2b	^{t}BuOLi	1.0	93	$1.9\mathrm{x}10^{5}$	1.95
2b	Ph_3COLi	1.0	84	$9.8\mathrm{x}10^{4}$	2.98
2b	$LiN(SiMe_3)_2$	1.0	61	$4.2\mathrm{x}10^{5}$	3.33
2b		1.0	77	$1.5\mathrm{x}10^{5}$	1.46
2b	LiF	1.0	0		
2b	LiCl	1.0	87	$3.7\mathrm{x}10^{5}$	4.09
2b	LiBr	1.0	80	$1.1\mathrm{x}10^{5}$	1.54
2b	LiI	1.0	87	$8.2\mathrm{x}10^{5}$	3.44
2c	none	0.0	0		
2c	*n*-BuLi	5.0	76	$1.1\mathrm{x}10^{3}$	1.39
2c	$LiN(SiMe_3)_2$	1.0	91	$1.3\mathrm{x}10^{4}$	1.73
2c		10.0	62	$5.2\mathrm{x}10^{3}$	2.04
2c	LiF	1.0	0		
2c	LiCl	10.0	84	$6.8\mathrm{x}10^{3}$	1.51
2c	LiBr	10.0	88	$9.5\mathrm{x}10^{3}$	1.61
2c	LiI	10.0	88	$1.9\mathrm{x}10^{3}$	2.49

a) Copolymerization was carried out in THF at 0 °C for 3h.
b) Isolated yield.
c) Determined by GPC.

Table 3. Copolymerization of Germylene 1b with Cyclic α,β-Unsaturated Ketones[a)]

comonomer	cat.	cat. (mol%)	yield(%)[b)]	M_w [c)]	M_w/M_n [c)]
2a	none	0	0		
2a	*n*-BuLi	1.0	40	1.1×10^4	1.95
2a	$LiN(SiMe_3)_2$	1.0	41	7.6×10^3	1.60
2a	LiCl	1.0	0		
2b	none	0	0		
2b	*n*-BuLi	1.0	55	7.3×10^3	1.77
2b	$LiN(SiMe_3)_2$	1.0	65	1.2×10^4	2.16
2b	LiCl	1.0	0		
2c	none	0	0		
2c	*n*-BuLi	1.0	0		
2c	$LiN(SiMe_3)_2$	1.0	0		
2c	LiCl	1.0	0		

a) Copolymerization was carried out in THF at 0 °C for 3h.

b) Isolated yield.

c) Determined by GPC.

reasonably assigned to an *O*-germylated enolate structure (Figure 1). The signal at δ = 0.60 ppm is due to the protons of the trimethylsilyl group. The signals at δ = 1.8-3.0 ppm (a,b,c and d) are ascribed to the methylene protons and methine proton in the cyclohexene ring, respectively. The doublet-like signal around δ = 5.4 ppm (e) is assigned to be the olefinic proton of the enolate structure. The ^{13}C NMR spectrum of the copolymer **3b** shows seven peaks at δ = 6.4, 23.8, 25.7, 31.5, 37.0, 102.8 and 152.7 ppm, assignable to the all carbon atoms of the product copolymer (spectrum not shown). No signal due to the carbonyl carbon atom derived from that of **2b** was observed around 180-220 ppm, indicating that the isomeric *C*-germylated structure was not formed by this reaction. The IR spectrum of **3b** shows an absorption due to the C=C bond of the enolate structure at 1624 cm^{-1} (Figure 2). The elemental analysis of the product also supported the structure of the 1:1 alternating copolymer. These results clearly indicate that a regioselectively *O*-germylated enolate type polymer was formed; a repeat unit derived from the isomeric *C*-germylated enolate structure was not detected. The ^{1}H and ^{13}C NMR spectra of the other copolymers **3a** and **3c** also exhibited the signals derived from the alternating *O*-germylated enolate structure. The ^{1}H and ^{13}C NMR spectra of the copolymer **4b** prepared by the reaction of **1b** and **3b** are shown in Figure 3 and 4, respectively. All signals in these spectra can be reasonably assigned to the 1:1 alternating structure of the *O*-germylated enolate structure which consists of an α,β-unsaturated carbonyl moiety and a tetravalent germanium moiety. The copolymer **4a** was also characterized to be an alternating poly(germanium enolate).

