

Synthesis of organosilanylene–pentathienylene alternating polymers and their application to the hole-transporting materials in double-layer electroluminescent devices

Joji Ohshita^{a,*}, Kazuhiro Yoshimoto^b, Mimi Hashimoto^b, Daisuke Hamamoto^b,
Atsutaka Kunai^{b,*}, Yutaka Harima^b, Yoshihito Kunugi^c, Kazuo Yamashita^c,
Masaya Kakimoto^d, Mitsuo Ishikawa^e

^a Institute for Fundamental Research of Organic Chemistry, Kyushu University, Fukuoka 812-8581, Japan

^b Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

^c Division of Materials Science, Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan

^d Osaka R&D Laboratories, Sumitomo Electric Industries Ltd., 1-1-3 Shimaya, Konohana-ku, Osaka 554-0024, Japan

^e Department of Chemical Technology, Kurashiki University of Science and the Arts, Kurashiki 712-8505, Japan

Received 13 August 2002; received in revised form 16 October 2002; accepted 18 October 2002

Abstract

Polymers composed of an alternating arrangement of organosilanylene and pentathienylene units, $[\text{SiBu}_2\text{-X-SiBu}_2\text{-(2,5-C}_4\text{H}_2\text{S)}_5]_n$ (**1**: X = none, **2**: X = O) were prepared and their application to the hole-transport in double-layer electroluminescent (EL) devices was studied. The EL devices with the structure of ITO/I or 2/Alq/Mg:Ag emitted a green light resulting from Alq emission by applying the bias voltage. The device with **1** showed a lower turn-on voltage than that with **2**, while almost the same maximum luminance of 4000 cd m^{-2} was obtained from both of the devices.

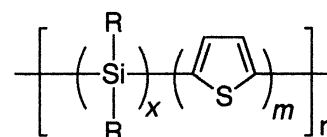
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Keywords: Organosilicon polymer; Oligothienylene; Hole-transport; EL device

1. Introduction

Polymers having an alternating arrangement of an organosilanylene and oligothienylene unit have been well studied regarding their conducting properties on the doped states [1–4]. In addition, current attention has been focused on their applications to the materials in electrode devices, such as the emitter of long lived electroluminescent (EL) devices [5] and semi-conducting photodiodes [6,7]. Recently, we have been interested in the hole-transporting properties of poly[silanylene(oligothienylenes)] and examined some of them (R = Et, $x = 1\text{--}2$, $m = 3\text{--}5$ in Chart 1) as the hole-transport in a double layer EL device system [4]. Thus, the devices with the structure of ITO/polymer film/Alq/Mg:Ag where the

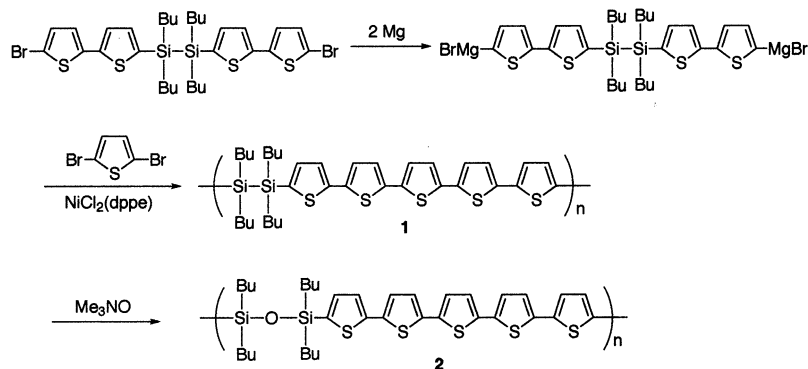
polymer film and Alq (tris(8-quinolinolato)aluminum (III)) layer are the hole-transport and electron-transporting emitter, respectively, were found to emit a green light arising from the Alq emission. Interestingly, the device performance is improved by increasing the number of x from 1 to 2 and m from 3 to 5. The highest luminance of 2000 cd m^{-2} was obtained from the device with disilanylene-tetrathienylene alternating polymer (**3**, R = Et, $x = 2$, $m = 4$ in Chart 1). However, due to the poor film quality, poly[tetraethyldisilanylene-penta(2,5-thienylene)] (**4**, R = Et, $x = 2$, $m = 5$ in



Poly[organosilanyleneoligo(2,5-thienylene)]

Chart 1.

* Corresponding authors. Fax: +81-824-24-5494
E-mail addresses: johshita@ms.kyushu-u.ac.jp (J. Ohshita),
akunai@hiroshima-u.ac.jp (A. Kunai).



Scheme 1.

