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Novel Oxidation−Reduction Copolymerization of a Germylene with Ethylene or Propylene Sulfide Producing a 1:1:α Periodic Copolymer

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The development of a new polymerization reaction makes it possible to create polymers having a monomer unit structure which is difficult to construct by conventional procedures. Organometallic polymers having a germanium(IV) unit in the main chain have become interesting substances from the viewpoint of material science.[1] The conventional methods for preparation of germanium-containing polymers have been based on the concept of polycondensation by using a tetravalent germanium species and a bifunctional monomer as building blocks. Normally, these procedures are accompanied by the elimination of small molecules as a result of acid−base reactions or a dehydration process. It is, therefore, necessary to remove them by using an appropriate acid scavenger or a dehydrating agent in order to promote the copolymerization effectively.[2]

In previous papers, we have reported new copolymerization reactions promoted by an oxidation−reduction process (*oxidation−reduction copolymerization*).[3] The reductant monomer of a divalent germanium species, germylene, was found to copolymerize with various oxidant monomers such as *p*-benzoquinone derivatives,[3g−i] cyclic α,*β*-unsaturated ketones,[3j,k] and acetylene derivatives[3l] to afford high molecular weight copolymers containing a germanium(IV) unit in the main chain. These reactions proceed smoothly without using any catalysts, acid scavengers, or dehydrating agents. The present paper describes a synthesis of novel germanium-containing polymers **3** having a germanium(IV) unit and a dithioether unit alternatingly in the main chain by using bis[bis(trimethylsilyl)aminato]germanium(II)[4] (**1**) as the reductant monomer and ethylene or propylene sulfide (**2**) as the oxidant monomer. This is a new class of the oxidation−reduction copolymerization where two molar amounts of **2** toward **1** are consumed, giving rise to a 1:1:α periodic copolymer **3** (α = 0.53 for **3a** and 0.43 for **3b**) by liberating ethylene or propylene (**4**) during the copolymerization (Scheme 1).[5]

The copolymerization involves a redox process; the divalent germanium species is oxidized to the tetravalent germanium unit and the episulfide structure is converted to the thioether unit in the resulting copolymer **3**. Interestingly, the organic unit (−SCH_2CHRS−) of the resulting copolymer is composed of two parts, −SCH_2CHR− and −S−. The structure of the former part corresponds to the ring-opened unit of the starting ethylene or propylene sulfide (**2**), whereas the latter consists of a single sulfur atom, lacking the −CH_2CHR− part. These results suggest that the copolymerization requires two molar amounts of ethylene or propylene sulfide to form the organic unit (−SCH_2CHRS−) by eliminating ethylene or propylene (**4**) during the copolymerization. In fact, the formation of propylene could be confirmed by a ^{1}H NMR spectrum of the reaction mixture of **1** and **2b**.[6]

Scheme 1

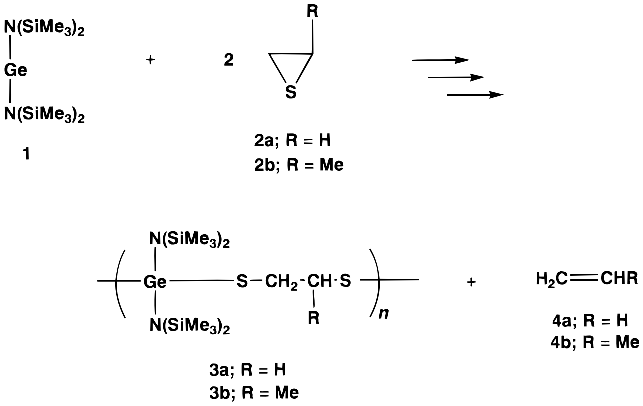

Table 1. Copolymerization of Germylene 1 with Ethylene Sulfide 2a or Propylene Sulfide 2b[a]

