Notes

Synthesis of Organosilanylene−Oligothienylene Alternate Polymers and Their Applications to EL and FET Materials

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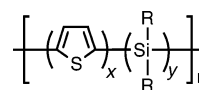
*Summary: Monosilanylene−oligothienylene alternating polymers, $[T_x\text{-}(SiBu_2)]_n$ (**MSxT**, T = 2,5-thienylene or 3-butyl-2,5-thienylene, x = 8, 10, 12, and 14), were synthesized and their applications to electroluminescent (EL) devices and field effect transistors (FETs) were examined. The onset voltages for the luminance of EL devices with the structure of ITO/**MSxT**/Alq3/Mg:Ag were reduced on going from x = 10 to 14. However, the highest maximum luminance was achieved for x = 12 (900 cd/m^2). The field effect carrier mobilities of the **MSxT** films were determined to be $(3.4−6.9) \times 10^{-5}$ cm^2 V^{-1} s^{-1}, which increased with the length of the oligothiophene unit from x = 8 to 12, while increasing x from 12 to 14 barely affected the FET properties.*

Introduction

Polythiophenes and oligothiophene-containing polymers have been extensively studied as active layers in EL devices[1] as well as in FETs.[2,3] Previously, we prepared polymers having an oligothienylene−organosilanylene alternating unit (see Chart 1). In these polymers, the silicon linkage is anticipated to provide sufficient solubility of the polymers and to elevate the HOMO energy level of the oligothienylene unit by its electron-donating properties, making it possible to use the polymer films as hole-transporting materials.[4] In fact, double-layer EL devices composed of a disilanylene−oligothienylene polymer film and an Alq3 (aluminum tris(8-hydroxyquinoline)) layer, as the hole-transporting and emitting layers, respectively, emit a

Chart 1

X = 3-5
y = 1-3
R = Me, Et, Bu

green light by applying a bias voltage. Interestingly, the performance of the devices is improved by elongating the oligothienylene unit from x = 3 to 5, and the device with poly(disilanylenequinquethiophene) (**DS5T**, R = Bu, x = 5, y = 2) exhibits the best performance among them.[5,6]

In the hope of obtaining EL device materials with even better properties, based on the organosilanylene−oligothienylene alternating system, we prepared this type of polymer with longer oligothienylene units, $[T_x\text{-}(SiBu_2)]_n$ (**MSxT**, T = 2,5-thienylene or 3-butyl-2,5-thienylene, x = 10, 12, and 14), and examined them as the hole-transport in the double-layer EL system. We also evaluated field effect carrier mobilities of spin-coated films of **MSxT** (x = 8, 10, 12, and 14).

Results and Discussion

Polymers **MSxT** were prepared by Stille coupling reactions as shown in Scheme 1 and were purified by reprecipitation from chloroform−ethanol. They are dark orange solids and soluble in common organic solvents, such as diethyl ether, THF, toluene, and chloroform, but barely soluble in alcohols and saturated hydrocarbons. Table 1 summarizes molecular weights and optical properties of **MSxT**. UV absorption and emission bands of **MSxT** appeared at almost the same energy regions as those of oligothiophenes with the same chain lengths.[7] It was also noted that the absorption bands of the spin-coated films were red-shifted by 20−40 nm from those in solutions, suggesting higher coplanarity of thienylene