The resulting copolymers (**3** and **4**) are fine white powders and are soluble in common organic solvents such as *n*-hexane and chloroform. The copolymers obtained by the reaction of **1a** and **2a** or **1a** and **2b** have high molecular weights ($M_w > 10^5$) and give transparent films by casting. Differential scanning calorimetry (DSC) analysis of the polymer prepared from germylene **1a** and **2a** (Table 1, entry 6) showed a glass transition temperature and a melting point at 40.2° and 220.8 °C, respectively. All of the copolymer are stable at room temperature. In order to examine the stability toward moisture, the following hydrolysis experiment has been performed. An aqueous THF (95%) solution of **3a** (Table 1, entry 6) was stirred for 24 h at room temperature. The GPC analysis of the recovered copolymer indicated little change of the molecular weight. It is well known that Si-N, Ge-N, and Ge-O bond of the enolate moiety are easily cleaved by the attack of nucleophiles such as an alcohol or water.[12] In the case of copolymer **3a**, however, the steric hindrance of the bulky trimethylsilyl group may prevent a water molecule from attacking the silicon or germanium atom.

Reaction Mechanism: The following mechanism has been proposed for the present copolymerization (Scheme 2). The first step is the formation of a germyl anion species **5** as a result of the reaction of the germylene and a lithium salt. The resulting germyl anion species then attacks the β-position of the cyclic α,β-unsaturated ketone via a Michael-type addition, giving rise to an enolate anion **6**. The germyl anion **7** is regenerated by the reaction of **6** with germylene. By repeating these processes, the propagation of the polymer chain is achieved. The steric hindrance of the bulky silyl amide group of germylene and the very poor homopolymerizability of the α,β-unsaturated ketone prevent the homo unit formation, which allows the *alternating propagation* leading to copolymers.

