Notes

Synthesis of Polymers Composed of Alternating Diphenylenedithienosilole and Diethynylenesilylene Units and Their Applications to Hole Transport in Double-Layer EL Devices

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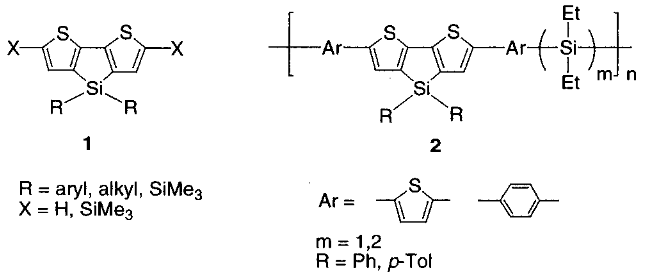
Introduction

There has been current interest in the chemistry of silole (silacyclopentadiene) ring system, because of the low-lying LUMO energy level, arising from the interaction between the silicon σ^* and butadiene π^* orbitals.[1] In an effort to obtain silole-based functionality materials,[2] we have synthesized dithienosiloles (**1** in Chart 1) as the novel silole-containing conjugated compounds.[3,4] Dithienosilole has a silole ring fused with two thiophene rings and was found to have the low-lying LUMO, as do simple siloles, being applicable to the electron transport of electroluminescent (EL) devices.[4,5] We have also synthesized polymers having the dithienosilole units in the backbone (**2** in Chart 1), which can be used as both electron- and hole-transport for EL devices.[6] Of these, polymer **2a** (Ar = thienylene, $m = 1$, R = Ph) shows the highest hole-transporting properties, which are a little inferior but almost compatible to a typical hole-transporting polymer, poly(*N*-vinylcarbazole) (PVK). However, the layers prepared from vapor deposition of monomeric dithienosiloles **1** and spin-coating of dithienosilole-containing polymers **2** in EL devices were found to be thermally unstable, and applying high voltage to the EL devices leads to decomposition of the dithienosilole layer. This is probably due to melting or crystallization, as is often observed for organic materials used for EL devices.

On the other hand, polymers composed of an alternating arrangement of an organosilicon unit and π-electron system have received much attention regarding their heat-resistant properties.[7,8] In particular, a class of polymers with ethynylenesilylene units in the backbone have been synthesized as excellent heat-resistant materials, and it has been proposed that the high heat-resistant properties of the materials obtained from these polymers are ascribed to the cross-linking reactions concerning the ethynylene bonds.[9] To obtain dithienosilole-based materials with sufficient thermal stability, we designed polymers whose backbone is composed of alternating di(phenylene)dithienosilole and diethynylenesilylene units.

Chart 1



Scheme 1

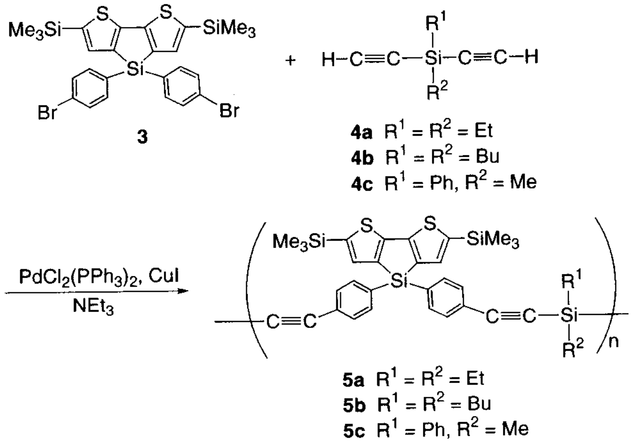


Table 1. Synthesis of Dithienosilole Polymers

polymer	R^1, R^2	yield/%[a]	M_w (M_w/M_n)[b]
5a	Et$_2$	58	33 000 (2.3)
5b	Bu$_2$	35	52 000 (2.5)
5c	Ph, Me	49	27 000 (2.5)

[a] After reprecipitation. [b] Determined by GPC, relative to polystyrene standards.

