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Synthesis and Electric Conductivity of Poly[(dodecamethyl-1,6-hexasilanediyl)-1,1′-ferrocenediyl]

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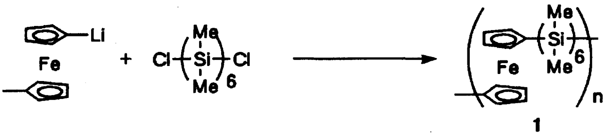
Synopsis. Poly[(dodecamethyl-1,6-hexasilanediyl)-1,1′-ferrocenediyl] was prepared from dilithioferrocene and 1,6-dichlorododecamethylhexasilane. The polymer exhibited electric conductivities of 3×10^{-5} S cm^{-1} upon iodine doping and 2×10^{-6} S cm^{-1} upon SbF_5 doping.

Organosilicon polymers featured with σ or σ-π conjugation along the backbone are known to exhibit intriguing properties such as conductivity, photoconductivity, thermochromism, nonlinear optical effect, and photoreactivity.$^{1)}$ However, these properties have been examined only for polysilanes and polycarbosilanes. On the other hand, a polymer with ferrocene units placed in the backbone, poly(1,1′-ferrocenediyl), is known to exhibit conductivities.$^{2—5)}$ Accordingly, introduction of ferrocene units into organosilicon polymers appears interesting. Ferrocene-containing organosilicon polymers have been known. However, the polymers are limited to those having siloxane linkages$^{6)}$ or isolated silylene units,$^{7)}$ and no polymer having both catenated silylenes and ferrocene units has been prepared until recently. Pannel et al.$^{8)}$ synthesized a polysilane with ferrocenyl groups as side chains, but its conductivity was not reported. A Chinese group$^{9)}$ prepared copolymers consisting of ferrocenediyl and oligosilanediyl units and reported conductivities ranging from 10^{-12} to 10^{-7} S cm^{-1}. However, these polymers are random copolymers and ferrocene-containing polysilanes with regularly alternating structure have not been synthesized yet. We now report the synthesis and conductivity of poly[(dodecamethyl-1,6-hexasilanediyl)-1,1′-ferrocenediyl] (**1**) in which ferrocenediyl and 1,6-hexasilanediyl units are alternatively arranged in the backbone (Scheme 1).



Scheme 1.

Experimental

Molecular weight distribution was measured with GPC (polystyrene standards) using Shodex KF-801, KF-802, and KF-80M columns and THF eluent at 1 ml min^{-1}. UV-vis, ^{1}H NMR, and IR spectra were recorded on Shimadzu UV-3100, Hitachi R-40, and JASCO A-302 spectrometers, respectively. Thickness of thin solid films was measured by a Taylor Hobson's Talystep instrument. An Advantest TR-8652 electrometer was used for conductivity measurements.

Synthesis of 1. An adduct of 1,1′-dilithioferrocene with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine$^{10)}$ (154 mg, 0.49 mmol) and 1,6-dichlorododecamethylhexasilane$^{11)}$ (155 mg, 0.37 mmol) were refluxed in toluene (5 ml) for 5 h. After cooling, the reaction mixture was filtered and the filtrate was concentrated. The residue was dissolved in THF (5 ml), and treated with a Grignard reagent which was prepared from 100 mg of *p*-bromotoluene. The resulting mixture was evaporated, and the solid residue was extracted with toluene. The extract was washed with water, filtered, dried with $MgSO_4$, and was evaporated. The polymer dissolved in THF was reprecipitated into methanol (twice, THF/methanol=1 : 5) to give 110 mg (56%) of pale yellow powder. UV-vis (THF) 272 (ε=35000) and 450 nm (ε=430); ^{1}H NMR (C_6D_6) δ=0.25—0.45 (m, 24H), 0.45—0.60 (m, 12H), and 4.05—4.45 (m, 8H); IR (KBr) 3100w, 2960m, 2900m, 1400m, 1250s, 1160s, 1040s, 820s, 760s, 690m, and 630m cm^{-1}. Found: C, 49.30; H, 8.79%. Calcd for $(C_{22}H_{44}Si_6Fe)_n$: C, 49.58; H, 8.32%.

Conductivity Measurement. A THF solution (1—2%) of **1** was cast on a quartz substrate to give a thin solid film, to which copper wires were attached with gold paste (Tokuriki Chemical, 8560-1A). Electric conductivity was measured with two-probe method by applying direct current of 10 nA or 100 pA. For iodine doping, iodine vapor was introduced with nitrogen stream into the vessel. For SbF_5 doping, about 0.5g of SbF_5 was placed in the vessel which was then sealed up. In both cases, conductivity measurement was started before doping and continued without exposure to the atmosphere.

