

Synthesis of Polymers with Alternating Organosilanylene and Oligothiénylene Units and Their Optical, Conducting, and Hole-Transporting Properties

Joji Ohshita,[†] Atsuhiko Takata,[†] Hiroyuki Kai,[†] Atsutaka Kunai,^{*,†}
Kenji Komaguchi,[†] Masaru Shiotani,[†] Akira Adachi,[‡] Koichi Sakamaki,[‡]
Koichi Okita,[‡] Yutaka Harima,[§] Yoshihito Kunugi,[§] Kazuo Yamashita,[§] and
Mitsuo Ishikawa^{||}

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Higashi-Hiroshima 739-8527, Japan, Japan Chemical Innovation Institute, Tsukuba Research
Center (D-7), 2-1-6 Sengen, Tsukuba 305-0047, Japan, Division of Material and Life Sciences,
Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521,
Japan, and Department of Chemical Technology, Kurashiki University of Science and the Arts,
2640 Nishinoura, Tsurashima, Kurashiki 712-8505, Japan

Received April 10, 2000

Polymers with alternating mono-, di-, or trisilanylene units and 2,5-oligothienylene groups, $[(\text{SiR}_2)_x(\text{C}_4\text{H}_2\text{S})_m]_n$ ($\text{R} = \text{Me, Et}$, $x = 1-3$, $m = 2-5$), were synthesized and their optical, conducting, and hole-transporting properties were investigated. The UV absorption and emission maxima of the polymers shift to lower energies as the number of thienylene groups (m) between the silanylene units increases, while they are little affected by the silicon chain length (x). When the polymer films were exposed to FeCl_3 vapor, semiconducting films with the conductivities of 1.3×10^{-4} – 2.3×10^{-1} S/cm were obtained. The conductivities tend to increase with m but decrease with increasing x . The double-layer-type EL devices were fabricated using some of the polymers ($x = 1$, $m = 3-5$; $x = 2$, $m = 4$) as the hole-transporting layer and tris(8-quinolinolato)aluminum(III) (Alq) as the electron-transporting-emitter layer. Reducing the number of m and x resulted in a high-voltage shift in the turn-on voltage and a decrease in the maximum current density of the device. The highest luminance of 2000 cd/m^2 was obtained from a device based on the disilanylene–tetrathiénylene alternating polymer ($x = 2$, $m = 4$).

Introduction

There has been a current interest in the chemistry of polymers composed of an alternating arrangement of an organosilicon and π -electron unit in the backbone.¹ Enhanced through-space interaction between the π -electron systems by the silicon bridge² and/or delocalization of π -electrons through the organosilicon units by σ – π conjugation in the backbone^{1,3–5} provide the potential utilities of the polymers as organic semiconductors and hole-transporting materials for electroluminescent (EL) devices.

In efforts to understand the relationship between the properties of the polymers and their structures, we have recently synthesized a series of poly[(tetraethyldisilanylene)oligo(2,5-thienylenes)], $[(\text{SiEt}_2\text{SiEt}_2)(\text{C}_4\text{H}_2\text{S})_m]_n$ (DSmT, $m = 1-5$), and investigated their photochemical and conducting properties.³ These polymers show a strong UV absorption that shifts to longer wavelength along the number of thienylene units in the repeating unit for $m = 1-5$. Interestingly, the degree of σ – π conjugation in the polymer chain which may be estimated from the red shifts of the polymer UV absorption maxima from those of the corresponding oligothiophenes, $\text{H}(\text{C}_4\text{H}_2\text{S})_m\text{H}$, decreases with increasing m . The reduced degree of σ – π conjugation along the extension of the π -electron system is general for this type of polymer, and a similar tendency is observed also for poly[(disilanylene)oligophenylenes].⁴ However, despite the unfavorable σ – π conjugation for the polymers having extended π -electron systems, the conductivities of I_2 - and FeCl_3 -doped DSmT tend to increase along m . We have also examined DSmT with respect to their

[†] Faculty of Engineering, Hiroshima University.

[‡] Japan Chemical Innovation Institute.

[§] Faculty of Integrated Arts and Sciences, Hiroshima University.

^{||} Kurashiki University of Science and the Arts.

(1) (a) Ohshita, J.; Kunai, A. *Acta Polym.* **1998**, *49*, 379. (b) Ishikawa, M.; Ohshita, J. Silicon and Germanium Containing Conductive Polymers. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: New York, 1997; Vol. 2, Chapter 15.

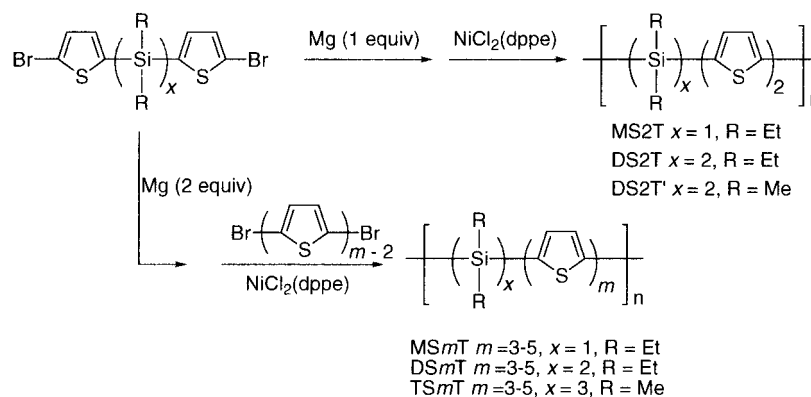
(2) (a) Chen, R.-M.; Chien, K.-M.; Wong, K.-T.; Jin, B.-Y.; Luh, T. Y. *J. Am. Chem. Soc.* **1997**, *119*, 11321. (b) van Walree, C. A.; Roest, M. R.; Schuddeboom, W.; Jenneskens, L. W.; Verhoeven, J. W.; Warman, J. M.; Kooijman, H.; Spek, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 8395.