Chart 1), whose film may be anticipated as a better hole-transport than **3**, could not be examined. In order to improve the film quality, we introduced longer alkyl groups on the disilanyl unit and examined the resulting polymer film as the hole-transport of the double layer EL device system. We also examined a disiloxanyl–pentathienylene alternating polymer, to know how the existence of the Si–Si bond influences in the hole-transporting properties of the film.

2. Results and discussion

2.1. Synthesis of polymers and the optical properties

Poly[tetrabutyl-disilanyl-penta(2,5-thienylene)] (**1**) and poly[tetrabutyl-disiloxanyl-penta(2,5-thienylene)] (**2**) were prepared as shown in Scheme 1. Thus, nickel-catalyzed cross-coupling [8] of the di-Grignard reagent prepared from bis(bromobithienyl)disilane with dibromothiophene afforded polymer **1** as dark orange solids. The yields of **1** from several runs varied from 70 to 85%. Polymer **2** was obtained as orange solids in 86% yield, by treatment of polymer **1** with an excess of trimethylamine oxide [9]. The resulting polymer **2** exhibited larger M_w and smaller M_n values than those of the starting **1**, as shown in Table 1. Presumably, both the cleavage of the polymer backbone and cross-linking reactions were involved in this reaction. Higher melting point of **2** compared to **1** may also reflect the cross-linked structure of polymer **2**.

UV absorption and emission maxima of **2** were slightly blue-shifted from those of **1**, indicating that introduction of the siloxane bonds in **2** interrupted the interaction between the Si–Si σ -orbital and thienylene π -electron system in polymer **1** [1]. When compared with **4** ($R = Et$, $x = 2$, $m = 5$ in Chart 1) reported previously [4], the absorption maximum of **1** appeared at 9 nm lower energy. Replacement of the ethyl groups on the disilanyl unit by more electron-donating butyl groups would elevate the HOMO energy level. Similar

red shifts are also observed when methyl groups on the poly[tetramethyldisilanyl-penta(2,5-thienylene)] ($R = Me$, $x = 2$, $m = 2$ in Chart 1) are replaced by ethyl groups [4]. Interestingly, polymer **2** showed solvatochromic behavior and changing the solvent from THF to hexane resulted in a blue shift by 12 nm, although the origin is still unclear [10].¹ The emission band did not move by changing the solvent from THF to hexane. Polymer **1** was barely soluble in hexane and therefore the solvatochromism could not be examined.

2.2. Performance of EL devices with polymers 1 and 2

Double layer EL devices having a spin-coated film of polymer **1** or **2** as the hole-transport and vapor-deposited layer of Alq as the electron-transporting emitter were fabricated. Fig. 1 represents the current density–voltage (I – V) and luminance–voltage (L – V) plots of the devices. The performance of a device with polymer **3** was reinvestigated with using a newly prepared polymer sample and the results are also depicted in Fig. 1. The presently fabricated device with **3** exhibited higher maximum luminance (4000 cd m^{-2} at 14 V), as compared with the previously reported one (2000 cd m^{-2} at 12–13 V) [4]. This may be ascribed to thermal stability of the polymer layer due to the higher molecular weight ($M_w = 22\,000$, $M_n = 8500$) of the present sample than the previous one ($M_w = 11\,000$, $M_n = 6500$). However, the I – V and L – V characteristics of the present device with **3** in low voltage region (4–10 V) were quite similar to those reported previously. Probably, the molecular weight did not exert significant influence on the polymer electronic state, but affected the thermal stability of the polymer film to allow a higher voltage to be applied, leading to higher luminance from the presently fabricated device.

As shown in Fig. 1, the device with polymer **1** showed the lowest turn-on voltage among the devices examined

¹ Clear solvatochromism of organosilanyl–thienylene alternating polymer in the emission spectra has been reported.

Table 1
Properties of polymers **1** and **2**

Polymer ^a	M_w ^b	M_n ^b	M_w/M_n ^b	M.p. (°C) ^c	UV λ_{max} (nm) ^d	Emission λ_{max} (nm) ^d
1	76 000	30 000	2.5	106	436	537, 513
2	94 000	25 000	3.8	138	426	530, 505

^a Purified by reprecipitation from ethanol–toluene for **1** and methanol–chloroform for **2**.

^b Determined by GPC, relative to polystyrene standards.

^c Determined by DSC.

^d Measured in THF.

