CHEMISTRY LETTERS, pp. 647-650, 1992.

Synthesis and Conductivity of Germanium- or Silicon-Containing Polymers

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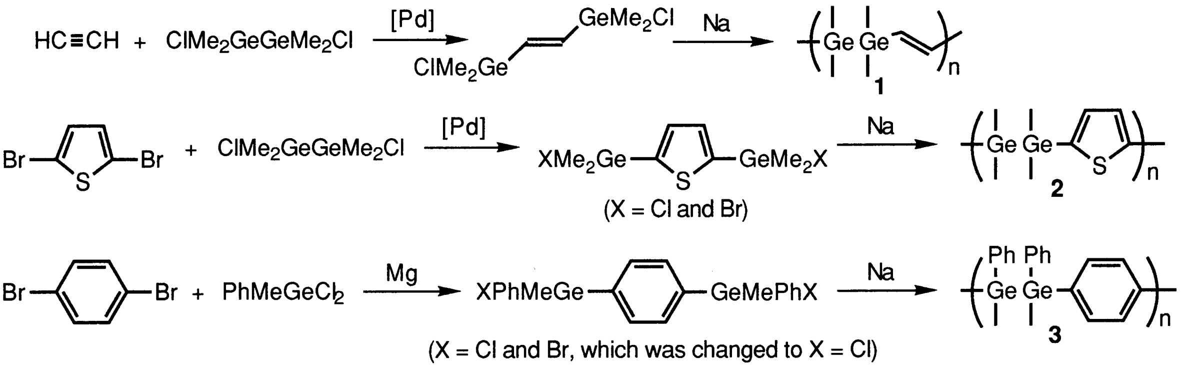
Poly[{(*E*)-1,1,2,2-tetramethyldigermanylene}ethenylene], poly[(1,1,2,2-tetramethyldigermanylene)-2,5-thienylene], poly[(1,2-dimethyl-1,2-diphenyldigermanylene)-*p*-phenylene], and poly(methylphenylgermylene) were synthesized. SbF_5 doping of above polymers showed the conductivities of the order of 10^{-4} S/cm, which were similar to, or a little higher than, those of corresponding silicon analogues.

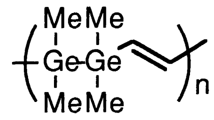
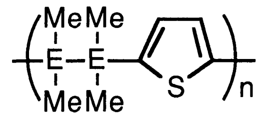
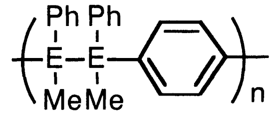
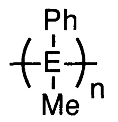
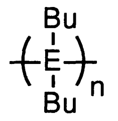
Organosilicon polymers featured by σ or σ-π conjugation exhibit characteristic physical properties and are attracting much attention as semiconductors, photoconductors, photoresists, and nonlinear optical materials.1) Recently, Ishikawa *et al.*2) synthesized several poly(disilanylene-π-electron system)s and reported the conductivities of these polymers upon SbF_5 doping. On the other hand, organic polygermanes are also known3) to exhibit σ conjugation like organic polysilanes. Indeed, thermochromism,4) photoconductivity5) and nonlinear optical effect6) of some polygermanes have been investigated. We now wish to report the synthesis of several germanium-containing polymers and their conductivity upon doping with SbF_5.

We recently developed double germylation reaction of acetylenes7) and germylation reaction of organic halides8) by use of palladium catalysts. (*E*)-1,2-Bis(chlorodimethylgermyl)ethene and a mixture of 2,5-bis(chloro- and/or bromodimethylgermyl)thiophenes were prepared by these methods, respectively. On the other hand, *p*-bis(chloromethylphenylgermyl)benzene9) was prepared from *p*-dibromobenzene and dichloromethylphenylgermane according to the procedure for *p*-bis(chlorodimethylgermyl)benzene10) with a slight modification.



Wurtz-type polycondensations of the above monomers as well as corresponding silicon analogues gave germanium- or silicon-containing polymers as shown in Table 1. Polymers **1**, **2**, **3**, and **6** were newly prepared.11) Poly(dibutylgermylene) (**7**),12) and silicon-analogues **4**,13) **5**,14) **8**, and **9**15) were prepared according to literatures.