(3) (a) Kunai, A.; Ueda, T.; Horata, K.; Toyoda, E.; Ohshita, J.; Ishikawa, M.; Tanaka, K. *Organometallics* **1996**, *15*, 2000. (b) Tanaka, K.; Ago, H.; Yamabe, T.; Ishikawa, M.; Ueda, T. *Organometallics* **1994**, *13*, 5583.

(4) Ohshita, J.; Watanabe, T.; Kanaya, D.; Ohsaki, H.; Ishikawa, M.; Ago, H.; Tanaka, K.; Yamabe, T. *Organometallics* **1994**, *13*, 5002.

(5) (a) Kunugi, Y.; Harima, Y.; Yamashita, K.; Ohshita, J.; Kunai, A.; Ishikawa, M. *J. Electroanal. Chem.* **1996**, *414*, 135. (b) Harima, Y.; Zhu, L.; Tang, H.; Yamashita, K.; Takata, A.; Ohshita, J.; Kunai, A.; Ishikawa, M. *Synth. Met.* **1998**, *98*, 79. (c) Tang, H.; Zhu, L.; Harima, Y.; Yamashita, K.; Ohshita, J.; Kunai, A.; Ishikawa, M. *Electrochim. Acta* **1999**, *44*, 2579.

Scheme 1



cyclic voltammograms, which indicate that they undergo multistep electrochemical oxidation and the first oxidation potentials of DS m T shift to lower voltage as m increases.⁵

Matsuda et al. have studied the optical and electrochemical properties of σ - π alternating polymers composed of oligosilanylene and π -conjugated units, $[(\text{SiMe}_2)_x\text{-A-}]_n$ ($x = 1, 3, 4, 6$; A = ethynylene, thienylene, bithienylene, biphenylene, anthrylene) and demonstrated that a longer organosilicon chain leads to a higher degree of σ - π conjugation along the polymer chain.⁶

It is of interest to us to investigate how the extension of the π -electron system and the chain length of the organosilicon unit affect the electronic state and electrical properties of the σ - π conjugated polymers. In this paper, we report the synthesis of polymers with alternating mono- and trisilanylene and oligothienylene units and optical, conducting, and hole-transporting properties of the resulting polymers in comparison with those of DS m T.

Results and Discussion

Synthesis of Organosilanylene-Oligothienylene Polymers. Poly[(tetraethylidisilanylene)oligothienylenes] (DS m T) were obtained as reported in the literature.^{3a} Poly[(diethylsilanylene)oligothienylenes] (MS m T) and poly[(hexamethyltrisilanylene)oligothienylenes] (TS m T) were obtained in a fashion similar to that of DS m T (Scheme 1). Thus, treatment of bis(bromothiophenyl)-substituted mono- or disilane with 1 molar equiv of Mg in THF, followed by heating the resulting mixture containing the starting dibromide and its mono- and di-Grignard reagent in a ratio of 1:2:1 in the presence of a catalytic amount of $\text{NiCl}_2(\text{dppe})$, afforded the bithienylene polymer ($m = 2$). The polymers with $m = 3-5$ were obtained from cross-coupling of the respective di-Grignard reagent obtained from bis(bromothiophenyl)silanes ($x = 1-3$ in Scheme 1) with dibromomono-, dibromobi-, or dibromoterthiophene. These polymers are orange-red solids and soluble in organic solvents, such as chloroform, THF, and toluene but insoluble in hexane and ethanol. For monosilanylene and disilanylene poly-

Table 1. Properties of Organosilanylene-Oligothienylene Polymers

polymer	$M_w (M_w/M_n)^a$	UV abs $\lambda_{\text{max}}/\text{nm}$		emissn $\lambda_{\text{max}}/\text{nm}$	
		in THF ($\epsilon \times 10^{-3}$)	film	in dioxane	film
MS2T	19 000 (2.6)	336 (17)	334	372	505
MS3T	17 000 (2.2)	384 (17)	391	423	561
MS4T	11 000 (1.7)	414 (35)	414	469	572
MS5T	5 000 (2.0)	425 (63)	425	498	578
DS2T ^b	53 000 (4.8)	343 (21)		384	
DS2T'	13 000 (3.3)	338 (24)	334	383	524
DS3T	12 000 (1.3)	388 (26)	390	434	564
DS4T	11 000 (1.7)	415 (38)	403	474	570
DS5T	17 000 (2.1)	427 (40)	405	504	563
TS3T	13 000 (2.0)	384 (21)	390	432	562
TS4T	14 000 (1.4)	412 (34)	400	470	575
TS5T	4 000 (1.3)	426 (41)	412	501	567

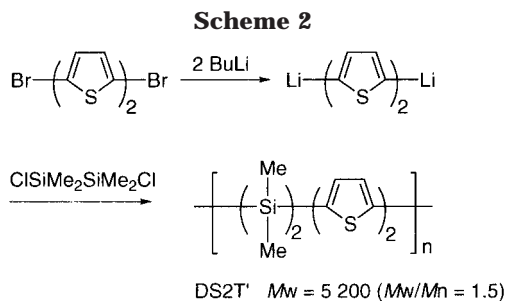
^a Determined by GPC, relative to polystyrene standards. ^b See ref 3a.

mers with three or more thiophene rings in a repeating unit, it was necessary to introduce ethyl groups on the silicon atoms in order to reduce the crystallinity to obtain polymers with sufficient solubility in common organic solvents. Tetraethylidisilanylene-dithienylene polymer DS2T, on the other hand, was obtained as a viscous oil, and therefore, we prepared tetramethylidisilanylene-dithienylene polymer DS2T' as the solids.