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(1) For example, see: (a) Pei, P.; Yu, W. L.; Ni, J.; Lai, Y. H.; Huang, W.; Heeger, A. J. *Macromolecules* **2001**, *34*, 7241. (b) Aubert, P. H.; Knipper, M.; Groenendaal, L.; Lutsen, L.; Manca, J.; Vanderzande, D. *Macromolecules* **2004**, *37*, 4087.
(2) (a) Halik, M.; Klauk, U. T.; Schmid, G.; Ponomarenko, S.; Kirchmeyer, S.; Weber, W. *Adv. Mater.* **2003**, *15*, 917. (b) Melucci, M.; Gazzano, M.; Barbarella, G.; Cavallini, M.; Biscarini, F.; Maccagnani, P.; Ostoja, P. *J. Am. Chem. Soc.* **2003**, *125*, 10266.
(3) (a) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108. (b) Katz, H. E.; Laquindanum, J. G.; Lovinger, A. J. *Chem. Mater.* **1998**, *10*, 633. (c) Ong, B. S.; Wu, Y. L.; Liu, P.; Gardner, S. *J. Am. Chem. Soc.* **2004**, *126*, 3378. (d) Murphy, A. R.; Frechet, J. M. J.; Chang, P.; Lee, J.; Subramanian, V. *J. Am. Chem. Soc.* **2004**, *126*, 1596.
(4) Kunai, A.; Ueda, T.; Horata, K.; Toyoda, E.; Ohshita, J.; Ishikawa, M.; Tanaka, K. *Organometallics* **1996**, *15*, 2000.
(5) Ohshita, J.; Takata, A.; Kai, H.; Kunai, A.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Sakamaki, K.; Okita, K.; Harima, Y.; Kunugi, Y.; Yamashita, K.; Ishikawa, M. *Organometallics* **2000**, *19*, 4492.
(6) Ohshita, J.; Yoshimoto, K.; Hashimoto, M.; Hamamoto, D.; Kunai, A.; Harima, Y.; Kunugi, Y.; Yamashita, K.; Kakimoto, M.; Ishikawa, M. *J. Organomet. Chem.* **2003**, *665*, 29.
(7) Sumi, N.; Nakanishi, H.; Ueno, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 979, and references therein.

Scheme 1
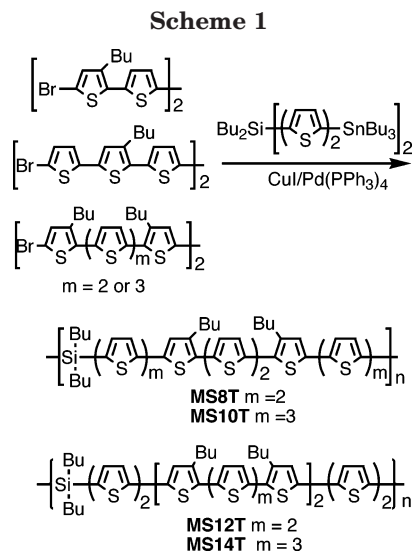
Table 1. Molecular Weights and Optical Properties of MSxT

polymer	M_w $(M_w/M_n)^a$	mp/°C	abs λ_{max}/nm $(\lambda_{edge}$/eV) in CHCl$_3$	film	emissn λ_{max}/nm^b in CHCl$_3$	film
MS8T	14 200 (1.7)	118−122	443 (2.30)	464 (2.08)	564	602
MS10T	7300 (1.4)	92−95	446 (2.28)	476 (2.06)	566	605
MS12T	9100 (1.3)	78−82	454 (2.25)	485 (2.04)	568	607
MS14T	11 400 (1.7)	112−116	457 (2.20)	499 (2.00)	578	616

^{a} Determined by GPC, relative to polystyrene standards. ^{b} Each emission band bears a shoulder around 620 nm in CHCl$_3$ and 660 nm in the solid state.

Table 2. Performance of EL Devices with MSxT

|	EL				FET	
polymer	max. luminance/ cd m^{-2} (voltage^a/V)	onset voltage^b/ V	EL^c λ_{max}/ nm	efficiency^d/ %	μ_{FET}/ cm^2 V^{-1} s^{-1}	on/ off ratio
MS8T					3.4×10^{-5}	1000
MS10T	400 (10.5)	8.5	606	0.08	4.6×10^{-5}	1000
MS12T	900 (11.5)	8.0	604	0.15	6.9×10^{-5}	1000
MS14T	800 (10.0)	7.0	612	0.15	6.7×10^{-5}	1000

^{a} Applied bias voltage, giving the maximum luminance. ^{b} Applied voltage giving a luminance of 10 cd/m^2. ^{c} EL maximum at the maximum luminance. ^{d} External quantum efficiency at the maximum luminance.

rings in the repeating unit and/or $\pi-\pi$ interaction between them in the solid states.