	copolymerization		copolymer **3**		
entry	comonomer **2**	feed molar ratio [monomer**1**: monomer **2**]	yield[b] (%)	M_w[c]	M_w/M_n
1	**2a**	1:1	32	8.5×10^3	1.51
2	**2a**	1:2	51	1.2×10^4	2.00
3	**2a**	1:4	37	2.8×10^3	1.79
4[d]	**2a**	1:2	99	1.8×10^5	1.76
5	**2b**	1:1	50	2.6×10^4	1.67
6	**2b**	1:2	78	5.0×10^4	1.60
7	**2b**	1:4	54	8.5×10^3	1.71
8[d]	**2b**	1:2	79	1.3×10^5	1.68
9[e]	**2b**	1:2	75	1.6×10^4	2.57

[a] Copolymerization was carried out at 0 °C for 4 h in toluene. [b] Isolated yield based on monomer **1**, assuming that the stoichiometries of copolymers **3a** and **3b** were 1:1.53 and 1:1.43, respectively, for **1** and **2**. [c] Determined by GPC. [d] Solvent, *n*-hexane. [e] Solvent, THF.

The resulting copolymers are white fine powders, soluble in benzene and chloroform, and insoluble in acetonitrile and acetone. Table 1 summarizes the effect of the monomer feed ratio (monomer **1**:monomer **2**) and the reaction solvent on the yield and molecular weight of **3**. The yield of the resulting copolymers was moderate to quantitative. An excess amount of **2** brought about the reduced molecular weight of **3** (entries 3 and 7). The molecular weight increased when the copolymerization was carried out in *n*-hexane (entries 4 and 8) and that of **3b** decreased slightly when THF was used as solvent (entry 9). It is to be noted that in all runs the stoichiometry of the reaction was 1:2 and the copolymers having a 1:1:α periodic structure composed of −$Ge[N(SiMe)_3]_2$−, −SCH_2CHR−, and −S− were obtained regardless of the monomer feed ratio (monomer **1**:monomer **2**) (Table 1). The third unit (−S−) comprises 53% and 43% of the ethylene sulfide (**2a**) and propylene sulfide (**2b**), respectively, by weight. Thus, copolymer **3** can be regarded as a 1:1:α periodic copolymer where α = 0.53 and 0.43 for **3a** and **3b**, respectively.

The structure of copolymers **3** was determined by ^{1}H and ^{13}C NMR and IR spectroscopies as well as elemental analysis. Figure 1 shows the ^{1}H NMR spectrum of copolymer **3b** obtained from **1** and **2b** at 0 °C in toluene (entry 6). The signal at around δ 0.34 is assigned to the trimethylsilyl protons (denoted by a in Figure 1) of the ligand on the germanium atom. The signal at δ 1.57 is due to the methyl protons d derived from propylene sulfide. Two signals at δ 2.90 and 3.08 are ascribed to the methylene protons b in the polymer main chain. The