Polymer structures were verified by spectrometric analysis. The ^1H , ^{13}C , and ^{29}Si NMR spectra of the polymers are consistent with the proposed structures (see Experimental Section). Molecular weights of the polymers were determined by GPC relative to polystyrene standards, as shown in Table 1. Polymers DS m T prepared from the present syntheses have lower molecular weights but smaller polydispersities than those reported previously. The lower molecular weights of MS5T and TS5T in comparison to the others are due to the low solubility of the polymers, and the polymers with high molecular weights, which are insoluble in organic solvents, were removed by filtration of the reaction mixtures. Rather low polydispersities (M_w/M_n) of the polymers clearly indicate that no cross-linking reactions are involved in this polymerization. In some cases, however, the carbon content was determined to be slightly lower than the calculated value by combustion elemental analysis. This is not unexpected for organometallic polymers and is probably due to the formation of carbon-containing ceramics during the analysis.

Next, we analyzed the nickel contamination into the resulting polymers which may influence the properties

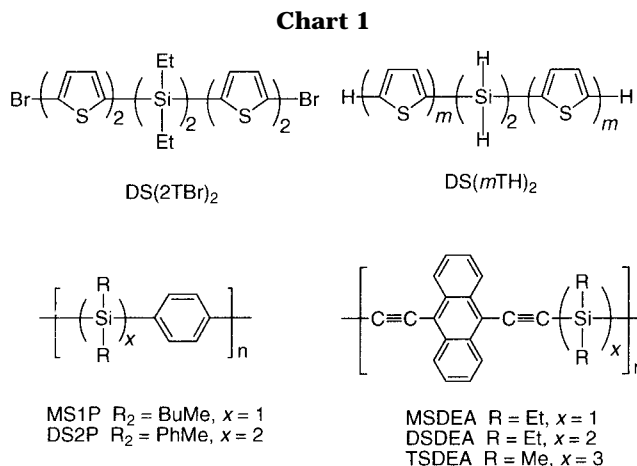
(6) (a) Fang, M.-C.; Watanabe, A.; Matsuda, M. *Chem. Lett.* **1994**, 13. (b) Fang, M.-C.; Watanabe, A.; Matsuda, M. *J. Organomet. Chem.* **1995**, 489, 15. (c) Fang, M.-C.; Watanabe, A.; Matsuda, M. *Macromolecules* **1996**, 29, 6807. (d) Fang, M.-C.; Watanabe, A.; Ito, O.; Matsuda, M. *Chem. Lett.* **1996**, 417. (e) Fang, M.-C.; Watanabe, A.; Matsuda, M. *Polymer* **1996**, 37, 163.



of materials obtained from the polymers. However, only a small amount of nickel contamination (0.005–0.16 wt %) in the polymers was detected. Furthermore, we prepared DS2T' by the reaction of 5,5'-dilithio-2,2'-bithiophene with 1,2-dichlorotetramethyldisilane in 18% yield, without using the nickel catalyst as shown in Scheme 2, and examined the resulting polymer with respect to UV and emission spectra and CV in comparison with those of DS2T' prepared by the nickel-catalyzed dehalogenative coupling. As expected, the UV and emission spectra and CV profile of DS2T' are identical regardless of the methods of polymerization, indicating that the influence of the nickel contamination into the polymers on the polymer properties is negligible if at all present.

Optical Properties of the Polymers. Since some photophysical properties of the present polymers in the solution phase have been already reported,⁷ we describe them only briefly in this paper. The UV absorption and emission maxima of MS m T and TS m T in solutions shifted to longer wavelength as the number of thienylene groups between the silanylene units increased for $m = 1$ –5 (Table 1), similar to the case of DS m T.³ The silanylene chain length in the polymer unit, on the other hand, slightly influences the optical properties of the polymers. DS2T exhibits an absorption λ_{\max} value slightly red-shifted from that of MS2T by 7 nm, probably due to the σ – π conjugation between the Si–Si σ -bonds and the oligothiophene units. Such red shifts, however, are no longer evident for the polymers with $m = 3$ –5, and polymers DS3T–DS5T and TS3T–TS5T show no remarkable shifts in UV maxima, compared to MS3T–MS5T, respectively. This is in accordance with our recent finding that the introduction of the more extended π -electron system into the σ – π alternating polymers leads to the less favorable σ – π conjugation.^{1,3,4}

The UV absorption maxima in the solid state appear at almost the same regions as those in the solution phase, although a slight blue shift is observed for DS4T–5T and TS4T–5T. On the other hand, the emission maxima of the polymers in the solid states are remarkably red-shifted from those in solutions. Since the excitation spectra of the polymers are essentially the same in the solid state and in solution, this is presumably due to the aggregation of the π -electron systems in the solid state to form excimers and/or exciplexes.^{8a} Interestingly, all of the polymer films with $m = 3$ –5 emit the fluorescence at almost the same region of 560–



570 nm, while the emission maxima for dithienylene polymers MS2T and DS2T appear at 505 and 524 nm, respectively. This can be understood by the difference in the nature of the lowest energy excitation in these polymers. As reported previously,^{3b} the results of SCF–CO calculations for simplified poly[disilanyleneoligo(2,5-thienylenes)] $[(\text{SiH}_2)_2(\text{C}_4\text{H}_2\text{S})_m]_n$ predict that the nature of both the highest occupied (HO) and lowest unoccupied (LU) bands interchanges from σ -type to π -type as the number of thienylene rings increases. Thus, polymers MS2T and DS2T may suffer a σ – σ^* type transition, whereas the polymers with $m = 3$ –5 undergo a π – π^* type excitation favorable to the formation of excimers/exciplexes between the oligothiophene π -units.