Figure 1. ^{1}H NMR Spectrum of Copolymer 3b

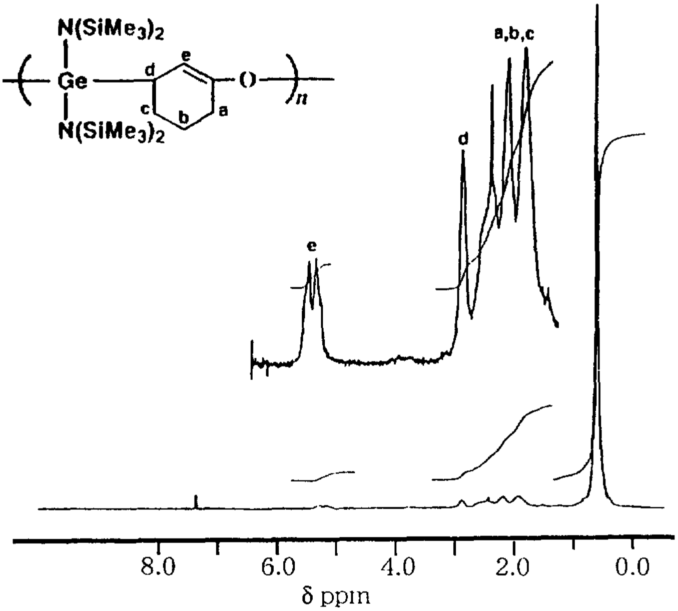


Figure 2. IR Spectrum of Copolymer 3b

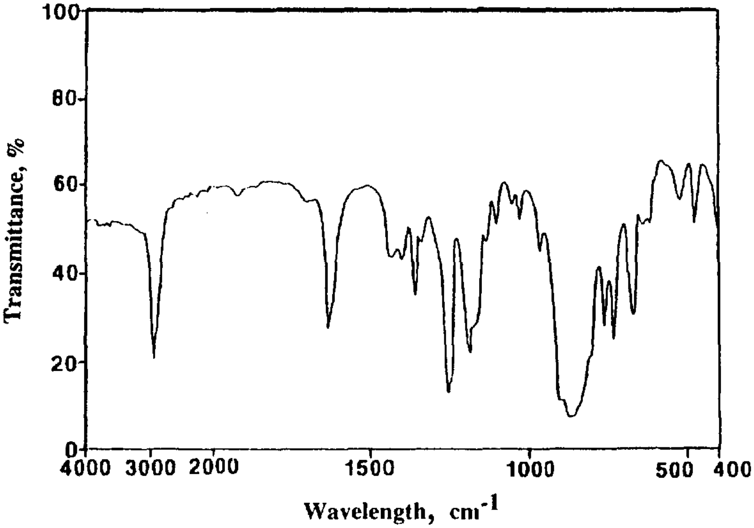


Figure 3. ^1H NMR Spectrum of Copolymer 4b

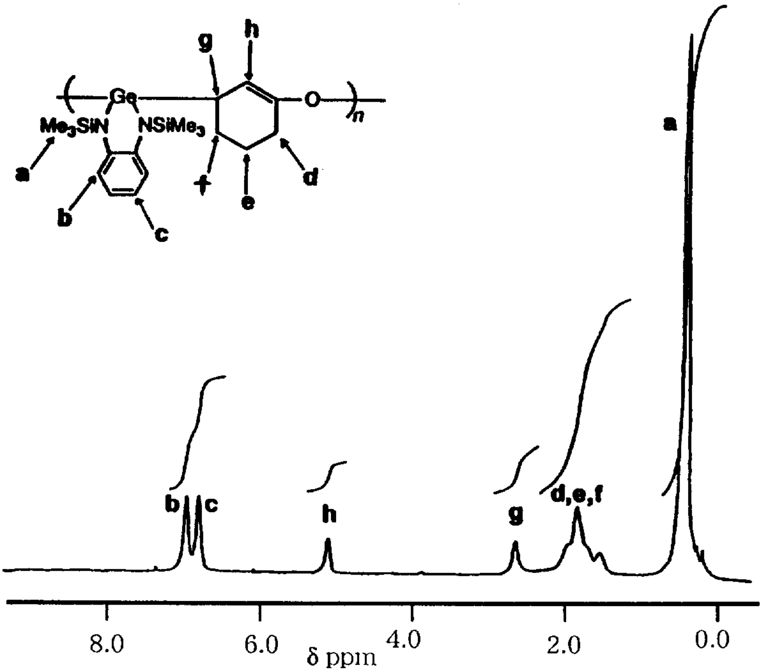
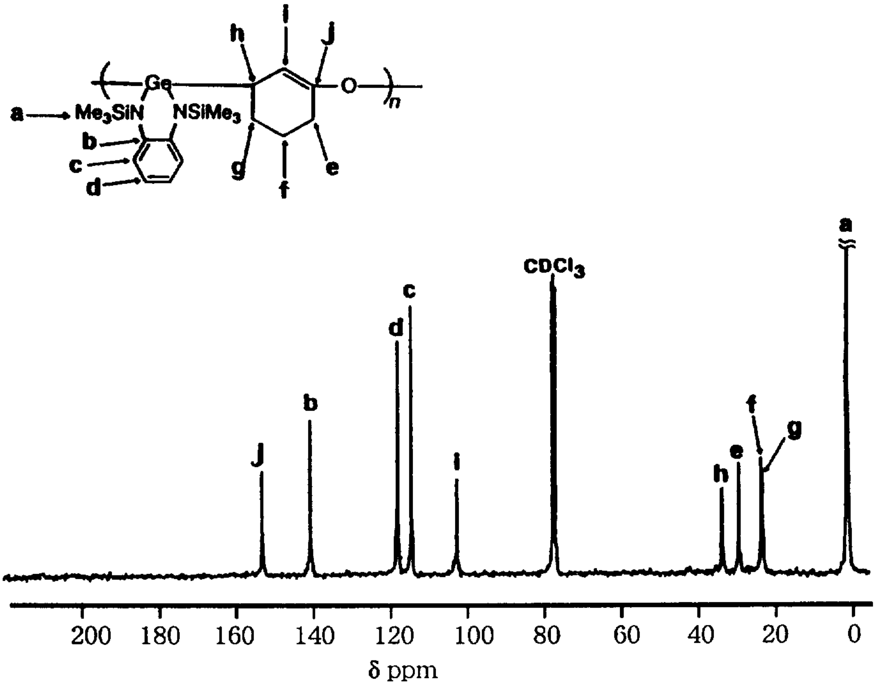
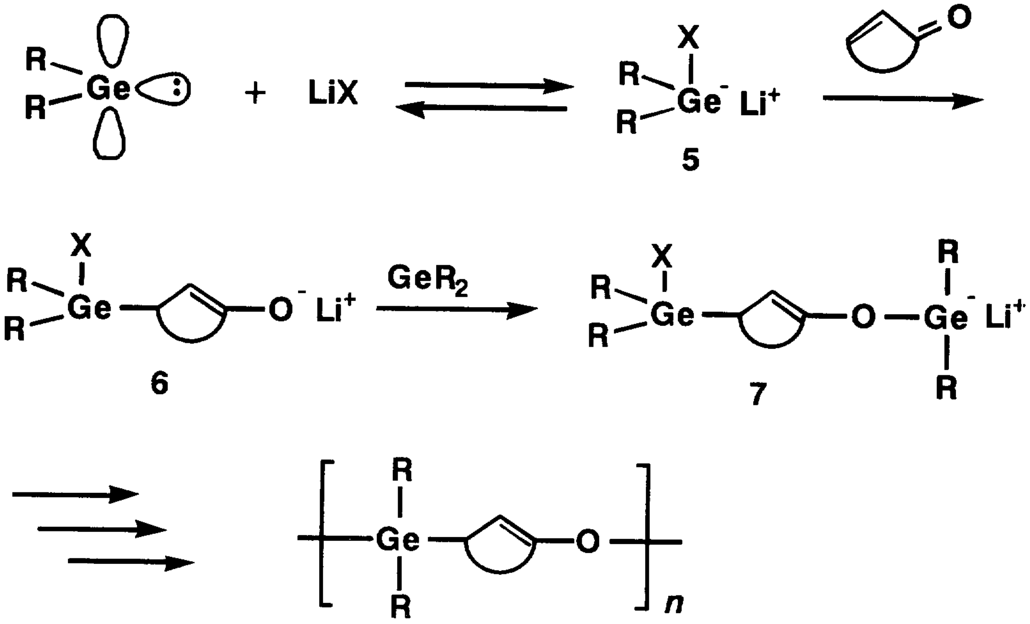


