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Copolymerization of a Germylene with Acetylene Monomers by Rhodium Catalysis

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A germylene with a bulky ligand, bis[bis(trimethylsilyl)amido] germanium, was copolymerized for the first time with acetylene monomers under the catalysis of a rhodium compound, to give rise copolymers with a structure having acetylene units in excess. Among the catalysts used, a rhodium norbornadiene complex was found to be most effective for the copolymerization.

Along with the vigorous progress of organosilicon chemistry, organogermanium chemistry has also attracted much attention in recent years not only from the view point of synthetic chemistry but in the potential application of organogermanium compounds and germanium-containing polymers. As the heavy analogues of carbenes, germylenes were found to be highly reactive towards many kinds of organic compounds.[1,2] This explored us to synthesize germanium-containing polymers by using a germylene as monomer. A germylene has been copolymerized successfully with p-benzoquinone[3] and cyclic α,β-unsaturated ketone[4] derivatves to produce alternating copolymers in both cases.

The present paper describes the new synthesis of germanium-containing polymers (**3**) by copolymerization of a germylene, bis[bis(trimethylsilyl)amido] germanium (**1**),[5] with acetylene monomers (**2**). Germylene **1** is present in a monomer form as a stable species under ambient conditions. In relevant to the present study, reactions of a germylene with an acetylenic compound resulted in the formation of cyclic germanium compounds in most cases.[2,6,7]

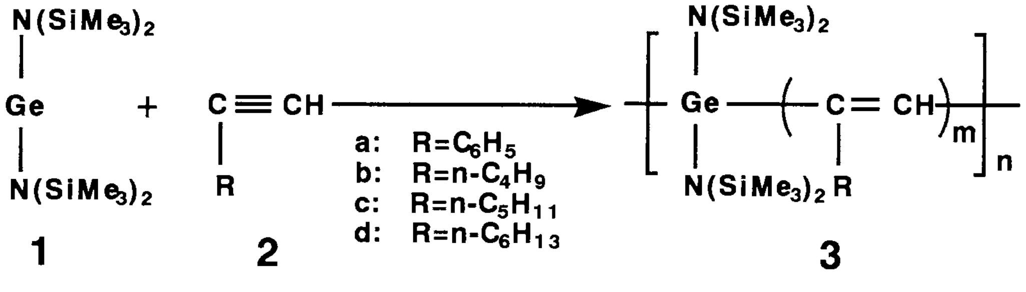

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Table 1. Copolymerization of **1** with **2** by a Rhodium Catalyst under Various Conditions[a)]

	Copolymerization					Copolymer			
Entry	**1** (mmol)	**2**	[Rh][b)] mmol	Solvent mL	Time h	Yield of **3**/%[c)]	*Mn* (x10^3)[d)]	*Mw*/*Mn*	**1**:**2** Molar ratio[e)]
1	1.10	**2a**	0	Toluene (4.0)	48	0			
2	0.84	**2a**	0.012	NEt_3 (6.0)	5 min	30	21.6	2.1	1 : 8.3
3	1.11	**2a**	0.017	Toluene (4.0)	1	36	16.7	6.6	1 : 5.0
4	1.10	**2a**	0.017[f)]	NEt_3 (4.0)	21	10	10.2	1.5	1 : 1.5
5	0.49	**2b**	0.0054	Toluene (3.0)	13	35	4.9	2.3	1 : 2.6
6	1.22	**2c**	0.021	NEt_3 (4.0)	5	31	4.4	2.1	1 : 2.9
7	0.97	**2d**	0.021	NEt_3 (4.0)	5	30	3.9	1.8	1 : 2.5

a) With the equimolar feed ratio of **1** and **2** carried out at room temperature under argon.
b) $[Rh(norbornadiene)Cl]_2$ except for Entry 4. c) Methanol insoluble parts. d) Determined by GPC.
e) Calculated from ^1H NMR. f) $[Rh(C_2H_4)_2Cl]_2$ as catalyst.

It has been found that a catalyst is necessary (Entry 1, Table 1) and some of rhodium compounds are effective for the present copolymerization. In a typical run (Entry 6, Table 1), 0.480 g (1.22 mmol) of germylene **1** and 0.117 g (1.22 mmol) of 1-heptyne (**2c**) were dissolved in 3.0 mL of triethylamine under argon. To this solution, was added 8.0 mg (0.021 mmol) of $[Rh(norbornadiene)Cl]_2$ in 1.0 mL of triethylamine. After 5 h with stirring at room temperature, the reaction mixture was poured into 8.0 mL of methanol to precipitate polymeric materials, which were isolated by filtration, followed by vacuum drying at about 50 °C to give 0.185 g (31% yield) of the polymeric product, which was a pale yellow powder soluble in a common organic solvent such as chloroform and toluene. The structure of the product was analyzed by ^{13}C and ^1H NMR and IR spectroscopy as well as gel permeation chromatography (GPC) and confirmed as copolymer **3c**.