A single crystal of 1,2-bis(5'-bromo-2,2'-bithien-5-yl)-tetraethyldisilane (DS(2TBr)₂ in Chart 1)³ was obtained, and the crystal structure was determined by an X-ray diffraction study. Cell dimensions, data collection details, and refinement parameters are listed in Table 2. Figure 1 depicts the ORTEP drawing of DS(2TBr)₂, indicating that two bromobithienyl units are located in a trans fashion with respect to the central Si–Si bond. As indicated by torsion angles for C3–C4–C5–C6 (171(1)°) and C11–C12–C13–C14 (159(1)°) listed in Table 3, the adjacent thiophene rings in each of the bithienyl units are slightly rotated but retain coplanarity to some extent. The Si–Si bond is arranged to possess torsion angles of –124(1) and 71(1)° with the attached thiophene rings, respectively, to permit the σ – π conjugation. This is in contrast to the results of SCF–CO calculations on polymers $[(\text{SiH}_2)_2(\text{C}_4\text{H}_2\text{S})_m]_n$ which suggest that a planar conformer having an Si–Si bond on almost the same plane as that of the oligothiophene unit is the most stable one.^{3b} However, the nonplanar conformer with the Si–Si bond, perpendicular to the oligothiophene unit, similar to the crystal structure of DS(2TBr)₂, is calculated to be less stable by only 0.06 eV than the planar conformer, suggesting the flexibility of the organosilanylene–oligothiophene structure.

For the present polymers, the oligothiophene units in the backbone are unlikely to retain always high coplanarity to permit the high degree of π -conjugation in the unit. The high flexibility of the oligothiophene unit, suggested by crystal structure analysis of DS(2TBr)₂, may allow significant twisting of the adjacent thiophene rings partly due to the packing of the polymer chains in the solid state. This is evident from the slight

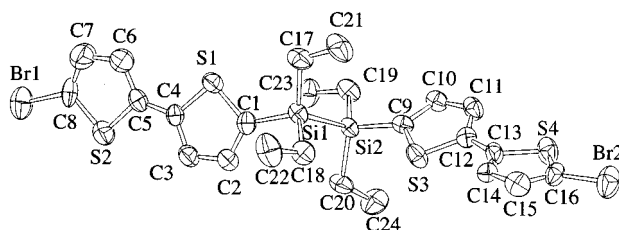
(7) Tang, H.; Zhu, L.; Harima, Y.; Yamashita, K.; Ohshita, J.; Kunai, A. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1873.

(8) (a) Manhart, S. A.; Adachi, A.; Sakamaki, K.; Okita, K.; Ohshita, J.; Ohno, T.; Hamaguchi, T.; Kunai, A.; Kido, J. *J. Organomet. Chem.* **1999**, *592*, 52. (b) Adachi, A.; Manhart, S. A.; Okita, K.; Kido, J.; Ohshita, J.; Kunai, A. *Synth. Met.* **1997**, *91*, 333.

Table 2. Crystal Data, Experimental Conditions, and Summary of Structural Refinement for DS(2TBr)₂

mol formula	C ₂₄ H ₂₈ Br ₂ S ₂ Si ₂
mol wt	660.70
space group	<i>P</i> $\bar{1}$ (No. 2)
cell dimens	
<i>a</i> , Å	11.432(2)
<i>b</i> , Å	14.463(3)
<i>c</i> , Å	8.858(1)
α, deg	95.48(2)
β, deg	97.90(1)
γ, deg	83.48(2)
<i>V</i> , Å ³	1436.5(5)
<i>Z</i>	2
<i>D</i> _{calc} , Mg/m ³	1.527
<i>F</i> ₀₀₀	668.00
cryst size, mm ³	0.8 × 0.8 × 0.3
cryst color	colorless
μ, cm ⁻¹	71.84
diffractometer	Rigaku AFC-6
temp, K	298
wavelength, Å	1.5418 (Cu Kα)
monochromator	graphite cryst
scan type	ω-2θ
scan speed, deg/min	4
scan width, deg	0 < 2θ < 126.1
no. of unique rflns	4228
no. of obsd rflns (<i>I</i> > 3σ(<i>I</i>))	3103
corrections	Lorentz-polarization absorption
transmissn factors	0.4358-0.9973
rfln/param ratio	10.74
<i>R</i>	0.096
<i>R</i> _w ^a	0.116

^a The weighting scheme is (σ(*F*_o)² + 0.0004|*F*_o|²)⁻¹.

**Figure 1.** ORTEP drawing of DS(2TBr)₂. Protons are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.**Table 3.** Selected Torsion Angles (deg) for DS(2TBr)₂ with Thier Esd's in Parentheses

C1-Si1-Si2-C9	-173.5(7)
Si2-Si1-C1-C2	71(1)
C11-C12-C13-C14	159(1)
Si1-Si2-C9-C10	-124(1)
C3-C4-C5-C6	171(1)

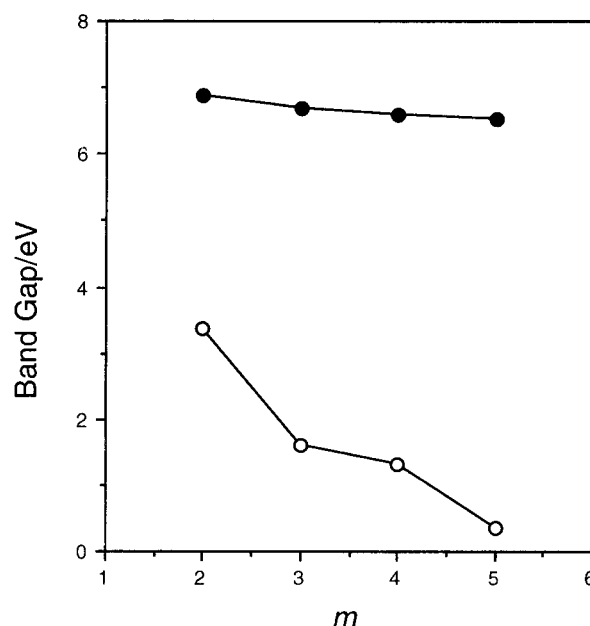
blue-shifted UV absorption maxima in the solid state from those in solution phase for DS*m*T and TS*m*T with *m* ≥ 4.