Results and Discussion

Synthesis and Properties of Dithienosilole Polymers. The Sonogashira-type coupling reactions[10] of bis(4-bromophenyl)dithienosilole (**3**) with diethynylsilanes (**4a**−**c**) in the presence of a catalytic amount of PdCl$_2$(PPh$_3$)$_2$ and CuI in Et$_3$N afforded the corresponding polymers **5a**−**c** (Scheme 1 and Table 1). Molecular weights of the polymers (after reprecipitation) were determined to be M_w = 27 000−52 000 by GPC, relative to polystyrene standards. The rather low yields of the polymers are due to the formation of oligomers with low molecular weight. For example, GPC analysis of polymer **5b** as prepared showed a peak at M_n = 500 and a shoulder at M_n = 1600, which disappeared by reprecipitation, in addition to a large peak due to the polymer. Polymers **5a**−**c** are light yellow solids and soluble in

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Table 2. Optical and Electrochemical Properties of Polymers 5a−c

polymer	absorption[a] λ_{max}/nm	oxidation potential[b] Ep/V vs SCE	TGA[c] Td$_5$[d]/°C	wt loss[e]/%
5a	359	1.31, 1.52	436	37
5b	351, 360 (sh)	1.37, 1.52	410	40
5c	350, 360 (sh)	1.30, 1.52	373	41
1 (X = SiMe$_3$)[f]				
R = Ph	356	1.22		
R = *p*-Tol	358	1.25		
2a[g]	332, 441, 537	0.97, 1.32, 1.80	232	61

[a] λ_{max} in THF, sh indicates peak shoulder. [b] On a polymer film, prepared by spin-coating on an ITO electrode, in acetonitrile containing 100 mM of Et$_4$NBF$_4$. [c] In nitrogen, with a rate of 10 °C/min. [d] Temperature resulting in 5% weight loss based on the initial weight. [e] Total weight loss at 1000 °C. [f] See ref 4. [g] See ref 6.

common organic solvents, such as aromatic solvents, halocarbons, and ethers, but barely soluble in saturated hydrocarbons and insoluble in alcohols. They do not show softening points up to 300 °C. The structures of the polymers were verified mainly by the NMR spectra, and all spectral data obtained for the polymers are consistent with the regular alternating structures shown in Scheme 1 (see Experimental Section).

Optical and electrochemical properties of polymers **5a**−**c** are summarized in Table 2. Their UV absorption maxima are around 360 nm. The cyclic voltammograms (CVs) of the polymers were measured on the thin films prepared by spin-coating of the polymer solutions on ITO glass plates, in the range of 0.0−2.0 V vs SCE. All the films underwent irreversible electrochemical oxidation in two steps, and no cathodic counterparts were observed in the CVs. As shown in Table 2, the UV and CV data of **5a**−**c** closely resemble those of monomeric dithienosiloles **1** with aryl and trimethylsilyl substituents on the silole silicon and thiophene α-carbons, respectively, indicating that the optical and electrochemical properties of the polymers are little affected by the ethynylenesilylene bridge, but mainly reflect those of dithienosilole units. The irreversible electrochemical properties of the polymers are also characteristics of the dithienosilole units. It has been reported that dithienosiloles **1**[4] and dithienosilole polymers **2**[6] undergo irreversible anodic oxidation in the CVs in the same scanning range, leading to decomposition of the dithienosilole ring system.

Thermal properties of polymers **5a**−**c** were examined by thermogravimetric analysis (TGA)−thermal differential analysis (TDA) in nitrogen. Temperature resulting in a 5% weight loss based on the initial weight (Td$_5$) and final weight loss at 1000 °C were noted as listed in Table 2. As can be seen in Table 2, the materials obtained from heating of the present polymers exhibit much higher heat-resistant properties than polymer **2a** (Ar = thienylene, *m* = 1, R = Ph in Chart 1) probably due to the cross-linking reactions of **5a**−**c**. In fact, TDA curves of polymers **5a**−**c** show a broad exothermic peak centered at 250 °C. When polymer **5b** was heated at 250 °C for 20 min in vacuo, the polymer became insoluble in organic solvents. However, no significant changes were observed in the IR spectrum on heating, and the UV spectra of the polymer film are essentially the same before and after heating the film, although the UV absorptions were slightly broadened and the IR spectrum revealed the slight decrease of the absorption due to the ethynylene unit at 2159 cm^{-1}.

