Syntheses and Electrical Properties of Organosilicon Polymers Containing Thiophene and Anthraquinone Units

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Organosilicon polymers containing thiophene and anthraquinone units in the main chain were synthesized using palladium catalyst. These polymers were soluble and showed a small UV absorption change by the substituents on the silicon atom. Some of the polymers exhibit cation doping (*n*-doping) by the electrochemical reduction, and this doping process seemed to depend on the kinds of substituents on silicon atom. These polymers showed electrical conductivity of 3×10^{-5} S cm^{-1} when doped with sodium naphthalenide.

Recently, various organosilicon polymers containing π-conjugation unit in the main chain were synthesized and their electrical properties were investigated by several groups.[1—8] These polymers could be doped by strong acceptor dopants such as SbF_5 or $NOBF_4$ and showed the conductivity in the range of $10^{-5}-10^{0}$ S cm^{-1}. The conductivities of these polymers are considered to appear by the pπ–dπ conjugation between the empty d orbital of silicon atom and π-conjugating system.[9,10] The conductivity also seemed to be affected by the π-conjugation length of main chain or the kinds of substituents of silicon atom.[11—14]

Some organosilicon polymers which consist of terthiophene and silicon atom with various substituents were synthesized and electrochemically characterized in our laboratory.[14] These polymers showed good reversible redox reactions and electrical semiconductivities by chemical doping. By using the same method, we synthesized some organosilicon polymers containing thiophene and anthraquinone units in the main chain and their *n*-doping properties were also investigated.

Results and Discussion

The polymers were synthesized by the reported method[13] using palladium catalyst as shown in Scheme 1.

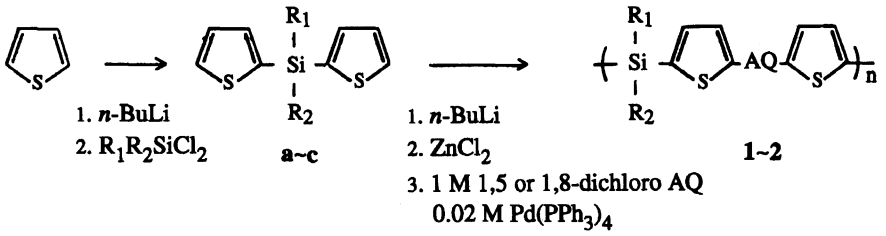
Although coupling reaction between 9,10-dibromoanthracene and zinc derivatives had not proceeded by the palladium catalyst, 1,5-dichloro or 1,8-dichloroanthraquinone was coupled with zinc metalated di(2-thienyl)-silane at 50°C, and the reaction mixture became dark black after 30 min of dropping time. All the polymers were purified by reprecipitation in chloroform–ethanol system followed by Soxhlet extraction in hot ethanol for 48 h. The synthesis results are shown in Table 1. The polymers were obtained as deep yellow powders, which were soluble in general organic solvent. However, polymer **1c** which had the hexyl side chain on silicon atom was obtained as hard yellow grease.

Figure 1 shows the ^{1}H NMR spectrum of polymer **1a**. Methyl proton resonated at $\delta=0.6$—0.8 and thiophene and benzene ring proton signals appeared in the range of $\delta=7.1$—7.4, 7.6—7.8, and 8.1—8.3. The area ratio of the aromatic to methyl proton signal is 5 : 3 which shows good agreement with the expected structure. All the other polymers also exhibited NMR spectra consistent with the structure shown in Scheme 1. The peaks corresponding to carbon atoms in polymer end groups were observed in ^{13}C NMR spectra. The carbonyl carbon signal of the anthraquinone unit was observed at $\delta=183.2$ in polymer **1a**.

IR spectra of polymer **1a** showed the characteristic carbonyl absorption band at 1678 cm^{-1} and out of plane vibration absorption of 2,5-disubstituted thiophene ring was observed in 804 cm^{-1}.