Conducting Properties of the Polymers. When polymer films were exposed to FeCl₃ vapor, the films became conducting. The conductivities of the polymer films increased with increasing the doping period and reached to the maximum values listed in Table 4. As shown in Table 4, the maximum conductivities tend to increase along the extension of the oligothienylene unit, although they slightly drop at *m* = 4. The conductivities are affected also by the silanylene chain length (*x*) and tend to decrease along the increase of *x*. This is probably due to the higher concentration of oligothienylene units in the unit volume in the solid phase and indicate that

Table 4. Conductivities (S/cm) of Organosilanylene-Oligothienylene Polymer Films Doped with FeCl₃

<i>m</i>	MS <i>m</i> T	DS <i>m</i> T	TS <i>m</i> T
2	5.8 × 10 ⁻⁴	1.3 × 10 ⁻⁴ ^a	
3	5.5 × 10 ⁻²	3.3 × 10 ⁻³	8.5 × 10 ⁻⁴
4	2.1 × 10 ⁻²	1.5 × 10 ⁻³	2.7 × 10 ⁻⁴
5	2.3 × 10 ⁻¹	1.3 × 10 ⁻²	3.5 × 10 ⁻¹

^a DS2T'.

**Figure 2.** Plots of band gap energy vs oligothienylene chain length for (●) neutral molecules and (○) radical cations of DS(*m*TH), derived from PM3 calculations.

the electric conduction arises primarily from interchain hopping of holes between oligothienylene units rather than the conduction along the polymer chains.

To learn the changes of electronic states of the polymers as *m* increases, we carried out semiempirical molecular orbital calculations of model compounds, bis-(oligothienyl)disilanes (DS(*m*TH))₂, *m* = 2-5 in Chart 1) at PM3 level whose results are depicted in Figure 2. As can be seen in Figure 2, the band gaps of the neutral model compounds decrease monotonically for *m* = 2-5. Similarly, those of radical cations of the models decrease along *m*. However, the band gaps of the radical cations do not monotonically decrease along *m* and the difference of the band gaps between *m* = 3 and *m* = 4 is calculated to be only 0.29 eV, much smaller than those between *m* = 2 and *m* = 3 (1.77 eV) and between *m* = 4 and *m* = 5 (0.97 eV). These results agree with the changes of the conducting properties of the FeCl₃-doped polymers along *m*.

Performance of EL Devices. To evaluate the hole-transporting properties of the present polymers, we constructed double-layer EL devices with layers of ITO/polymer/Alq/Mg:Ag, in which (8-hydroxyquinoline)aluminum (Alq) is used as the electron transporting-emitting layer and ITO and Mg:Ag are the anode and cathode, respectively. Figure 3 shows the voltage dependence of the current density of the devices with the use of MS*m*T (*m* = 4, 5) and DS*m*T (*m* = 3, 4). The EL devices based on the other polymers, however, show low reproducibility of the data due to the poor quality of the

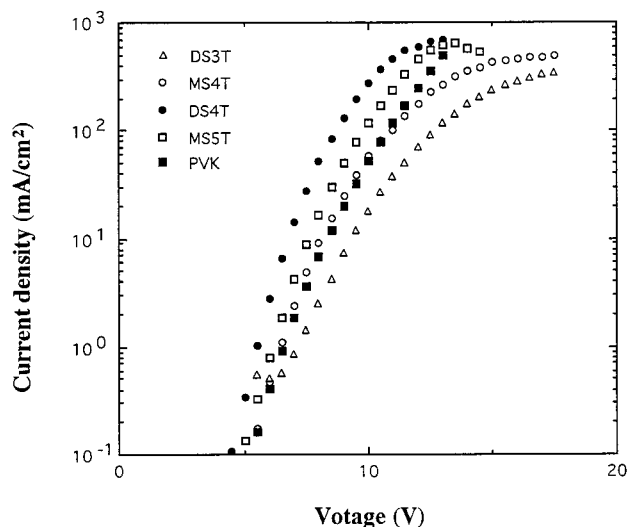


Figure 3. Current density–voltage curves for double-layer EL devices having organosilanylene–oligothienylene polymers and PVK as the hole-transporting material and Alq as the electron-transporting emitting material.

polymer films on constructing the devices. Although the origin of the lower film processability of TSM m T is still unclear, low affinity of the films to the ITO surface might be one of the reasons. Of those devices, the DS4T-based device exhibits the best electrical properties. The turn-on voltage of the device is about 4 V and the maximum current density is 700 mA/cm² at the applied voltage of 13 V. As the number of the thiophene rings or the silanylene chain length is reduced, the current density of the device decreases at any applied voltage. The expansion of the π -conjugation affects the hole-transporting properties more significantly than the elongation of silicon chain, as indicated by the improved current density–voltage (I – V) characteristics in the order DS3T < MS4T < DS4T. The I – V curve of the device with MS4T is almost identical with that of the device with a typical hole-transporting material, PVK. As the number of the thiophene rings is increased from $m = 4$ to $m = 5$ in monosilanylene polymers (MS m T), the current density of the device increases slightly. In organosilicon polymers with a larger number of thiophene rings than quaterthiophene (4T), the extension of the π -conjugation seems to exert little influence on the hole-transporting properties.

We have recently reported that a disilanylene–phenylene polymer (DS1P in Chart 1) reveals better hole-transporting properties than the monosilanylene analogue (MS1P).⁹ In contrast, for organosilanylene–diethynylanthracene polymers (MSDEA-TSDEA in Chart 1), the hole-transporting properties are improved by reducing the silicon chain length.^{8,9} These results indicate that the σ – π conjugation is significantly operative for the polymers with a rather small π -electron system, but for the polymers with an extended π -electron system, reducing the silicon chain length leads to higher concentration of the π -conjugated units in the unit volume of the polymer film to facilitate the hole transport by the hopping process between the π -conjugated units. As discussed in the preceding section, some

of the oligothiénylene units in the present polymers would possess a limited degree of extension of the π -conjugation in the units in the solid states due to the flexibility of the oligothiénylene units, which would allow significant twisting between the rings in part, and hence, the σ – π conjugation still plays an important role for the hole-transporting properties of the polymers.