Figure 4. ^{13}C NMR Spectrum of Copolymer 4b

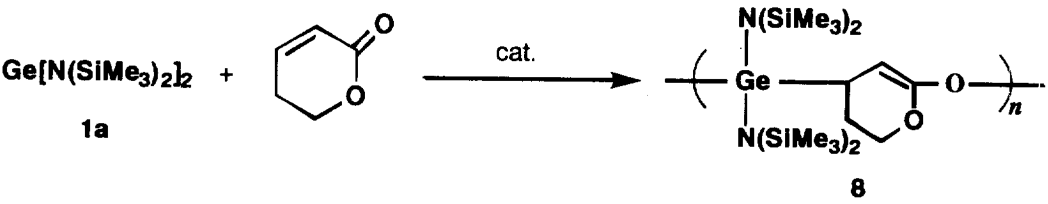


Scheme 2



Copolymerization of Germylene 1a with α, β-unsaturated lactone: Bis[bis(trimethylsilyl)amino]germanium(II) (**1a**) was copolymerized with 5,6-dihydro-2H-pyran-2-one to afford a novel germanium containing polymer **8** having a ketene acetal structure in the main chain (Scheme 3). The copolymerization requires a catalytic amount of anionic initiator such as *n*-butyllithium, methyllithium, and lithium chloride. The copolymerization was carried out in THF for 3h at -78 or 0 °C. The copolymerization was completed within 3h even at - 78 °C. The copolymer could not be obtained when the reaction was carried out at 50 °C. Toluene and benzene are also usable as solvent. Lithium fluoride did not work as initiator probably because of its low solubility in THF.