EL devices with the structure ITO/**MSxT**/Alq3/Mg: Ag were fabricated, and their performance was examined. The results are summarized in Table 2. Figure 1 represents the luminance−voltage ($L-V$) and current density−voltage ($I-V$) plots for the device with **MS12T** as a typical example. As can be seen in Figure 1a, the device with **MS12T** afforded the maximum luminance of 900 cd/m^2 at the bias voltage of 11.5 V. By applying higher voltages, however, the luminance decreased to about 200 cd/m^2. In contrast, the current density of the device increased continuously along the bias voltage up to 13 V (Figure 1b), indicating that the decrease of the luminance in the high-voltage region was not due to decomposition of the device, but presumably ascribed to suppressed efficiencies of the current−luminance conversion. Interestingly, a clear EL spectral change was observed around 11.5 V (Figure 2). Up to 11.5 V, the EL spectra were composed of the emissions from
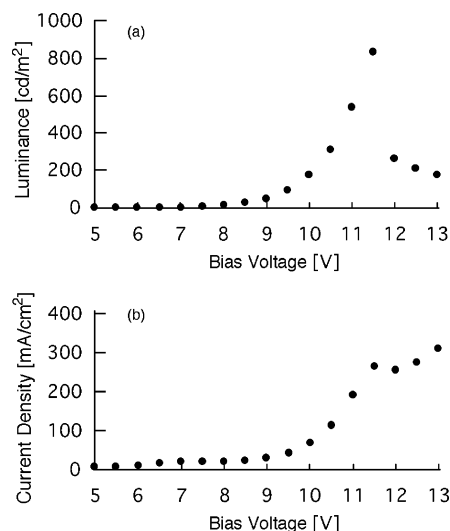
Figure 1. (a) Luminance−voltage ($L-V$) and (b) current density−voltage ($I-V$) plots for the EL device of ITO/ **MS12T**/Alq3/Mg:Ag.
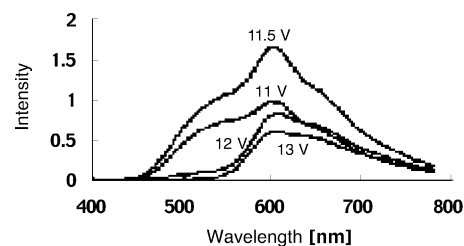

**Figure 2.** EL spectra from the device of ITO/**MS12T**/Alq3/ Mg:Ag.

Alq3 and the polymer around 520 and 610 nm, respectively, while applying voltages higher than 11.5 V led to disappearance of the emission from Alq3 and the color change from orange to red. This process was irreversible, and the device, to which voltage higher than 11 V had been once applied, emitted a red light from the low-voltage region.

The EL devices with **MS10T** and **MS14T** exhibited $I-V$ and $L-V$ profiles and EL spectral changes similar to those of the device with **MS12T**. The maximum luminances from these devices were 400 and 800 cd/ m^2, respectively. Onset voltages for these devices were slightly reduced by increasing x (Table 2). The external quantum efficiencies of the devices with **MSxT** were about 0.1−0.2% at the maximum luminance. The present devices showed much lower maximum current densities and luminances, when compared to the device with **DS5T**, for which maximum current density and luminance were 500 mA/cm^2 and 4000 cd/m^2, respectively.[6] This may be due to the different emission mechanism between the devices. The devices having a polymer layer with a short oligothienylene unit ($x \leq 5$ in Chart 1) emitted a green light arising from Alq3 emission, in contrast to the present devices.[6] Single-layer devices (ITO/**MSxT**/Mg:Ag) were also fabricated. However, these devices emitted no detectable light at all.