In order to investigate the electron delocalization which occurred through the polymer main chain, the lowest energy absorption maximum and reduction potential of polymers **1a** and **2a** were compared with those of anthraquinone. Under the same measuring conditions of polymers **1a** and **2a**, the λ_{max} and reduction potentials of anthraquinone were observed at 323 nm, −0.98, and −1.43 V, respectively. These values are nearly the same as are reported previously.[15] Compare these values with those of polymers, an 8 nm red-shift of λ_{max} was observed in polymer **1a** and **2a** (Table 1). The reduction potentials of polymer **1a** and **2a** also shifted to the lower negative value by 0.15—0.24 V than those of anthraquinone (Table 2). These findings indicate that the electron delocalization occurred to a little extent, although the thiophene ring of the polymer is considered to take a conformation nearly perpendicular to the plane of anthraquinone unit.[16] On the other hand, UV absorption spectra showed no absorption change between 1,5-disubstituted and 1,8-disubstituted anthraquinone which is considered to have different polymer structure. There was also little change of UV absorption by the substituents on the silicon atom of the polymers (Table 1).

The chloroform solution of polymers **1**—**2** was casted on a platinum electrode and cyclic voltammetry was performed in acetonitrile containing 0.1 M (1 M = 1 mol dm^{-3}) of tetraethylammonium tetrafluoroborate at the scan rate of 100 mV s^{-1}. All the polymers exhibited the successive two anodic peaks by the first scan which potentials are summarized in Table 2. However,



1 : AQ=1,5-disubstituted anthraquinone
R_1=methyl, R_2=methyl (**1a**)
R_1=methyl, R_2=phenyl (**1b**)
R_1=hexyl, R_2=hexyl (**1c**)

2 : AQ=1,8-disubstituted anthraquinone
R_1=methyl, R_2=methyl (**2a**)
R_1=methyl, R_2=phenyl (**2b**)

Scheme 1.

Table 1. Synthesis Result of Polymers **1**—**2**

Polymer	Yield (%)	M_w	M_w/M_n	n[a]	λ_{max}[b]	Td/°C[c]	Appearance
1a	82	3400	1.4	8	331	246	Yellow powder
1b	56	1550	1.2	3	330	241	Yellow powder
1c	69	1800	1.3	3	331	—	Yellow grease
2a	37	1640	1.2	4	331	258	Yellow powder
2b	41	2300	1.4	5	329	244	Yellow powder

a) Repeating units. b) The longest wavelength of absorption maximum is read and measured in THF. c) Decomposition temperature.

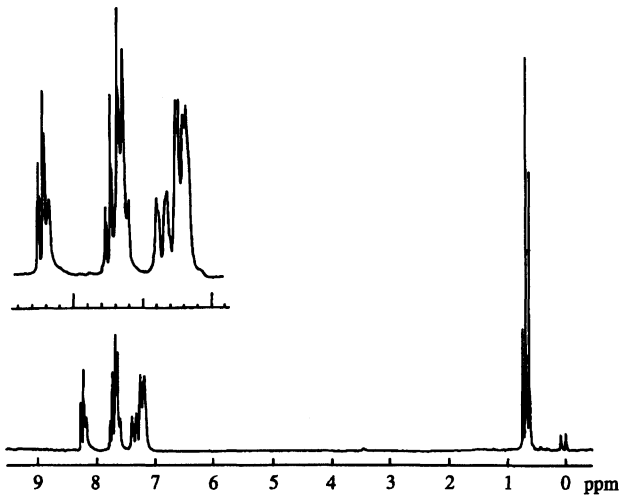


Fig. 1. ^{1}H NMR spectrum of polymer **1a**.

the corresponding cathodic peak was not observed and the polymer film showed no electroactivity at the second scan. All the polymers also showed the same electrochemical inactivities by sweeping to the first anodic potential.

Although polymers **1a** and **2a** did not show any *n*-doping property in the $LiClO_4$ electrolyte solution,[17] a large amount of charge current corresponding to cation doping process was observed in the presence of Et_4NBF_4 electrolyte. As the potential was sweeped to the negative direction, the polymer was doped by cation electrolyte and the color of polymer film became bluish black. The polymers **1a** and **2a** showed two reversible cathodic peaks corresponding to formation of the quinone anion radical and dianion by cation doping process.[18] However, the polymer film was gradually dissolved to the electrolyte solution after the cation doping, which resulted in the small anodic charge current as shown in Fig. 2. Reduction doping potential of polymer **1a** was 0.04—0.08 V lower than that of polymer **2a** and the value of ΔE_p of polymer **1a** was also smaller than that of polymer **2a**, which is attributed to the difference of polymer structure (Table 2). While polymers **1a** and **2a** showed electroactive *n*-doping property, polymers **1b**, **2b**, and **1c** did not show such a property under the same conditions. It is reported that *n*-doping process depends strongly on the substituents of polymer and required a more ordered polymer structure.[17] The relation between polymer structure and *n*-doping property is now under investigation.