Scheme 3



The ^1H NMR spectrum of the resulting copolymer **8** indicates a signal ascribable to the olefinic proton (e) of the ketene acetal moiety at δ = 4.18 ppm (Figure 5). The methyne proton on the carbon atom (c) bonded to the germanium atom was observed at δ = 2.72 ppm. These data clearly shows that a structure of -Ge-CH-HC=C-O- unit is exclusively formed by the Michael type addition of the germylene to the carbon-carbon double bond of the α,β-unsaturated ester moiety. The ^{13}C NMR also supported the above structure (Figure 6). However, the resulting copolymer was so unstable that one can not measure its molecular weight by GPC because the ketene acetal is more reactive than the germanium enolate toward moisture and the germanium-oxygen bond of the resulting polymer is easily cleaved by the attack of water molecule to the germanium atom.

Conclusions

The poly(germanium enolate), polymers having a germanium enolate structure in the main chain, has been synthesized for the first time. The present reaction is a new example of "oxidation-reduction copolymeization", where the germylene is oxidized and the α,β-unsaturated ketone is reduced. The resulting copolymer has a potential utility as a novel functional polymer based on characteristic feature of the unusual structure of the metal enolate. It is to be noted that this is the first example of a regioselectively *O*-germylated metal enolate.

Experimental

Measurements: NMR spectra (^1H, ^{13}C) were recorded on a Bruker AM-250T spectrometer. IR spectra were taken on a Shimazdu IR-460 spectrometer. 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).

Materials: All reactions were carried out under argon atmosphere. Toluene, benzene, *n*-hexane, THF, ether and 1,4-dioxane were distilled from sodium/benzophenone before use. Acetonitrile and 1,1,3,3,-hexamethyldisilazane were distilled from calcium hydride. Germylenes were prepared by the reaction of $GeCl_2$ 1,4-dioxane complex and appropriate lithium amides according to the literature.[13]

Copolymerization of Germylene 1a with 2-cyclopenten-1-one (2a). Following is a typical example of copolymerization of **1a** and **2a** using $LiN(SiMe_3)_2$ as an initiator. To a THF solution (1.2 mL) of germylene **1a** (471 mg, 1.20 mmol) was added a THF solution of $LiN(SiMe_3)_2$ (1.1 x 10^{-2} mmol) and the resulting mixture was stirred at room temperature for 2 h. A THF (1.2 mL) solution of 2-cyclopenten-1-one (116 mg, 1.41 mmol) was then added dropwise at 0 °C with stirring. After being stirred for 3 h, the reaction mixture was poured into 50 mL of acetonitrile under argon. The white precipitates were collected by filtration and dried in vacuo to give 512 mg of copolymer **3a** (90 % yield): T_g = 40.2 °C, T_m = 220.8 °C. ^1H NMR ($CDCl_3$) δ 0.25 (s, SiMe, 36H), 2.30 (br, CH_2, 4H), 2.88 (br, GeCH, 1H), 4.70 (br, =CH, 1H); ^{13}C NMR