Fig. 1 (A) shows the ^{13}C NMR spectrum of the product. Signals at 145.6 and 144.0 ppm were attributed to two carbon atoms of the olefinic unit attached to the germanium atom. Other olefinic carbon atoms in the main chain appeared at 139.3 and 127.0 ppm as two singlets **a** and **b** respectively. Signals **c**, **c** ', **d**, **e**, and **f** were assigned as four methylene carbons of n-pentyl group. Signals **g** and **h** are due to terminal methyl of n-pentyl group and Si-methyl group, respectively. In the ^1H NMR spectrum, Fig. 1 (B), the olefinic proton adjacent to the germanium appeared at δ 6.70 and the other olefinic protons in the main chain at δ 5.92. Proton signals of methylenes and methyls are assigned in the figure. From the integral values of proton peaks **e** due to $SiCH_3$ group in the germylene unit and **d** due to CH_3 group derived from **2c**, the unit ratio of **1** and **2c** in the product was calculated as 1.0 : 2.9. GPC analysis of the product showed one peak with *Mn* as 4400 (*Mw*/*Mn*=2.1) based on polystyrene standard. The IR spectrum of the product (Fig. 2) showed a characteristic absorption of the C=C group at 1626 cm^{-1}, and the two sharp absorptions at 2940 and 1259 cm^{-1} and the two broad absorptions around 1050 and 830 cm^{-1} are due to the germylene units. All the above data strongly suggest the structure of the product as copolymer **3 c**.

The rhodium complex of norbornadiene[8] was active for copolymerization of **1** with phenylacetylene(**2a**), 1-hexyne (**2b**), 1-heptyne (**2c**) and 1-octyne (**2d**). In the combination of **1** with **2a**, this catalyst seems to be too active for the homopropagation of **2a**, resulting in the less germylene unit content in copolymer **3a** (Entries 2 and 3, Table 1) compared with the copolymerization of **1** with 1-alkynes (**2b-d**). A less active catalyst for the homopolymerization of phenylacetylene, $[Rh(C_2H_4)_2Cl]_2$,[9] gave a copolymer **3a** with a much higher germylene unit content (Entry 4, Table 1).

The lower content of germylene units in the copolymer **3** in almost all cases is probably due to the relatively high homopropagation tendency of the acetylene monomers, while the germylene monomer is not able to homopropagate because of its bulky ligand. The relatively lower copolymer yield may be ascribed to the less copolymerizability of the germylene monomer.