In order to measure the electrical conductivities of polymers **1a** and **2a**, sodium naphthalenide in THF was added to the polymer solution (0.5g/1 cm^3 THF) at 0.33

Table 2. Electrochemical Data[a)] for Polymers **1**—**2**

Polymer	*p*-Doping			*n*-Doping					
	E_{pa}^1	E_{pa}^2	E_{pc}	E_{pa}^1	E_{pa}^2	E_{pc}^1	E_{pc}^2	ΔE_p^1	ΔE_p^2
1a	1.49	1.73	—	−0.75	−1.30	−1.13	−1.59	0.38	0.29
1b	1.54	1.84	—			No *n*-doping			
1c	1.53	1.82	—			No *n*-doping			
2a	1.48	1.79	—	−0.74	−1.25	−1.17	−1.67	0.43	0.42
2b	1.54	1.83	—			No *n*-doping			

a) E in volts vs. Ag/AgCl, 0.1 M Et_4NBF_4/CH_3CN solution, Potential scan rate: 100 mV s^{-1}.

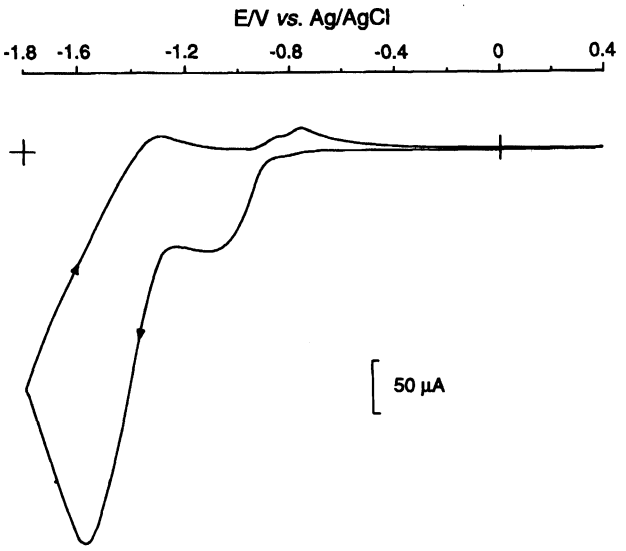


Fig. 2. Cyclic voltammogram of cathodic charging/discharging of polymer **1a** in 0.1 M Et_4NBF_4/CH_3CN solution (potential scan rate: 100 mV s^{-1}).

mol ratio. The doped blue polymer solution was cast on the ITO glass, dried in vacuum for 24 h, and measured the conductivity by Shlumberger 1260 impedance/gain-phase analyzer under argon atmosphere. The conductivities of polymers **1a** and **2a** at room temperature were 3.3×10^{-5} and 4.2×10^{-5} S cm^{-1}, respectively. All the polymers were thermally stable below 240°C in the neutral state.

Experimental

Materials. Tetrahydrofuran, diethyl ether (Kanto Chemical Co.) were dried over sodium for 24 h and distilled from sodium–benzophenone system. Thiophene (Janssen), chloroform, and acetonitrile (Kanto Chemical Co.) were distilled over calcium hydride before use. Dichlorodimethyl-, dichlorodihexyl-, and dichloromethylphenylsilanes (Shin-Etsu Silicon Chemical Co.), and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (Tokyo Kasei Chemical Co.) were fractionally distilled before use. 1,5- or 1,8-Dichloroanthraquinone, butyllithium (Tokyo Kasei Chemical Co.), zinc chloride (Kishida Chemical Co.), tetrakis(triphenylphosphine)palladium(0), and tetraethylammonium tetrafluoroborate (Aldrich) were used as received.