FETs having a spin-coated **MSxT** film as the active layer were fabricated (Figure 3), and the field effect hole mobilities μ_{FET} and on/off ratios were noted. In these experiments, we prepared three or four devices based on each of the polymers. The deviation of the data depending on the runs was within 10%, and the best
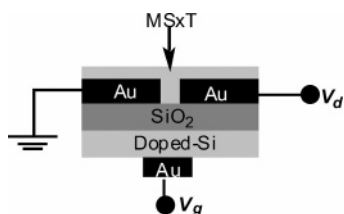
Figure 3. Schematic illustration of the FETs.
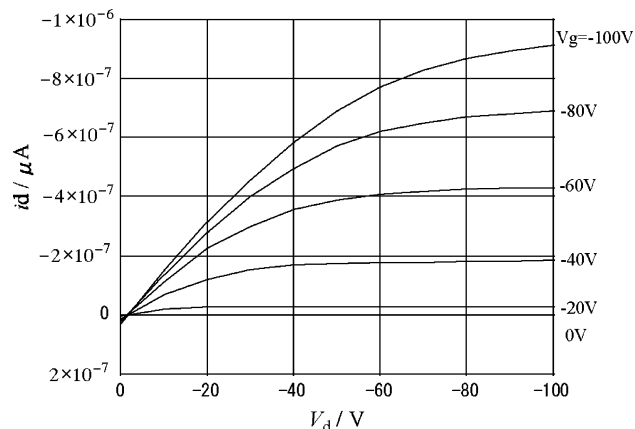
Figure 4. i_d vs V_d curves at different gate biases for the FET device using the thin film of polymer **MS12T** as an active layer.

ones are given in Table 2. Figure 4 shows curves of drain current (i_d) versus drain voltage (V_d) at various gate voltage (V_g) for the FET based on **MS12T** as a typical example. The channel conductances increased as V_g became more negative for the present devices, implying that the **MSxT** films behaved as *p*-channel semiconductors. The carrier mobilities of the devices slightly increased by elongation of the oligothienylene unit from $x = 8$ to 12. However, increasing x from 12 to 14 barely affected the FET properties. There might be a concern about the tin contamination in the polymers that would affect the FET properties. However, washing **MS12T**

(8) The EDS analysis of a spin-coated film of **MS12T** on a silicon wafer showed the existence of tin. However, the fact that the ^{1}H NMR integration ratios were consistent with the ideal structure seemed to indicate that the tin contamination was low.

with 10% hydrochloric acid under ultrasonic irradiation did not exert a clear influence, giving rise to only a little inferior FET properties with $\mu_{FET} = 4.9 \times 10^{-5}$ and on/off ratio = 1000 for the film.[8]

The mobilities of the present polymer films were lower than that previously reported for a cast film prepared from a chloroform solution of regioregular poly(3-hexylthiophene) ($\mu_{FET} = 4.5 \times 10^{-2}$ cm^2 V^{-1} s^{-1}). However, it is noteworthy that the on/off ratios of the present devices (ca. 1000) were higher than that of the polythiophene-based device, although the ratio of the polythiophene-based device was reported to be improved from 340 to 9000 by exposing the film to NH$_3$.[3a] We also prepared FETs with **DS5T** (see Chart 1; R = Bu, $x = 5$, $y = 2$) and **MS7T** (R = Bu, $x = 7$, $y = 1$). However, **DS5T** was not FET active and **MS7T** showed inferior activity, with $\mu_{FET} = 5.6 \times 10^{-6}$ cm^2 V^{-1} s^{-1} and on/off ratio = 100, to those of **MSxT** with $x = 8$, 10, 12, and 14.

In conclusion, we found that the present polymers **MSxT** were potentially useful as emissive materials in EL device systems, as well as FET active materials. The performance of the present FETs was inferior to those reported for highly oriented polythiophene and oligothiophene films.[2,3] The XRD analyses of the present **MSxT** films used for the FETs showed no clear peaks, indicating the amorphous-like morphologies of the films without highly oriented oligothienylene units. Optimization of the conditions of film preparation for ordering the π-conjugated systems, which are known as an important factor for the FET properties, may be necessary to improve the performance.

Supporting Information Available: Experimental details for the synthesis of polymers **MSxT** and fabrication of EL devices and FETs. This material is available free of charge via the Internet at http://pubs.acs.org.

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