Results and Discussion

Synthesis and Properties of 1. Condensation reaction of 1,1′-dilithioferrocene with 1,6-dichlorododecamethylhaxasilane gave **1**. ^{1}H NMR signals of dimethylsilylenes were divided into two bunches, the integral ratio of which was almost 2 : 1, showing that hexasilanediyl structure was retained. Though its synthesis was worked up with *p*-tolylmagnesium bromide, ^{1}H NMR spectrum did not show any terminal *p*-tolyl group. Thus, **1** seemed to have ferrocenyl terminals or a cyclic structure.

Molecular weight of **1** was 3500 (peak top) and showed a monomodal distribution (Fig. 1), indicative of the polymer consisting of six units. The UV-vis spectrum of **1** had absorption maxima at 272 and 450 nm. The former was assignable to the polysilane structure and the latter to the ferrocene unit, respectively. The absorption maximum of tetradecamethylhexasilane is reported to appear at 260 nm.$^{12)}$ The bathochromic

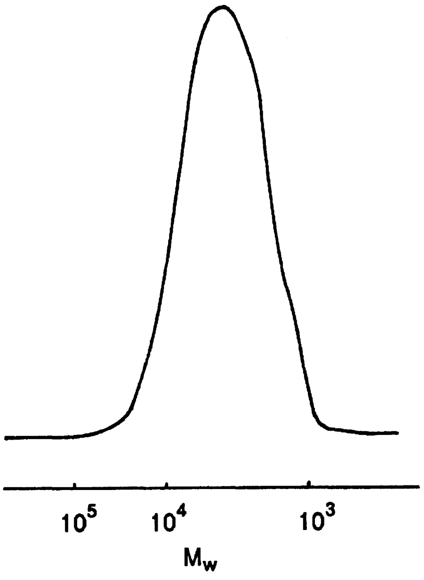


Fig. 1. GPC profile of **1**. Column: Shodex KF801+KF802+KF80M, Eluent: THF 1 ml min^{-1}, Detector: UV 265 nm.

shift by 12 nm observed for **1** can be ascribed to σ–π conjugation between the polysilane and ferrocene moieties. The polymer **1** was readily soluble in THF or toluene. The THF solution gave a thin solid film by casting method.

Conductivity upon Iodine Doping. Si–Si bonds in disilanes are known to be cleaved by the reaction with iodine.[13)] In order to see the possible cleavage of **1** under iodine doping, UV-vis spectra were compared before and after the doping (Fig. 2). Before the doping, $\lambda_{\max}$ values were 272 (ε=35000) and 450 nm (ε=430). They shifted to 268 (ε=27000) and 366 nm (ε=2400) after iodine doping over 12 h. Since ferrocenium polyiodide has absorptions at 295 and 370 nm,[14)] the absorption at 268 nm seems to originate from the polysilane structure. Thus, the cleavage of the polysilane structure by iodine vapor does not seem to be so serious under the doping conditions.

Upon the exposure of the cast film of **1** to iodine vapor, the electric resistance value decreased down to the order of 10^{-6} S cm^{-1} (Fig. 3). The stream of pure nitrogen changed **1** to insulator again. This cycle could be repeated several times as illustrated in Fig. 3, although the resistance value observed upon doping was increasing gradually with the repetition of the cycle.

Table 1 summarizes electric conductivities calculated from resistance values measured after 30 min to 1 h exposure to iodine vapor and film thickness measured after doping. Since two samples with different thickness gave the similar conductivity values, surface conductance could be denied. The conductivity of **1** was 10^2 to 10^3 times higher than those of poly(dimethylsilylene) (octadecamer)[15)] and the mixture of the octadecamer and ferrocene. Therefore, the conjugated structure of the backbone consisting of ferrocenediyl and hexasilanediyl units seems to contribute to the conductivity.

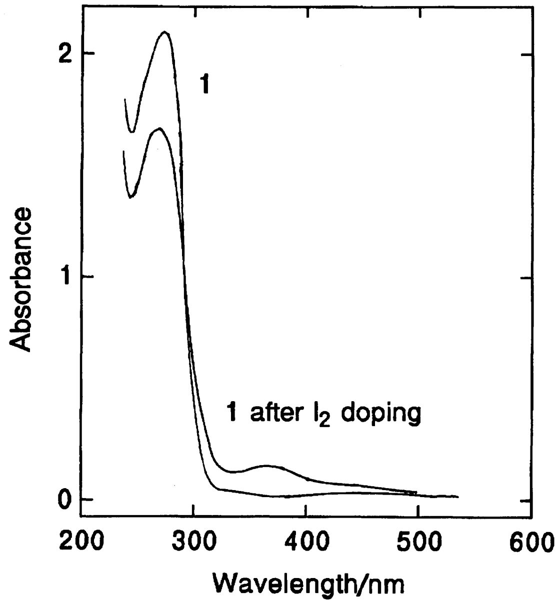


Fig. 2. UV spectra of **1** before and after iodine doping.