Di(2-thienyl)silanes (a, b, and c). Thiophene (0.3 mol) was introduced by the syringe into three necked flask equipped with an argon inlet, dropping funnel, and condenser under the argon atmosphere. Dry diethyl ether was added by the syringe as a solvent, and the reaction vessel was cooled to 0°C with ice–water bath. Butyllithium (0.3 mol) containing the same mol of TMEDA was added dropwise, and resulting clear yellow solution was allowed to react for 3 h with stirring. Dichlorosilane (0.15 mol) was slowly added dropwise at 0°C for 1 h and the reaction vessel was then allowed to warm slowly to room temperature. As reaction proceeded, white salt precipitated. After stirring for 12 h at room temperature, distilled water was added to the reaction mixture to remove the salt. The water layer was extracted with diethyl ether and the combined organic layer was washed with water, dried with anhydrous magnesium sulfate, filtered and solvent was evaporated. Di(2-thienyl)-silanes were obtained by distillation under reduced pressure (Scheme 1).

a: Bp 75—85°C (1 mmHg, 1 mmHg=133.322 Pa); ^{1}H NMR ($CDCl_3$) δ=0.62 (s, 6H, methyl), 7.16, 7.31, 7.58 (q, q, q, 6H, thiophene ring); ^{13}C NMR ($CDCl_3$) δ=0.01 (methyl), 128.2, 131.3, 135.4, 137.4 (thiophene ring).

b: Bp 105—110°C (0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ=0.91 (s, 3H, methyl), 7.15, 7.32, 7.61 (q, m, m, 11H, thiophene and phenyl ring); ^{13}C NMR ($CDCl_3$) δ=−1.00 (methyl), 127.9, 128.3, 129.9, 132.1, 134.7, 135.4, 135.8, 136.9 (thiophene and phenyl ring).

c: Bp 135—140°C (0.1 mmHg); ^{1}H NMR ($CDCl_3$) δ=0.63—1.58 (m, 26H, hexyl), 7.15, 7.31, 7.57 (m, q, q, 6H, thiophene ring); ^{13}C NMR ($CDCl_3$) δ=14.1, 15.1, 22.6, 23.7, 31.4, 33.1 (hexyl), 128.1, 131.2, 135.6, 135.9 (thiophene ring).

Poly(2, 5- thiophenediylsilanediyl- 2, 5- thiophenediyl-1,5 or 1,8-Anthraquinonediyl)s (1a, 1b, 1c, 2a, and 2b). Bis(5-lithio-2-thienyl)silanes (0.015 mol) which were prepared by lithiation of di(2-thienyl)silanes with butyllithium containing the same mol of TMEDA at 0°C were added slowly dropwise to a stirred solution of 0.3 mol of dry zinc chloride in THF at 0°C for 1 h. The reaction mixture was then added dropwise to the 0.015 mol of 1,5- or 1,8-dichloroanthraquinone solution in THF containing 0.15 mmol of $Pd(PPh_3)_4$ catalyst. After dropping, the temperature was slowly raised to 50°C, the reaction mixture was allowed to react for 24 h. The dilute aqueous hydrochloric acid was added to the cooled reaction mixture followed by separation of the aqueous layer which was extracted with diethyl ether. The combined organic layer was washed with aqueous sodium hydrogencarbonate, dried with anhydrous magnesium sulfate, filtered, and concentrated. After precipitating with methanol, the polymers were purified twice by reprecipitation using chloroform–methanol system (Scheme 1).

1a: ^{1}H NMR ($CDCl_3$) δ=0.60—0.78 (t, 6H, methyl), 7.12—7.40, 7.60—7.78, 8.17—8.26 (m, m, m, 10H, thiophene and phenyl ring).

1b: ^{1}H NMR ($CDCl_3$) δ=0.87—1.03 (t, 3H, methyl), 7.15—7.46, 7.59—7.75, 8.14—8.26 (m, m, m, 15H, thiophene and phenyl ring).

1c: ^{1}H NMR ($CDCl_3$) δ=0.80—0.95, 1.05—1.67 (t, m, 26H, hexyl), 7.15—7.43, 7.57—7.76, 8.16—8.25 (m, m, m, 10H, thiophene and phenyl ring).

2a: ^{1}H NMR ($CDCl_3$) δ=0.60—0.73 (t, 6H, methyl), 7.10—7.32, 7.51—7.77, 8.09—8.24 (m, m, m, 10H, thiophene and phenyl ring).

2b: ^{1}H NMR ($CDCl_3$) δ=0.79—0.98 (t, 3H, methyl), 7.06—7.42, 7.50—7.73, 8.13—8.24 (m, m, m, 15H, thiophene and phenyl ring).