The enhanced hole-transporting properties for DS4T relative to MS4T might seem to conflict with the increase in the conductivities of the FeCl₃-doped polymer films by reducing the silicon chain length. To understand the disagreement, we assume that the conformation of oligothiophene units would be significantly affected by the presence of counteranions. It is known that the oligothiophene radical cations strongly tend to have a planar structure due to the quinoid-type resonance structure.¹⁰ Permeation of counteranions into the polymer films may reduce the interchain steric congestion to permit the planar structures of the oligothiénylene units, resulting in a π -conjugation sufficiently extended to minimize the influence of the σ – π conjugation. On the other hand, in the polymer films not having the counteranions, such as in the hole-transporting layer in the EL devices, the structures of the oligothiénylene units may not readily change even when a hole appears on the unit.

Concerning the emission properties of the double-layer EL devices, bright green emission is observed from the EL device when operated in a continuous dc mode for a forward bias with ITO at positive polarity. The EL spectrum is identical with the PL spectrum of Alq in the solid state, and the spectral profile is independent of the current density, implying that the recombination of the injected holes and electrons takes place only in the emitting layer. This indicates that the layers of silanylene–oligothienylene polymers enable hole transport but block electron injection from Alq, thus controlling the recombination process.

As shown in Figure 4, the EL device with DS4T exhibits the highest luminance of 2000 cd/m² at 12 V and the lowest threshold voltage at 5 V, in accord with the I – V characteristics. Although the current density of the device with MS5T is always higher than that with MS4T (Figure 3), the L – V characteristics of the device with MS5T are almost the same as that with MS4T. These results may imply lower electron blocking properties of MS5T compared to that of MS4T. In fact, the oxidation potential of the MS5T film in CV (0.73 V vs Ag/Ag⁺) is lower than that of MS4T (0.84 V) and the UV absorption maximum of MS5T (425 nm) is at longer wavelength than that of MS4T (414 nm). These results indicate that the LUMO level of MS5T is at much lower energy than that of MS4T.

In conclusion, we prepared a series of polymers with alternating organosilanylene–oligothienylene units in the backbone and demonstrated that both silicon chain length and the number of thienylene rings in the oligothiénylene unit affect the properties of the polymers in doped and undoped states. It seems likely that the conformation of the polymers in the films, which would relate to the film morphology, plays an important role

(9) Adachi, A.; Ohshita, J.; Ohno, T.; Kunai, A.; Manhart, S. A.; Okita, K.; Kido, J. *Appl. Organomet. Chem.* **1999**, *13*, 859.

(10) Sauvajol, J. L.; Lère-Porte, J. P.; Moreau, J. J. E. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; Wiley: New York, 1997; Chapter 14.

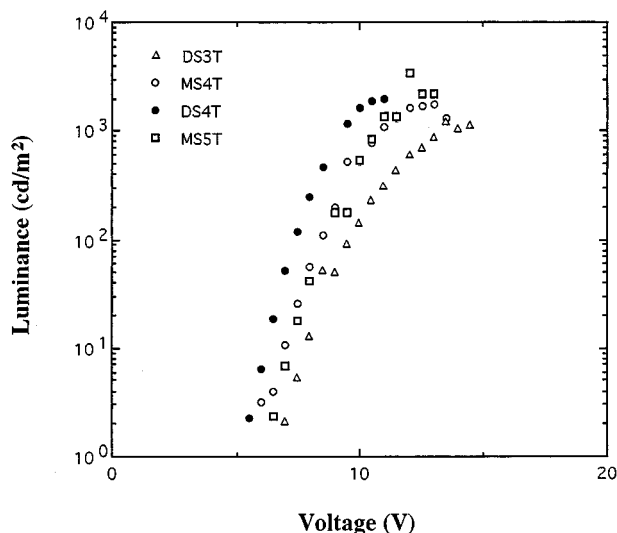


Figure 4. Luminescence-voltage curves for double-layer EL devices having organosilanylene-oligothienylene polymers and PVK as the hole-transporting material and Alq as the electron transporting-emitting material.

in the polymer functionalities such as conducting and hole-transporting properties.

Experimental Section

General Considerations. All reactions were carried out under a dry nitrogen atmosphere. ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on JEOL Model JNM-EX 270 and JNM-EX 400 spectrometers. UV spectra were measured with a Hitachi U-3210 spectrophotometer. IR spectra were measured on a Perkin-Elmer 1600-FT infrared spectrometer. Molecular weights of polymers were determined by GPC, using THF as the eluent, and are relative to polystyrene standards. The usual workup used for the following synthetic experiments involves hydrolysis of the mixture, separation of the organic layer, drying of the organic phase over anhydrous magnesium sulfate, and evaporation of the solvent.

Materials. The polymers DS m T ($m = 2-5$),^{3a} DS2T,¹¹ and 1,3-bis(5-bromothien-2-yl)hexamethyltrisilane¹¹ were prepared as reported in the literature. THF and ether were dried over sodium-potassium alloy and distilled just before use.