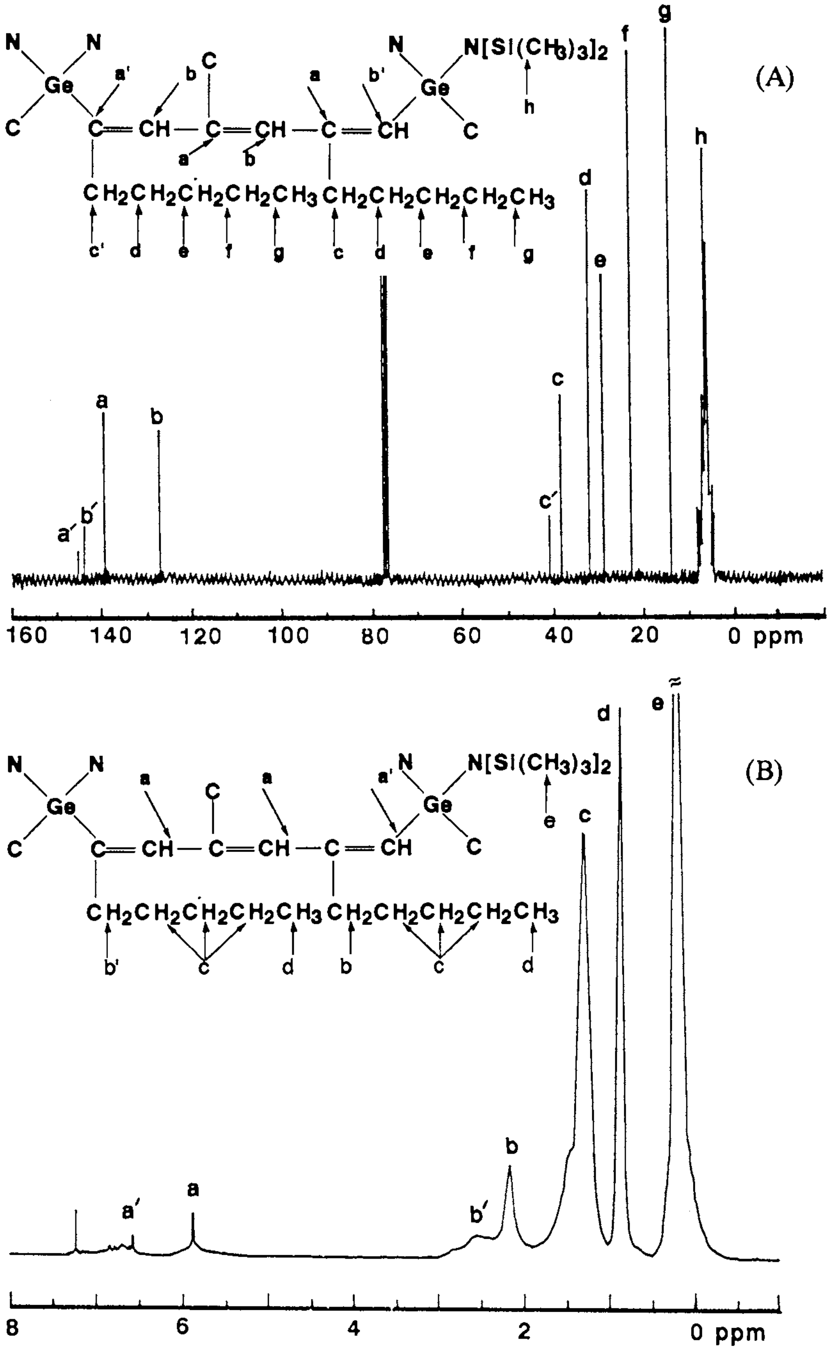

Fig. 1. ^{13}C NMR (A) and ^{1}H NMR (B) spectra of copolymer **3 c** (both in $CDCl_3$).

Besides catalysts used above, several other transition metal compounds were examined for the copolymerization of **1** with **2a**. A compound like $Pd[PPh_3]_4$ or $RhCl[PPh_3]_3$ which was not effective for the homopolymerization of **2a**, was also not able to catalyze the present copolymerization. It is well known that molybdenum and tungsten compounds were very effective for the homopolymerization of acetylenes.[10,11] When

$MoCl_5$ and WCl_6 were used in the present reaction, their catalytic activity was not so high and the copolymer yield was very low. In the case of di-substituted acetylenes, such as 2-hexyne and 1-phenyl-1-propyne, both of their homopolymerization and copolymerization with **1** were difficult by the catalysis of the rhodium norbornadiene complex.

More detailed studies including the copolymerization mechanism and copolymer properties are now under progress.

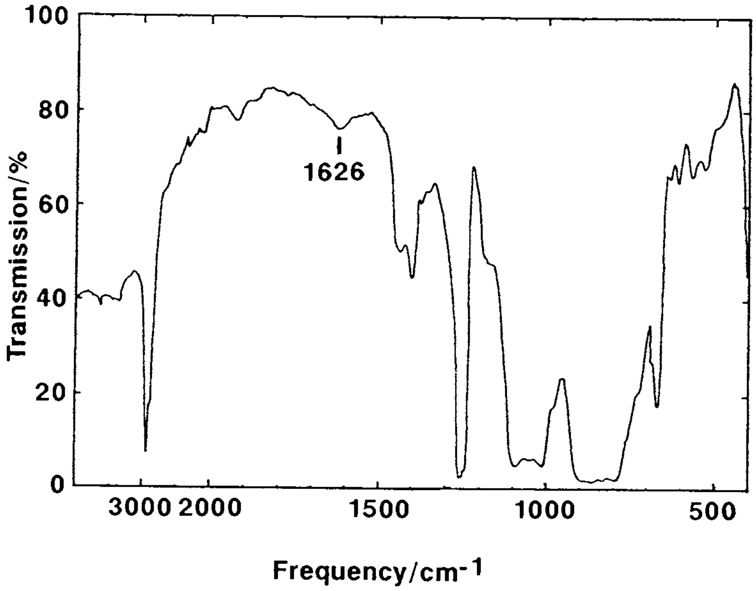

Fig. 2. IR spectrum of copolymer **3c**.

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