Figure 5. ^1H NMR Spectrum of Copolymer 8

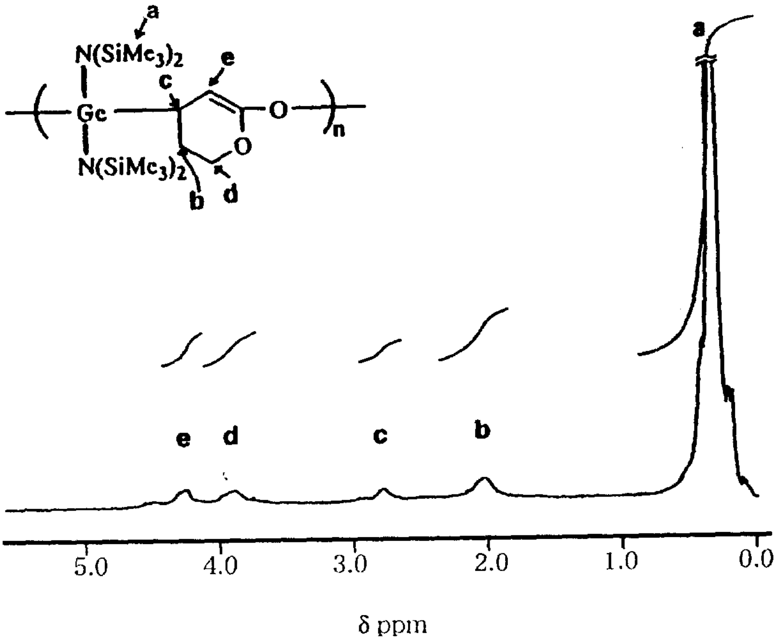
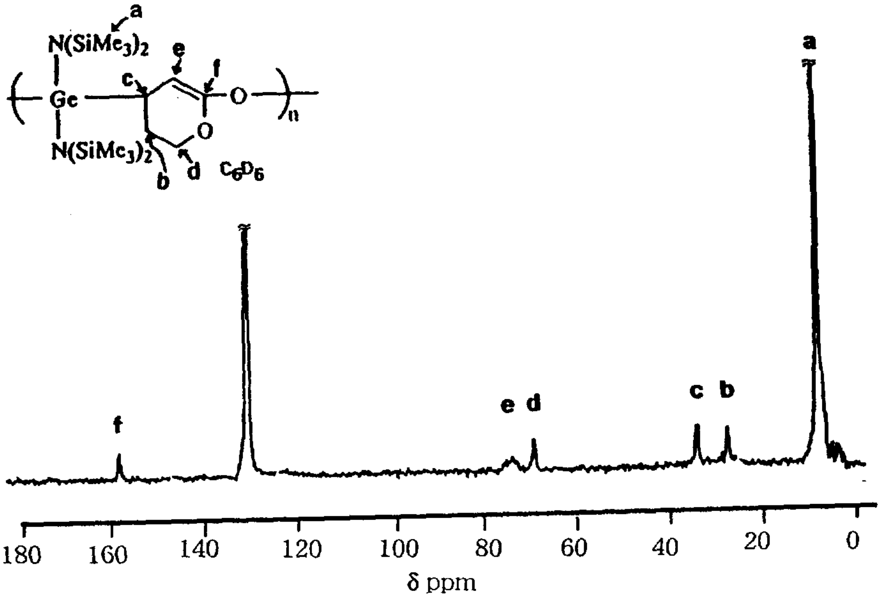


Figure 6. ^{13}C NMR Spectrum of Copolymer 8



($CDCl_3$) δ 6.4 ($SiMe_3$), 25.2 (CH*C*H_2), 34.6 (*C*H_2C=), 39.8 (GeCH), 103.1 (CH=), 157.1 (=C-O); IR: 2955, 1624, 1436, 1405, 1249, 1181, 870 cm^{-1}. Anal. Calcd for $(C_{17}H_{42}N_2OGeSi_4)_n$: C, 42.94; H, 8.90; N, 5.89. Found: C, 42.18; H, 9.19; N, 5.69. Copolymerizations of germylene **1a** and 2-cyclohexen-1-one (**2b**) and 2-cyclohepten-1-one (**2c**) and copolymerization of germylene **1b** and **2a** or **2b** were carried out in a similar manner.

Copolymer **3b**: T_g = 49.3 °C, T_m = 238.1 °C. ^{1}H NMR ($CDCl_3$) δ 0.60 (s, $SiMe_3$, 36H), 1.8-2.9 (br, CH_2, 6H), 3.01 (br, GeCH, 1H), 5.3-5.5 (br, CH=, 1H); ^{13}C NMR ($CDCl_3$) δ 6.4 ($SiMe_4$), 23.8 (CH*C*H_2), 25.7 (CH_2*C*H_2CH_2), 31.5 (*C*H_2C=), 37.0 (GeCH), 102.8 (CH=), 152.7 (=C-O); IR: 2948, 1634, 1359, 2253, 1192, 904, 867, 762, 659 cm^{-1}; Anal. Calcd for $(C_{18}H_{44}N_sOGeSi_4)_n$: C, 44.17; H, 9.06; N, 5.72. Found: C, 43.43; H, 9.22; N, 5.40.