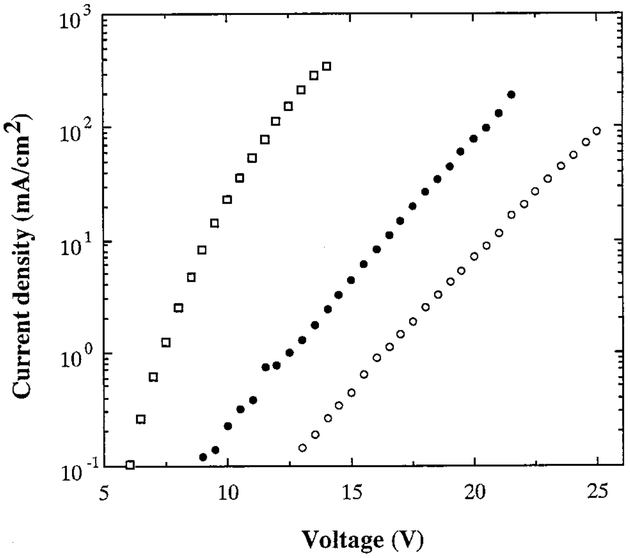

Figure 1. Current density−voltage curves for EL devices having a polymer film of (□) **2a**, (●) **5a**, and (○) **5b**, as the hole-transporting material.

These results indicate that the cross-linking reactions concerning ethynylene units occurred slightly, and the dithienosilole units remained unchanged. Powder X-ray diffraction analysis for polymer **5a** revealed no characteristic patterns. After heating polymer **5a**, however, broad and weak but certain peaks were observed at 2θ = 26° and 43° (Cu Kα), indicating that crystallization occurred to some extent. Presumably, occurrence of the cross-linking reactions and crystallization are both responsible for the formation of the insoluble materials by heating the polymers.

Performance of EL Devices Using Polymers 5a,b as the Hole Transport. We examined hole-transporting properties of the present polymers in a double-layer EL system, ITO/**5a**,**b**/Alq/Mg-Ag, in which Alq (tris(8-quinolinolato)aluminum(III)) is used as the electron-transporting-emitter layer and ITO (indium tin oxide) and Mg-Ag are the anode and cathode, respectively. Figure 1 depicts the current density−voltage curves of the devices, together with that of a device of ITO/**2a**/Alq/Mg-Ag for comparison.[6] As can be seen in Figure 1, the devices with polymers **5a**,**b** showed much higher turn-on voltage, relative to the device with polymer **2a**. This agrees well with the higher HOMO energy level for **2a** relative to **5a**,**b** indicated by the lower anodic peak potential of **2a** (Table 2). It is also likely that the existence of the long bridging unit between the dithienosilole units suppresses the hole transfer through the hopping between the dithienosilole units in both inter- and intramolecular ways. The device with **5a** showed higher current density, relative to that with **5b** at any applied voltages. Similar improvement of the hole-transporting properties by reducing the chain length of the alkyl substituents on the silylene bridge has been previously reported for poly[(dialkylsilylene)diethynylene-9,10-anthrylenes], and it has been pointed out that high concentration of diethynylanthracene units in the polymer layer favors the π−π interaction between diethynylanthracene units in an intermolecular way, which plays an important role for improved hole-transporting properties.[11] By applying voltage, the device exhibited green EL as shown in Figure 2, whose spectrum was almost identical with the photoluminescence spectrum of vacuum-deposited Alq, implying that the EL origi-

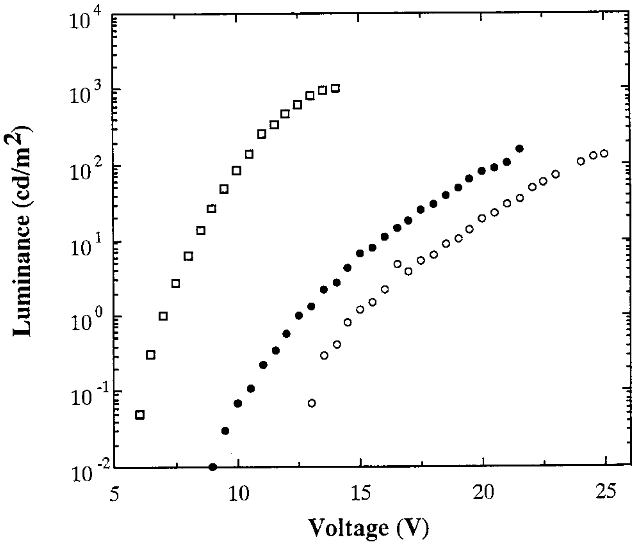

Figure 2. Luminescence–voltage curves for EL devices having a polymer film of (□) **2a**, (●) **5a**, and (○) **5b**, as the hole-transporting material.