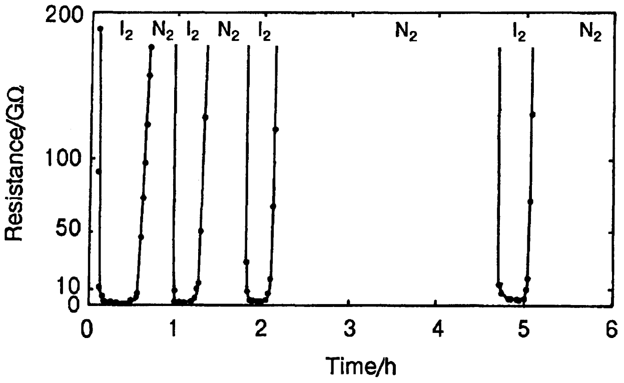


Fig. 3. Change in resistance with iodine doping and nitrogen flush cycle.

Some ferrocene-containing polymers are reported to become conductive upon iodine doping.[3)—5)] For poly(vinylferrocene) and amorphous poly(1,1′-ferrocenediyl), the conductivity is considered to result from hopping between ferrocene moieties.[3,4)] Accordingly, the conductivity of **1** may be partly due to the hopping mechanism. However, its conductivity value upon iodine doping is at least two order of magnitude higher than that of those polymers (10^{-7} S cm^{-1} or less).[3,4)] On the other hand, poly(1,1′-ferrocenediyl) prepared according to Refs. 4 and 5 is reported to be microcrystalline and to exhibit the conductivity in the order of 10^{-4} S cm^{-1} which is ascribed to the delocalization along the chain.[4)] Thus, the conductivity value as well as the UV spectrum of **1** supports the conductivity of **1** is substantially due to the delocalization of the cation radical along the main chain.

Table 1. Conductivity of Thin Films during Doping

Polymer	Thickness/mm	Dopant	Conductivity/S cm^{-1}
1	2.5	I_2	2.7×10^{-5}
1	0.3	I_2	3.2×10^{-5}
$Me(Me_2Si)_{18}Me$	1.5	I_2	3.5×10^{-8}
$Me(Me_2Si)_{18}Me$+Ferrocene[a)]	7.0	I_2	3.8×10^{-7}
1	7.0	SbF_5	1.8×10^{-6}

Two-probe method, under N_2. See Experimental section for measurement conditions.
a) Si/Fe=4.5 (atomic ratio).

SbF_5 Doping. When a cast film of **1** was doped with SbF_5, the resistance decreased with darkening of the film to gray with metallic luster, and became constant in 80 min. The conductivity is also shown in Table 1. A THF solution of the resulting film still showed an absorption at 272 nm, while ε had diminished to 1400, suggesting the irreversible chemical change of **1** during SbF_5 doping.

References

1) R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1359 (1989).

2) D. O. Cowan, J. Park, C. U. Pittman, Jr., Y. Sasaki, T. K. Mukherjee, and N. A. Diamond, *J. Am. Chem. Soc.*, **94**, 5110 (1972).

3) C. U. Pittman, Jr., Y. Sasaki, and T. K. Mukherjee, *Chem. Lett.*, **1975**, 383.

4) K. Sanechika, T. Yamamoto, and A. Yamamoto, *Polym. J.*, **13**, 255 (1981).

5) T. Yamamoto, K. Sanechika, A. Yamamoto, M. Katada, I. Motoyama, and H. Sano, *Inorg. Chim. Acta*, **73**, 75 (1983).

6) W. J. Patterson, S. P. McMarms, and C. U. Pittman, Jr., *J. Polym. Sci., Polym. Chem.*, **12**, 837 (1974).

7) H. Rosenberg, U. S. Patent 3426053 (1969). Very recently, Manners et al. reported the synthesis of poly(silyleneferrocenylene)s through ring opening polymerization: D. A. Foucher, B. Z. Tang, and I. Manners, *J. Am. Chem. Soc.*, **114**, 6246 (1992).

8) K. H. Pannel, J. M. Rozell, and J. M. Zeigler, *Macromolecules*, **21**, 278 (1988).

9) Z. Du, X. Wen, and J. Lin, *Shandong Daxue Xuebao, Ziran Kexueban*, **22**, 115 (1987); *Chem. Abstr.*, **108**, 56695w (1988).

10) M. S. Wrighton, M. C. Palazzotto, A. B. Bocarsly, J. M. Bolts, A. B. Fischer, and L. Nadjo, *J. Am. Chem. Soc.*, **100**, 7264 (1978).

11) H. Gilman and S. Inoue, *J. Org. Chem.*, **29**, 3418 (1964).

12) H. Gilman, W. H. Atwell, and G. L. Schwebke, *J. Organomet. Chem.*, **2**, 369 (1964).

13) A. Taketa, M. Kumada, and K. Tarama, *Nippon Kagaku Zasshi*, **78**, 999 (1957).

14) M. A. Wassef and S. H. Abou El Fitouh, *Indian J. Chem., Sect. A*, **14**, 282 (1976).

15) W. G. Boberski and A. L. Allred, *J. Organomet. Chem.*, **71**, C27 (1974).