Table 1. Synthesis and Conductivity of Ge- or Si-Containing Polymers

Polymer	E	Reaction conditions[a]/ Yield(Reprecipitation)	$M_w(M_w/M_n)$[b]	λ_{max}/nm	σ/S cm^{-1}[c]
	**1**	US,[d] 0.5 h/30%(A[e])	33,000 (peak)	260	4×10^{-4}
	Ge **2** Si **4**	100 °C, 6 h/10%(B[f]) Ref. 13	27,500 (2.47) 8,700 (2.34)	256 271	3×10^{-4} 1×10^{-4}
	Ge **3** Si **5**	Reflux, 2 h/10%(A) Ref. 14	21,300 (2.74) 48,000 (3.21)	244 254	4×10^{-4} 2×10^{-4}
	Ge **6** Si **8**	Reflux, 1.5 h/35%(A) Ref. 15	8,600 (2.07) 9,400 (2.80)	330 343	5×10^{-4} 2×10^{-4}
	Ge **7** Si **9**	Ref. 12 Ref. 15	10,000 (1.16) 170,000 (4.10)	329 319	6×10^{-4} 1×10^{-4}

a) Monomer solution was added to Na dispersion in toluene at reaction temperature. b) M_w: weight-average molecular weight, M_n: number-average molecular weight, both from GPC (polystyrene standards). c) Conductivity during SbF_5 doping. d) External irradiation of ultra sound (40°C). e) Reprecipitation solvent was toluene/isopropyl alcohol = 1/5. f) Reprecipitation solvent was toluene/hexane = 1/5.

All the polymers **1** - **9** were soluble in toluene and were spin-coated on glass-substrates. Two pieces of copper wire were attached to the resulting thin solid film by means of gold paste and the electric conductivity was measured by the two-probe method during SbF_5 doping. The doping was carried out with the vapor pressure of SbF_5 at room temperature. The film turned dark blue except that of **7** and **9**. From the conductivity data in Table 1, the following are pointed out. 1) Germanium-containing polymers show similar or a little higher conductivity as compared with the corresponding silicon analogues. This may be ascribed to a lower ionization potential (*Ip*) value, which correlates to readiness for acceptor doping, of Ge-Ge bonds than that of Si-Si bonds.3) 2) The conductivities of all the polymers **1**-**9** are in the same range (10^{-4} S/cm), which indicates that π-electron systems in polymer backbone or those as a substituent do not largely affect the conductivity of the doped polymers.16) This is consistent with the fact that band gap values calculated in CNDO/2 level for poly(disilanylene-ethenylene), poly(disilanylene-phenylene), and polysilanes are similar.18)

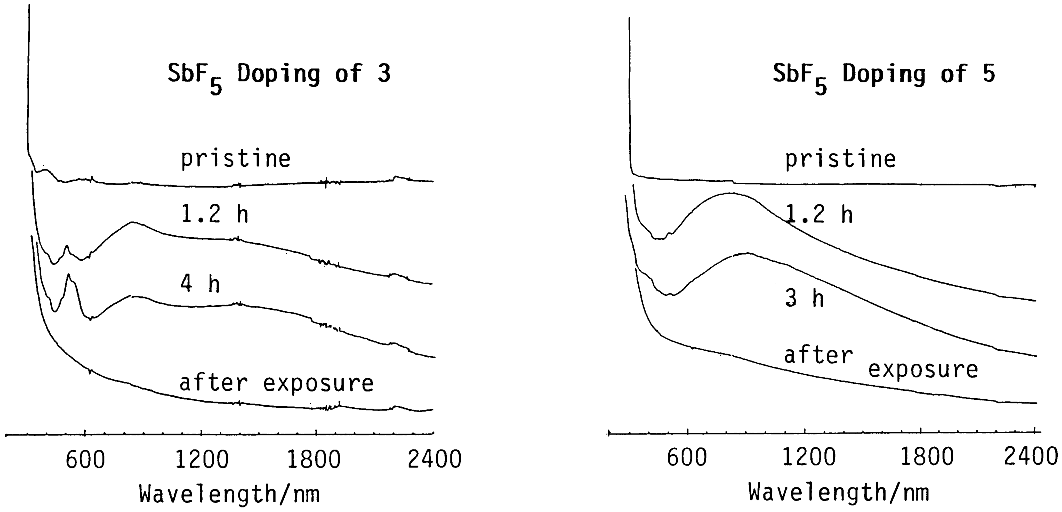


Fig. 1. UV-Vis-near IR spectra of **3** and **5** during SbF_5 doping.