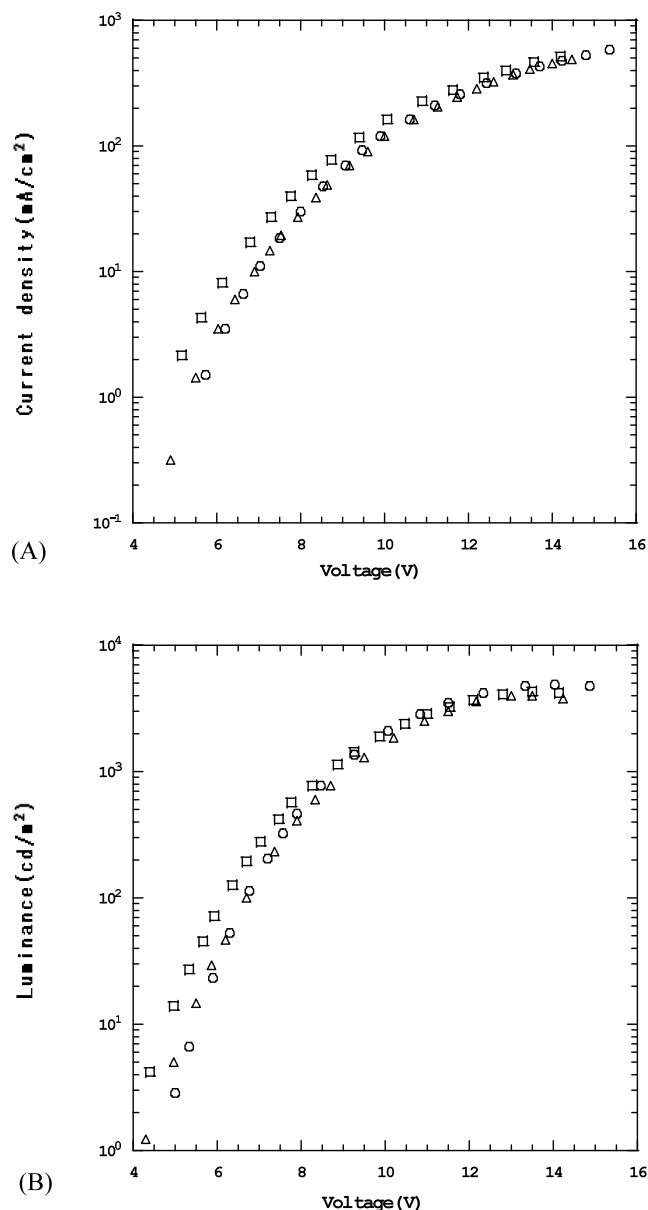


Fig. 1. (A) Current density–voltage and (B) luminescence–voltage plots for EL devices having a polymer film of (\square) **1**, (Δ) **2** and (\circ) **3**, as the hole-transporting material.

and always afforded higher current density and luminance in the applied voltage of 4–15 V than the others. The maximum current density and luminance obtained

from the present devices are 5000 mA cm^{-2} and 4000 cd m^{-2} , respectively, independent of the polymer structure. It seems to be noteworthy that polymer **1** film showed better hole-transporting properties than the device with **3**, despite the existence of bulkier butyl substituents on the disilanylene unit in **1** rather than ethyls in **3**. Our recent studies on the hole-transporting properties of the polymers with alternating organosilanylene and π -conjugated units indicate that the existence of bulkier substituents on the organosilanylene unit suppresses the hopping process between the π -conjugated systems, probably due to the steric requirement [11].

I – V and L – V characteristics of the device with **2** were found to be inferior to those of the device with **1**, indicating that the introduction of a siloxane linkage in place of the disilanylene unit in polymer **2** rather suppressed the hole-transporting properties of the polymer film. This may be due to the interruption of σ – π type interaction between the disilanylene unit and π -electron system, although we can not exclude the possibility of other operating factors. The elongation of the organosilanylene unit by introducing the siloxane bonds may reduce the density of the π -electron system in the film, leading to poor interaction between the oligothierylene units in the film. More simply, the introduction of electronegative oxygen atoms into the polymer chain may decrease the hole-affinity of the polymer.

3. Experimental

3.1. General

THF used as the solvent was dried over sodium–potassium alloy and distilled just before use. NMR spectra were recorded on a JEOL model JNM-EX spectrometer. UV spectra were measured with a Hitachi U-3210 spectrophotometer. IR-spectra were measured on a Shimadzu FT8000 infrared spectrometer. The detailed procedure for the preparation of polymer **1** will be described elsewhere [12].