Preparation of Bis(5-bromothien-2-yl)diethylsilane. Into a 300 mL three-necked flask was placed 11.681 g (48.3 mmol) of 2,5-dibromothiophene in 90 mL of ether. To this was added 31.2 mL (48.0 mmol) of a 1.54 M hexane solution of *n*-butyllithium at -80°C over a period of 1.5 h. After the mixture was stirred at -80°C for 1 h, 3.744 g (24.0 mmol) of dichlorodiethylsilane was added to the mixture at this temperature over 1 h. The mixture was warmed to room temperature and stirred for 1 day. After the usual workup, the residue was distilled under reduced pressure to give 5.830 g (59% yield) of bis(5-bromothien-2-yl)diethylsilane as a colorless oil: bp $135-136^\circ\text{C}$ (1 mmHg); ^1H NMR (δ in CDCl_3) 7.12 (d, 2H, $J = 3.6$ Hz), 7.07 (d, 2H, $J = 3.6$ Hz), 1.06 (br s, 10H); ^{13}C NMR (δ in CDCl_3) 5.82, 7.15, 118.14, 131.33, 136.62, 137.19; ^{29}Si NMR (δ in CDCl_3) -10.5 ; MS m/z 410 (M^+ as $^{79}\text{Br}^{81}\text{Br}$). Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{S}_2\text{Br}_2\text{Si}$: C, 35.13; H, 3.44. Found: C, 35.15; H, 3.44.

Preparation of Poly[(diethylsilanylene)bis(2,5-thienylene)] (MS2T). A mixture of 48.6 mg (2.0 mmol) of Mg and 0.820 g (2.0 mmol) of bis(5-bromothien-2-yl)diethylsilane in 3 mL of THF was stirred in a Pyrex tube at 50°C until all magnesium was consumed. To the resulting mixture of bis(5-bromothien-2-yl)diethylsilane and the mono- and di-Grignard

reagent in a ratio of 1:2:1 was added 10 mg (1.7 mol %) of $\text{NiCl}_2(\text{dppe})$ ($\text{dppe} = \text{bis}(\text{diphenylphosphino})\text{ethane}$), and the tube was degassed and sealed. The tube was heated at 230°C for 100 h. After the usual workup, the products were reprecipitated from hexane-chloroform to give 0.370 g (74% yield) of MS2T as orange-red solids: mp $56-70^\circ\text{C}$; $M_w = 19\,000$ ($M_w/M_n = 2.6$); ^1H NMR (δ in CDCl_3) 1.07 (br s, 10H), 7.20 (d, 2H, $J = 3.3$ Hz), 7.27 (d, 2H, $J = 3.3$ Hz); ^{13}C NMR (δ in CDCl_3) 6.13, 7.33, 125.30, 134.28, 136.94, 143.25; ^{29}Si NMR (δ in CDCl_3) -10.39 . Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{S}_2\text{Si}$: C, 57.55; H, 5.63. Found: C, 57.48; H, 5.59.

Preparation of Poly[(diethylsilanylene)tris(2,5-thienylene)] (MS3T). A mixture of the di-Grignard reagent, prepared from 48.6 mg (2.0 mmol) of Mg and 0.410 g (1.0 mmol) of bis(5-bromothien-2-yl)diethylsilane in 3 mL of THF, 0.242 g (1.0 mmol) of 2,5-dibromothiophene, and 10 mg (1.7 mol %) of $\text{NiCl}_2(\text{dppe})$ was heated at 150°C for 80 h in a degassed sealed Pyrex tube. After the usual workup, the products were reprecipitated from hexane-chloroform to give 0.089 g (27% yield) of MS3T as orange-red solids: mp $100-118^\circ\text{C}$; $M_w = 17\,000$ ($M_w/M_n = 2.2$); ^1H NMR (δ in CDCl_3) 1.07 (br s, 10H), 7.08-7.21 (m, 6H); ^{13}C NMR (δ in CDCl_3) 6.12, 7.33, 124.33, 124.70, 124.94, 136.19, 136.96, 143.21; ^{29}Si NMR (δ in CDCl_3) -10.39 . Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{S}_3\text{Si}$: C, 57.78; H, 4.85. Found: C, 56.21; H, 4.64.

The synthesis of polymers MS m T ($m = 4, 5$) and TS m T ($m = 3-5$) were performed in a fashion similar to that of MS3T, using an appropriate combination of the monomers as shown in Scheme 1. Data for MS4T: 50% yield; orange-red solids; mp $97-110^\circ\text{C}$; $M_w = 11\,000$ ($M_w/M_n = 1.7$); ^1H NMR (δ in CDCl_3) 1.09 (br s, 10H), 7.05-7.27 (m, 8H); ^{13}C NMR (δ in CDCl_3) 6.09, 7.35, 124.33, 124.74, 125.00, 125.31, 136.10, 136.96, 143.14; ^{29}Si NMR (δ in CDCl_3) -10.37 . Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{S}_4\text{Si}$: C, 57.92; H, 4.37. Found: C, 56.85; H, 4.19.

Data for MS5T: 20% yield; orange-red solids; mp $95-110^\circ\text{C}$; $M_w = 5000$ ($M_w/M_n = 2.0$); ^1H NMR (δ in CDCl_3) 1.08 (br s, 10H), 7.05-7.23 (m, 10H); ^{13}C NMR (δ in CDCl_3) 6.09, 7.33, 124.34, 124.54 (2C), 124.74, 134.28, 135.99 (2C), 136.01, 136.94, 143.10; ^{29}Si NMR (δ in CDCl_3) -10.39 . Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{S}_5\text{Si}$: C, 58.02; H, 4.06. Found: C, 56.25; H, 3.97.

Data for TS3T: 85% yield; orange-red solids: mp $52-65^\circ\text{C}$; $M_w = 13\,000$ ($M_w/M_n = 2.0$); ^1H NMR (δ in CDCl_3) 0.16 (s, 6H), 0.37 (s, 12H), 6.99-7.17 (m, 6H); ^{13}C NMR (δ in CDCl_3) -6.71 , -2.00 , 124.29, 124.91, 134.91, 136.10, 138.63, 142.27; ^{29}Si NMR (δ in CDCl_3) -20.78 . Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{S}_3\text{Si}_3$: C, 51.37; H, 5.75. Found: C, 48.78; H, 5.42.