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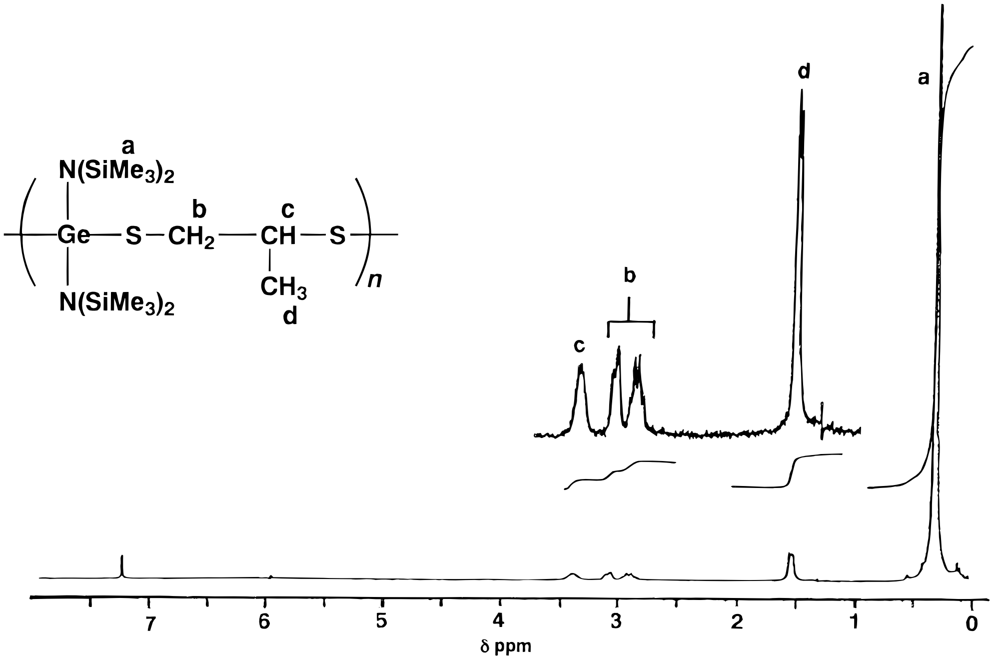


Figure 1. ^{1}H NMR spectrum of copolymer **3b** in $CDCl_3$.

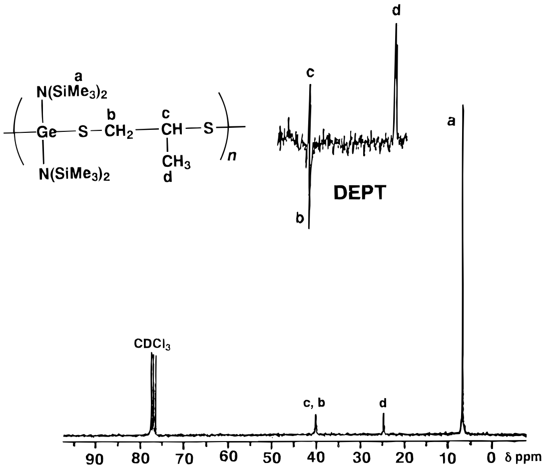


Figure 2. ^{13}C NMR spectrum of copolymer **3b** in $CDCl_3$.

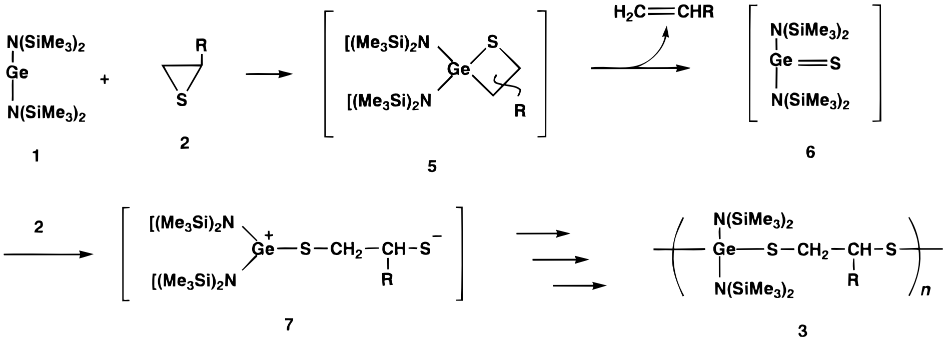
signal at δ 3.40 is assigned to the methine proton c in the polymer chain. By comparison of the integral value of the peaks a and b–d, the ratio of the germanium(IV) unit and the organic unit in the copolymer was calculated to be 1:1. The fairly lower chemical shifts of the signals b and c clearly indicate that both of the methylene protons and the methine proton are connected to the sulfur atoms. The incorporation of two sulfur atoms into the organic unit was also confirmed by the elemental analysis of the copolymers.