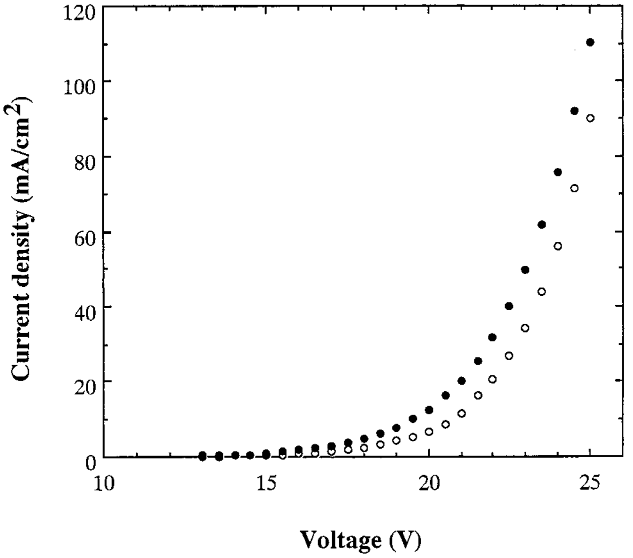

Figure 3. Current density–voltage curves for EL devices having a film of polymer **5b** (○) as-prepared and (●) thermally cross-linked.

nated from the Alq layer.

Next, we fabricated devices having thermally cross-linked polymers as the hole transport. Thus, a film of **5b** prepared on an ITO electrode was heated at 250 °C for 5 min, and then Alq and Mg-Ag were vapor-deposited on the surface of the film in this order. Interestingly, as shown in Figures 3 and 4, the device with thermally treated polymer **5b** exhibits superior EL properties to that with **5b** film as prepared. Thermally induced cross-linking in polymer **5b** layer seems to facilitate the interchain interaction between dithienosilole units. Similar treatment of polymer **5a**, however, led to the detach of the polymer film from the surface of the ITO electrode.

In conclusion, we prepared polymers **5a**–**c** as the heat-resistant hole-transporting materials and observed the enhancement of the hole-transporting properties of the polymer film by thermally induced cross-linking, which would provide a new opportunity to develop silicon-based EL materials.

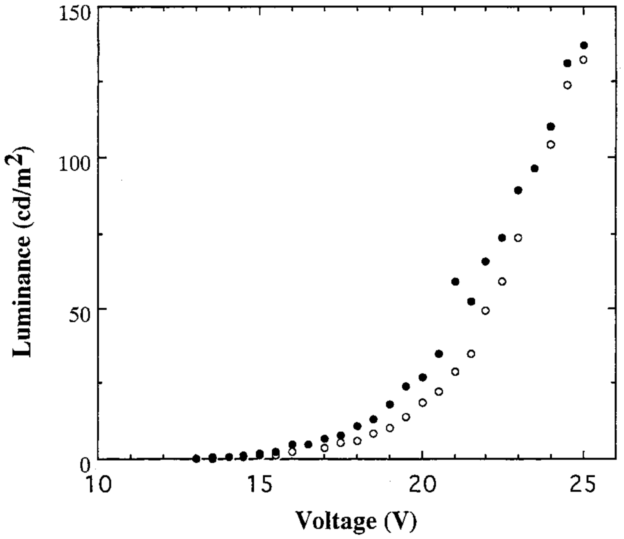

Figure 4. Luminescence–voltage curves for EL devices having a film of polymer **5b** (○) as-prepared and (●) thermally cross-linked.

Experimental Section

General Data. All reactions were carried out under an atmosphere of purified argon. Mass spectra were measured on a Hitachi M-80B spectrometer. NMR spectra were recorded on JEOL EX-270 and Lambda-400 spectrometers using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer FT1600 spectrophotometer.

Materials. Ether and THF were dried over sodium–potassium alloy and distilled just before use. Triethylamine was distilled from potassium hydroxide and stored over molecular sieves until use. Monomers **4a**–**c** were prepared as reported in the literature.[12]

Preparation of Monomer 3. To a solution of 3,3′-dilithio-5,5′-bis(trimethylsilyl)-2,2′-bithiophene,[4] prepared from 4.00 g (8.54 mmol) of 3,3′-dibromo-5,5′-bis(trimethylsilyl)-2,2′-bithiophene and 2 equiv of butyllithium in 100 mL of ether, was added 3.86 g (9.39 mmol) of bis(4-bromophenyl)dichlorosilane at −80 °C. The mixture was stirred for 2 h at this temperature. THF (30 mL) was added to the mixture, and the mixture was heated to reflux for 40 h. After hydrolysis of the mixture, the organic products were chromatographed on a silica gel column eluting with hexane to give crude solids which were recrystallized from ethanol to give 2.12 g (39% yield) of **3** as the colorless crystals: mp 152–154 °C; MS m/z 650 (M^+ for ^{81}Br). ^1H NMR (δ in $CDCl_3$): 0.33 (s, 18H), 7.23 (s, 2H), 7.46 (d, $J = 8.1$ Hz, 4H), 7.50 (d, $J = 8.1$ Hz, 4H). ^{13}C NMR (δ in $CDCl_3$): 0.1, 125.5, 130.6, 131.4, 136.1, 136.9, 140.6, 142.9, 155.8. ^{29}Si NMR (δ in $CDCl_3$): −22.0, −6.6. Anal. Calcd for $C_{26}H_{28}Br_2S_2Si_3$: C, 48.18; H, 4.35. Found: C, 48.19; H, 4.31.