Characterization. NMR spectra in $CDCl_3$ were recorded on a JEOL FX-200 spectrometer at room temperature, using TMS as an internal standard. Infrared spectra were obtained from KBr pellets and recorded by JASCO FT/IR-5300. UV spectra were obtained by JASCO Ubset-30 UV/visible spectrometer. Average molecular weight were determined by GPC using THF as an eluent and with a calibration curve of standard polystyrene. Electric conductivity was measured by Shlumberger 1260 impedance/gain-phase analyzer under argon atmosphere at room temperature. Thermal analyses were done by TAS-200 System (Rigaku Denki Co.) under the nitrogen atmosphere at a heating rate of $10°C\,min^{-1}$.

Cyclic Voltammetry. Cyclic voltammetry was carried out in a 20-ml single compartment cell using Toho Polarization Unit PS-06. Plots were made on a Yokogawa Model 3022 XY Recorder. The measurements were performed in dry acetonitrile containing the electrolyte of tetraethylammonium tetrafluoroborate (0.1 M). The electrochemical cell was rinsed with deionized water and then dried at the oven. The electrolyte solution was degassed with a dry argon for 20 min prior to use and maintained under argon throughout each experiment. Platinum electrode (BAS Co.) of 0.02 cm^2 geometric area was polished before use with α-alumina paste with a particle size of 0.06 μm and used as a working electrode. Platinum spiral was used as a counter electrode, the reference electrode was Ag/AgCl (all the potentials in this paper are expressed with respect to Ag/AgCl reference). In the experiment, the polymer films were cast on Pt electrode from chloroform solution and measured immediately in argon atmosphere.

References

1) J. Ohshita, D. Kanaya, M. Ishikawa, and Y. Yamanaka, *J. Organomet. Chem.*, **369**, C18 (1989).

2) M. Ishikawa, Y. Hasegawa, T. Hatano, A. Kunai, and T. Yamanaka, *Organometallics*, **8**, 2741 (1989).

3) M. Ishikawa, Y. Hasegawa, A. Kunai, and T. Yamanaka, *J. Organomet. Chem.*, **381**, C57 (1990).

4) J. Ohshita, K. Furumori, M. Ishikawa, and T. Yamanaka, *Organometallics*, **8**, 2084 (1989).

5) M. Tanaka, T. Kobayashi, and T. Sakakura, *Appl. Organomet. Chem.*, **2**, 91 (1988).

6) C. Biran, M. Bordeau, P. Pons, M. P. Leger, and J. Dunogues, *J. Organomet. Chem.*, **382**, C17 (1990).

7) T. Shono, S. Kashimura, M. Ishifune, and R. Nishida, *J. Chem. Soc., Chem. Commun.*, **1990**, 1160.

8) M. Umezawa, M. Takeda, H. Ichikawa, T. Ishikawa, T. Koizumi, T. Fuchigami, and T. Nonaka, *Electrochim. Acta*, **35**, 1867 (1990).

9) S. K. Ritter and R. E. Noftle, *Chem. Mater.*, **4**, 872 (1992).

10) H. Sakurai, *J. Organomet. Chem.*, **200**, 261 (1980).

11) T. Hayashi, Y. Uchimaru, N. P. Reddy, and M. Tanaka, *Chem. Lett.*, **1992**, 647.

12) J. Ohshita, D. Kanaya, M. Ishikawa, T. Koike, and T. Yamanaka, *Macromolecules*, **24**, 2106 (1991).

13) P. Chicart, R. J. P. Corriu, J. J. E. Moreau, F. Garnier, and A. Yassar, *Chem. Mater.*, **3**, 8 (1991).

14) S. H. Yi, J. Nagase, and H. Sato, *Synth. Met.*, in press.

15) K. Sasaki, T. Kashimura, M. Ohura, Y. Ohsaki, and N. Ohta, *J. Electrochem. Soc.*, **137**, 2437 (1990).

16) P. W. Kenny, T. H. Jozefiak, and L. L. Miller, *J. Org. Chem.*, **53**, 5007 (1988).

17) J. Roncali, H. K. Youssoufi, R. Garreau, F. Garnier, and M. Lemaire, *J. Chem. Soc., Chem. Commun.*, **1990**, 414.

18) P. W. Kenny, T. H. Jozefiak, and L. L. Miller, *J. Org. Chem.*, **53**, 5007 (1988).