The ^{13}C NMR spectrum of copolymer **3b** shows five peaks at δ 6.7, 24.4, 24.7, 39.8, and 40.0, assignable to carbon atoms denoted as a–d in Figure 2. Of the overlapped signals b and c, the existence of the methylene carbon atom was confirmed by DEPT measurement. The splitting of signal d assignable to the methyl carbon atom may be explained by assuming the formation of a head to tail or a head to head structure concerning the two organic units ($-SCH_2CHRS-$) across the germanium atom.

The mechanism of the present copolymerization is proposed as follows (Scheme 2). The first step of the reaction is an oxidative addition of **2** to **1** to form a germathietane intermediate **5** via formation of a germylene–sulfide complex. Then, **5** is converted into a key species, germanethione **6**, by liberating ethylene or propylene. In the next step, the resulting very reactive germanethione intermediate **6** attacks further to **2** to give a zwitterion **7** via ring-opening of the episulfide ring. The propagation proceeds via successive combination among the zwitterions leading to 1:1:α copolymer **3**.

In conclusion, a novel germanium-containing periodic copolymer **3** having a germanium(IV) unit, an ethane thioether unit, and a sulfide unit periodically in the main chain has successfully been prepared by combined use of a germylene, bis[bis(trimethylsilyl)aminato]germanium(II) (**1**), and ethylene or propylene sulfide (**2**).

Scheme 2



The present reaction provides a new example of oxidation−reduction copolymerization, where two ethylene sulfide or propylene sulfide molecules are consumed to construct the dithioether unit with the elimination of ethylene or propylene, respectively.

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(5) A typical procedure for the copolymerization of germylene **1** and ethylene sulfide **2a** (entry 4 in Table 1) was as follows: To a solution of bis[bis(trimethylsilyl)aminato]germanium(II) (775 mg, 1.97 mmol) in *n*-hexane (2 mL) was added an *n*-hexane (5 mL) solution of ethylene sulfide (237 mg, 3.94 mmol) slowly under argon at 0 °C, and the reaction mixture was stirred at the same temperature for 4 h. The solvent was removed, and the residue was dissolved in a minimum amount of chloroform. The resulting solution was poured into a large amount of acetonitrile to precipitate the polymeric products. The material was isolated by centrifugation followed by decantation and dried in vacuo to give 956 mg of copolymer **3a** (99% yield): ^{1}H NMR ($CDCl_3$) δ 0.33 ($SiMe_3$), 2.94 (CH_2); ^{13}C NMR ($CDCl_3$) δ 6.4 ($SiMe_3$), 31.4 (CH_2); IR 2945, 1425, 1401, 1250, 1210, 1096, 1017, 861, 760, 673, 617, 412 cm^{-1}. Anal. Calcd for $C_{14}H_{40}GeN_2S_2Si_4$: C, 34.63; H, 8.30; N, 5.77; S, 13.21. Found: C, 33.84; H, 8.33; N, 5.23; S, 12.87. The copolymerization of germylene **1** and propylene sulfide **2b** was carried out in a similar manner to afford the copolymer **3b**: ^{1}H NMR ($CDCl_3$) δ 0.34 ($SiMe_3$), 1.57 (CH_3), 2.90, (CH_2), 3.08 (CH_2), 3.40 (CH); ^{13}C NMR ($CDCl_3$) δ 6.7 ($SiMe_3$), 24.4, 24.7 (CH_3), 39.8 (CH_2), 40.0 (CH); IR 2950, 1425, 1390, 1249, 1215, 1163, 869, 760, 673 cm^{-1}. Anal. Calcd for $C_{15}H_{42}GeN_2S_2Si_4$: C, 36.06; H, 8.47; N, 5.61; S, 12.84. Found: C, 35.42; H, 8.49; N, 4.83; S, 13.92.

(6) When the copolymerization was carried out in a sealed NMR sample tube, the characteristic olefin peaks of the liberated propylene were detected at around δ 5.0−6.0 and their intensities were increased as the copolymerization proceeded, indicating that the copolymerization accompanies the elimination of propylene.

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