Data for TS4T: 20% yield; orange-red solids: mp $140-153^\circ\text{C}$; $M_w = 14\,000$ ($M_w/M_n = 1.4$); ^1H NMR (δ in CDCl_3) 0.17 (s, 6H), 0.38 (s, 12H), 6.97-7.15 (m, 8H); ^{13}C NMR (δ in CDCl_3) -6.68 , -2.02 , 124.18, 124.33, 124.97, 134.91, 135.83, 136.20, 138.72, 142.21; ^{29}Si NMR (δ in CDCl_3) -20.92 . Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{S}_4\text{Si}_3$: C, 52.54; H, 5.21. Found: C, 51.71; H, 5.14.

Data for TS5T: 37% yield; orange-red solids; mp $147-158^\circ\text{C}$; $M_w = 4000$ ($M_w/M_n = 1.3$); ^1H NMR (δ in CDCl_3) 0.15 (s, 6H), 0.37 (s, 12H), 6.98-7.15 (m, 10H); ^{13}C NMR (δ in CDCl_3) -6.68 , -2.04 , 124.27 (2C), 125.08, 128.21, 134.12, 134.91, 135.68, 135.90, 136.38, 142.19; ^{29}Si NMR (δ in CDCl_3) -20.92 . Anal. Calcd for $\text{C}_{26}\text{H}_{28}\text{S}_5\text{Si}_3$: C, 53.37; H, 4.82. Found: C, 49.47; H, 4.73.

Preparation of Poly[(tetramethyldisilanylene)bis(2,5-thienylene)] (DS2T') from Dilithiobithiophene and Dichlorodisilane.¹² To a solution of 4,4'-dilithiobithiophene prepared from 4,4'-dibromobithiophene and 2 equiv of *n*-BuLi in THF was added 1 equiv of 1,2-dichlorotetramethyldisilane at -80°C . The resulting mixture was warmed to room temperature. After the usual workup, the organic products were reprecipitated from ethanol-chloroform and then from hexane-chloroform to give the title polymer with $M_w = 5,200$ (M_w/M_n

(11) Ohshita, J.; Kanaya, D.; Ishikawa, M. *Appl. Organomet. Chem.* **1993**, *7*, 269.

(12) Corriu, R. J. P.; Guérin, C.; Henner, B.; Kuhlman, T.; Jean, A. *Chem. Mater.* **1990**, *2*, 351.

$M_n = 1.5$) in 18% yield. All spectral data for the polymer are identical with those reported in the literature.¹¹

CV Measurements. CV measurements for the disilanylene-oligothienylene polymers were carried out using a three-electrode system in an acetonitrile solution containing 100 mM of tetraethylammonium tetrafluoroborate as the supporting electrolyte. Thin solid films of the polymers were prepared by spin coating of the polymer solution in chloroform on ITO working electrodes. An Ag/0.1 M AgClO₄ electrode and a Pt plate were used as the reference and counter electrode, respectively. Peak potential was determined in a sweep rate of 50 mV/s. The current–voltage curve was recorded on a Hokuto Denko HAB-151 potentiostat/galvanostat.

X-ray Crystallographic Analysis of DS(2TBr)₂. All unique diffraction maxima with $0 < 2\theta < 126.1^\circ$ for DS(2TBr)₂ were recorded on a Rigaku AFC-6 automated four-circle diffractometer using graphite-monochromated Cu K α radiation ($\lambda = 1.5418$ Å). Refractions with $I > 3\sigma(I)$ were used in the least-squares refinement. The structure was solved by SIR92 direct methods¹³ and expanded using DIRDIF94 Fourier techniques.¹⁴ The non-hydrogen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber.¹⁵ Anomalous dispersion effects were included in F_o ; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.¹⁷ The values for the mass attenuation coefficients are those of Creagh and Hubbel.¹⁸ All calculations were performed using the teXsan¹⁹ crystallographic software package of Molecular Structure Corp.

Measurement of Conductivities of Polymer Films Doped with FeCl₃. A benzene solution of a polymer was cast

to a thin film on a glass plate. After the solvent was evaporated, the film was dried in vacuo overnight and then held over FeCl₃ powder, which was placed in a glass vessel. Doping was performed by heating the bottom of the glass vessel at 150 °C under reduced pressure (1 mmHg) for 15–42 h. The conductivities of the polymers were determined by the four-probe method.

Preparation of EL Devices. To construct the device with the structure of ITO/polymer/Alq/Mg:Ag, a thin film (30–40 nm) of the silanylene-oligothienylene polymers was prepared by spin-coating from a solution of polymer in dichloroethane on an anode, indium–tin oxide (ITO) coated on a glass substrate with a sheet resistance of 15 Ω /cm (Asahi Glass Co.). An electron transporting–emitting layer was then prepared by vacuum deposition of tris(8-quinolinolato)aluminum(III) (Alq) at 1×10^{-5} Torr with a thickness of 60–70 nm on the polymer film. Finally a layer of magnesium–silver alloy with an atomic ratio of 10:1 was deposited on the Alq layer surface as the top electrode at 1×10^{-5} Torr. The actual thickness of each layer on the EL devices was measured with a Sloan Dektak 3030 surface profiler. The emitting area was 0.5×0.5 cm². Luminance was measured with a Topcon BM-7 luminance meter at room temperature.

Acknowledgment. This work was supported by Grant-in Aid for Scientific Research on Priority Area (A) (2) No. 11120234 from the Ministry of Education, Science, Sports, and Culture of Japan. We thank Sankyo Kasei Co. Ltd. and Sumitomo Electric Industry for financial support.

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for DS(2TBr)₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM000302+

(18) Creagh, D. C.; Hubbell, J. H. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Boston, 1992; Table 4.2.4.3, pp 200–206.

(19) teXsan: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985, 1992.

(13) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(14) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 Program System; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1994.

(15) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2 A.

(16) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(17) Creagh, D. C.; McAuley, W. J. In *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic: Boston, 1992; Vol. C, Table 4.2.6.8, pp 219–222.