3.2. Preparation of polymer 2

To a 100 ml flask was placed 0.50 g (4.5 mmol) of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ and 50 ml of toluene and the flask was heated for azeotropic distillation of a mixture of toluene/water. After ca. 45 ml of toluene was distilled, the mixture was cooled to room temperature (r.t.) and 0.70 g (1.0 mmol) of polymer **1** and 50 ml of THF were added to the mixture. The mixture was heated at 60 °C for 3 h. The solvent was evaporated under reduced pressure and 5 ml of chloroform was added to the residue. Excess Me_3NO was filtered and the filtrate was poured into 200 ml of methanol to give 0.62 g (86% yield) of **2** as dark orange solids: ^{13}C -NMR (CDCl_3) δ 13.7, 16.2, 25.2, 26.4, 124.3, 124.5, 124.7, 135.4, 136.3 (*ipso* carbons can not be observed due to their low intensities); ^{29}Si -NMR (CDCl_3) δ -4.9; IR 1070 cm^{-1} ($\nu_{\text{Si-O}}$). Anal. Found: C, 60.10; H, 6.51. Calc. for $(\text{C}_{36}\text{H}_{46}\text{OS}_5\text{Si}_2)_n$: C, 60.79; H, 6.52%.

3.3. Preparation of EL devices

A thin film (ca. 70 nm) of polymer **1** or **2** was prepared by spin coating from the chloroform solution on an anode, indium–tin–oxide (ITO) coated on a glass substrate (Nippon Sheet Glass Co.). An electron-transporting emitting layer was then prepared by vacuum deposition of 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.

Acknowledgements

This work was supported in part by NEDO (project no. 01A26005a). We thank Sankyo Kasei Co. Ltd.,

Tokuyama Co. Ltd. and Mitsubishi Chemical Corporation Fund for financial support.

References

- [1] (a) J. Ohshita, A. Kunai, *Acta Polym.* 49 (1998) 379; (b) M. Ishikawa, J. Ohshita, in: H.S. Nalwa (Ed.), *Organic Conductive Molecules and Polymers*, Ch. 30, Wiley, Volume 2, New York, 1997.
- [2] R.J.P. Corriu, C. Guérin, B. Henner, T. Kuhlman, A. Jean, *Chem. Mater.* 2 (1990) 351.
- [3] (a) K. Tanaka, H. Ago, T. Yamabe, M. Ishikawa, T. Ueda, *Organometallics* 13 (1994) 5583; (b) A. Kunai, T. Ueda, K. Horata, E. Toyoda, J. Ohshita, M. Ishikawa, K. Tanaka, *Organometallics* 15 (1996) 2000; (c) J. Ohshita, A. Takata, A. Kunai, M. Kakimoto, Y. Harima, Y. Kunugi, K. Yamashita, *J. Organomet. Chem.* 611 (2000) 537.
- [4] J. Ohshita, A. Takata, H. Kai, A. Kunai, K. Komaguchi, M. Shiotani, A. Adachi, K. Okita, Y. Harima, Y. Kunugi, K. Yamashita, M. Ishikawa, *Organometallics* 19 (2000) 4492.
- [5] F. Garten, A. Hilberer, F. Cacialli, Y. van Dam, B. Schlattmann, R.H. Friend, T.M. Krapwijk, G. Hadziioannou, *Adv. Mater.* 9 (1997) 127.
- [6] K. Yoshino, S. Lee, A. Fujii, H. Nakayama, W. Schneider, A. Naka, M. Ishikawa, *Adv. Mater.* 11 (1999) 1382.
- [7] M. Kakimoto, H. Kashihara, T. Kashiwagi, T. Takiguchi, J. Ohshita, M. Ishikawa, *Macromolecules* 30 (1997) 7816.
- [8] K. Tamao, S. Kodama, I. Nishimura, M. Kumada, A. Minato, *Tetrahedron* 38 (1982) 3347.
- [9] For similar oxidation of a disilanylene polymer, see: M. Ishikawa, T. Hatano, Y. Hasegawa, T. Horio, A. Kunai, A. Miyai, T. Ishida, T. Tsukihara, T. Yamanaka, T. Koike, J. Shioya, *Organometallics* 11 (1992) 1604.
- [10] J. Ohshita, M. Hashimoto, T. Iida, H. Tang, A. Kunai, *Organometallics* 20 (2001) 4395.
- [11] (a) S.A. Manhart, A. Adachi, K. Sakamaki, K. Okita, J. Ohshita, T. Ohno, T. Hamaguchi, A. Kunai, J. Kido, *J. Organomet. Chem.* 592 (1999) 52; (b) J. Ohshita, T. Sumida, A. Kunai, A. Adachi, K. Sakamaki, K. Okita, *Macromolecules* 33 (2000) 8890.
- [12] M. Ishikawa, W. Schneider, K.-K. Lee, Y. Yasumura, M. Kakimoto, to be submitted to *Macromolecules* (manuscript in preparation).