In order to examine the doped state, UV-Vis-near IR spectra were measured (Fig.1). For the polymers **1-6** and **8**, an absorption was observed in visible to near IR region during doping. This new band can be ascribed to a charge transfer absorption relevant to the electric conductivity. Polymers **7** and **9** did not show distinct absorptions.[19)]

The conductivity values for **4** and **5** were lower by 10^3-10^4 times than those reported.[21)] In case of polyacetylene or polydiacetylene, it is known that exposure of the doped polymer to the moist atmosphere results in an increase of the conductivity.[22)] Similar phenomena were observed for the polymers **1-9**. Each polymer film on the glass substrate, after the doping with SbF_5 followed by evacuation of the doping vessel, was exposed to the atmosphere (relative humidity 45-55% at 22-26 °C). The conductivity rapidly rose up to the order of 10^{-1}-10^0 S/cm in 5-10 seconds. The exposure to dry air did not increase the conductivity. UV-Vis-near IR spectra exhibited that the absorption observed during doping (Fig. 1) disappeared immediately after the exposure to the atmosphere. Based on these observations, it can be safely concluded that the electric conductivities of polymers **1-9** originated from charge transfer on acceptor doping with SbF_5 are in the order of 10^{-4} S/cm.

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9) *p*-Phenylenebis(magnesium bromide) was treated with dichloromethylphenylgermane (1.15 equiv.) in THF/benzene (1:1) at 60 °C for 18 h. The reaction mixture was filtered at 60 °C and concentrated. The hexane extract was subjected to vacuum distillation to give pale yellow oil (34% yield). Since the oily product was a mixture of the bromide and the chloride, it was transformed to *p*-bis(methylphenylgermyl)benzene (130 °C/0.1 Torr, 55%) with $LiAlH_4$. Refluxing in CCl_4 afforded *p*-bis(chloromethylphenylgermyl)benzene (85%). Bp 135-138 °C/2.9×10^{-3} Torr; ^1H NMR ($CDCl_3$) δ 7.67 (s, 4H), 7.6-7.67 (m, 4H), 7.4-7.5 (m, 6H), 1.16 (s, 6H) ppm; Anal. Found: C, 50.58; H, 4.26%. Calcd for $C_{20}H_{20}Ge_2Cl_2$: C, 50.41; H, 4.23%.

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11) **1**: White powder; mp 87-89 °C; ^1H NMR (C_6D_6) δ 7.02 (s, 2H), 0.52 (s, 12H) ppm; ^{13}C NMR (C_6D_6) δ 148.3, -3.5 ppm; IR (nujol) 990 (trans CH=CH), 620, 590, 554 cm^{-1}; UV (THF) λ_{max} 260 nm (ε 4200). Anal. Found: C, 31.15; H, 5.86%. Calcd for $(C_6H_{14}Ge_2)_n$: C, 31.14; H, 6.10%. **2**: Pale yellow powder; mp 203-206 °C (softn.); ^1H NMR (THF-d_8) δ 7.20 (s, 2H), 0.58 (s, 12H) ppm; IR (KBr) 800 (thiophene CH), 610, 585, 510 (Ge-C) cm^{-1}; UV (THF) λ_{max} 256 nm (ε 19100). Anal. Found: C, 32.74; H, 4.72%. Calcd for $(C_8H_{14}Ge_2S)_n$: C, 33.43; H, 4.91%. **3**: Pale yellow powder; mp 117-119 °C; ^1H NMR ($CDCl_3$) δ 7.27 (br, 14H), 0.73 (br, 6H) ppm; IR (KBr) 1424, 1081, 454 (Ge-Ph) cm^{-1}; UV (THF) λ_{max} 244 nm (ε 21500). Anal. Found: C, 59.10; H, 5.01%. Calcd for $(C_{20}H_{20}Ge_2)_n$: C, 59.23; H, 4.97%. **6**: Pale brown powder; mp 129-132 °C (gelation); ^1H-NMR ($CDCl_3$) δ 6.3-7.2 (br, 5H, C_6H_5Ge), -0.5-0.5 (br, 3H, CH_3Ge) ppm; IR (film) 1483, 1081, 1065, 450 (Ge-Ph) cm^{-1}; UV (THF) λ_{max} 330 nm (ε 6500), 268 nm (ε 3800). Anal. Found: C, 50.88; H, 5.11%. Calcd for $(C_7H_8Ge)_n$: C, 51.04; H, 4.90%.

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16) In case of poly[(silanylene)diethynylene]s, introduction of a phenyl group onto the backbone showed higher conductivity than that of a methyl group under $FeCl_3$ doping.17)

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19) A pristine film of **7** exhibited red shifted absorption (λ_{max} 360 nm) in comparison with the absorption in solution (λ_{max} 329 nm). The shift may be ascribed to the change of the conformation of polygermylene backbone,20) to the state favorable for σ conjugation.

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(Received February 3, 1992)