Preparation of 5a. A mixture of 0.50 g (0.77 mmol) of **3**, 0.105 g (0.77 mmol) of **4a**, 15 mg of CuI, and 30 mg of $PdCl_2(PPh_3)_2$ in 15 mL of triethylamine was heated to reflux for 20 h. The resulting salts were filtered, and the solvent was evaporated. Reprecipitation of the residue from chloroform–ethanol gave 0.28 g (58% yield) of **5a**: softening point >300 °C. ^1H NMR (δ in $CDCl_3$): 0.31 (s, 18H, Me_3Si), 0.82 (q, $J = 7.7$ Hz, 4H, Et), 1.11 (t, $J = 7.7$ Hz, 6H, Et), 7.23 (s, 2H, thiophene ring H), 7.45 (d, $J = 7.8$ Hz, 4H, phenylene), 7.52 (d, $J = 7.8$ Hz, 4H, phenylene). ^{13}C NMR (δ in $CDCl_3$): 0.1, 6.5, 7.2, 90.4, 106.5, 124.7, 131.6, 133.0, 135.1, 136.2, 140.9, 142.7, 155.8. IR: $\nu_{C\equiv C}$ 2159 cm^{-1}. Anal. Calcd for $(C_{34}H_{38}S_2Si_4)_n$: C, 65.53; H, 6.15. Found: C, 63.76; H, 6.04.[13]

Polymers **5b**,**c** were obtained in a fashion similar to above. Data for **5b**: softening point >300 °C. ^1H NMR (δ in $CDCl_3$): 0.32 (s, 18H, Me_3Si), 0.70–0.80 (m, 10H, Bu), 1.30–1.50 (m, 8H, Bu), 7.23 (s, 2H, thiophene ring H), 7.45 (d, $J = 7.2$ Hz, 4H, phenylene), 7.53 (d, $J = 7.2$ Hz, 4H, phenylene). ^{13}C NMR (δ in $CDCl_3$): 0.1, 13.8, 14.5, 25.9, 26.0, 91.0, 106.4, 124.7, 131.6, 132.9, 135.1, 136.2, 140.9, 142.7, 155.8. IR: $\nu_{C\equiv C}$ 2159 cm^{-1}. Anal. Calcd for $(C_{38}H_{46}S_2Si_4)_n$: C, 67.19; H, 6.83. Found: C, 63.58; H, 6.56. Data for **5c**: softening point >300 °C. ^1H NMR (δ in $CDCl_3$): 0.32 (s, 18H, Me_3Si), 0.67 (s, 3H, MeSi), 7.24 (s, 2H, thiophene ring H), 7.30−7.80 (m, 13H, Ph and phenylene). ^{13}C NMR (δ in $CDCl_3$): −0.1, 0.1, 90.5, 107.2, 124.4, 127.8, 128.1, 131.1, 131.6, 134.1, 135.2, 135.3, 136.2, 140.8, 142.8, 155.9. IR: $\nu_{C\equiv C}$ 2160 cm^{-1}. Anal. Calcd for $(C_{37}H_{36}S_2Si_4)_n$: C, 67.62; H, 5.52. Found: C, 65.50; H, 5.49.

Preparation of EL Devices. A thin film (30−40 nm) of the polymer was prepared by spin-coating from a solution of polymer in dichloroethane on ITO coated on a glass substrate with a sheet resistance of 15 Ω/cm (Asahi Glass Company). An Alq layer was then prepared by vacuum deposition at 1×10^{-5} Torr with a thickness of 60−70 nm on the polymer film. Finally, a layer of Mg-Ag alloy with an atomic ratio of 10:1 was deposited on the Alq layer surface at 1×10^{-5} Torr.

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(13) Lower carbon content determined by combustion analysis than the theoretical value is often observed for organometallic polymers (see ref 8 and references therein). This would be due to the formation of silicon-containing ceramics, such as β-SiC during the analysis.

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