Copolymer **3c**: ^{1}H NMR ($CDCl_3$) δ 0.27 (s, $SiMe_3$, 36H), 1.4-2.8 (br, CH_2, GeCH, 9H), 5.14 (br, CH=, 1H); ^{13}C NMR ($CDCl_3$) δ 6.5 ($SiMe_3$), 24.5 ($CHCH_2$*C*H_2), 30.6 (*C*H_2CH_2C=), 32.3 (CH*C*H_2CH_2), 33. 0 (CH_2*C*H_2C=), 36.2 (GeCH), 104.6 (*C*H=), 159.4 (=C-O); Anal. Calcd for $(C_{19}H_{46}N_2OGeSi_4)_n$: C, 45.32; H, 9.21; N, 5.56. Found: C, 43.10; H, 9.01; N, 5.23.

Copolymer **4a**: ^{1}H NMR ($CDCl_3$) δ 0.26 (s, $SiMe_3$, 18H), 1.99 (br, CH_2, 4H), 2.72 (br, CH, 1H), 4.52 (br, CH=, 1H), 6.65 (br, aromatic, 1H), 6.78 (br, aromatic, 1H); ^{13}C NMR ($CDCl_3$) δ 0.4 ($SiMe_3$), 23.2 (*C*H_2CH_2), 32.37 (CH_2*C*H_2), 37.36 (CH), 100.9 (C=), 114.1 (aromatic), 117.7 (aromatic), 140.5 (aromatic), 157.7 (=C-O); Anal. Calcd for $(C_{17}H_{28}N_2OGeSi_2)_n$: C, 50.38; H, 6.96; N, 6.91, Found: C, 49.53; H, 6.87; N, 5.83.

Copolymer **4b**: ^{1}H NMR ($CDCl_3$) δ 0.36 (s, $SiMe_3$, 18H), 1.3-2.1 (br, CH_2, 6H), 2.55 (br, GeCH, 1H), 5.00 (br, CH=, 1H), 6.70 (br, aromatic, 2H), 6.86 (br, aromatic, 2H); ^{13}C NMR δ ($CDCl_3$) 0.4 ($SiMe_3$), 22.6 (CH*C*H_2), 23.0 (CH_2*C*H_2CH_2), 29.0 (*C*H_2C=), 33.10 (GeCH), 102.2 (C=), 114.0 (C(3), C(6) aromatic), 117.6 (C(4), C(5) aromatic), 140.4 (C(1), C(2) aromatic), 153.0 (=C-O); Anal. Calcd for $(C_{18}H_{30}N_2OGeSi_2)_n$: C, 51.57; H, 7.21; N, 6.68, Found: C, 48.38; H, 7.05; N, 6.17.

Hydrolysis Experiment of Copolymer 3a. Copolymer **3a** (80 mg) was dissolved in THF (20 mL) and water (1 mL) and the resulting solution was stirred at room temperature for 24 h. The solvent was evaporated and the residue was directly analyzed by GPC.

Copolymerization of Germylene 1a with 5,6-dihydro-2H-pyran-2-one. A typical procedure by using *n*-butyllithium as an initiator is as follows: To a THF solution (1.5 mL) of germylene **1a** (573 mg, 1.46 mmol) was added a hexane solution of *n*-butyllithium (1.60 N, 1.46 x 10^{-2} mmol) and the resulting mixture was stirred at room temperature for 1 h. A THF (1.5 mL) of 5,6-dihydro-2H-pyran-2-one (145 mg, 1.47 mmol) was then added dropwise at -78 °C with stirring. After being stirred for 3 h, the reaction mixture was poured into 50 mL of acetonitrile under argon. The white precipitate was collected by filtration under argon and dried in vacuo to give 657 mg of copolymer **5** (92 % yield): ^{1}H NMR ($CDCl_3$) δ 0.26 (s, SiMe, 36H), 1.97 (br, $CHCH_2$, 2H), 2.72 (br, CH, 1H), 3.83 (br, CH_2O, 2H), 4.18 (br, CH=, 1H); ^{13}C NMR ($CDCl_3$) δ 6.2 ($SiMe_4$), 25.1 (CH_2CH), 31.7 (CH), 66.9 (CH_2), 70.7 (CH=), 155.2 (=C-O).

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