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Synthesis of organosilanylene–thienylene alternating oligomers bearing ether side chains

Joji Ohshita *, Mimi Hashimoto, Kwang-Hoi Lee, Hiroto Yoshida, Atsutaka Kunai *

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

Abstract

Organosilanylene–thienylene alternating oligomers bearing ether side chains were synthesized and their optical properties were studied. The oligomers exhibited the emission maxima at 380–400 nm, which were slightly shifted to lower energies as the solvent polarity increased. In contrast, the UV absorption spectra were not evidently affected by the solvent polarity, indicating that the solvatochromic behaviors in the emission spectra may be due to the favored aggregation of chromophores in the polar solvents.
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1. Introduction

Polymers composed of π-conjugated units bridged by organosilanylene σ-linkages are of current interest, because of their unique properties arising from delocalization of π-electrons through the σ-bonds and/or electron donating properties of organosilanylene units that elevate the HOMO energy level of the π-electron system [1,2]. In particular, much attention has been focused on the polymers having thienylene units as the π-conjugated units, regarding their usefulness as functionality materials, such as organic semi-conductors [2–5], photoresists [6], and hole-transporting [5,7], photoconducting [4,8], and emitting materials [9]. However, the organosilanylene–thienylene polymers reported thus far are soluble only in organic solvents of moderate polarity, such as ethers, chlorocarbons, and aromatic compounds. No organosilanylene–thienylene polymers that are soluble in water and the lower alcohols have been reported until recently, although the solubility in such polar solvents would provide a better chance for their applications to functional materials. Recently, we

synthesized organodisilanylene– and organodisiloxanylene–thienylene alternating oligomers bearing ether side chains (**2** and **3** in Scheme 1) that were soluble even in methanol/water mixed solvents [10]. Interestingly, they exhibited clear solvatochromic shifts in the emission maxima, probably due to the changes in the oligomer conformations, and the emission maxima moved to longer wavelength as the solvent polarity increased. To know more about the solvatochromism of organosilanylene–thienylene oligomers, we prepared this type of an oligomer with organomonosilanylene units in the backbone and those with longer ether chains. The optical properties of the present oligomers are described in comparison with those of **2** and **3**, reported previously.

2. Results and discussion

2.1. Preparation of organosilanylene–thienylene oligomers with ether side chains

Oligomer **4** was obtained in a fashion similar to the preparation of **2** and **3**, reported previously (Scheme 1). Thus, treatment of monomer **1** with 2.1 equiv of *sec*-butyllithium in THF, followed by addition of 2,5-bis(chlorodimethylsilyl)thiophene to the resulting solu-

* Corresponding authors. Tel.: +81-824-24-7727; fax: +81-824-24-5494.
E-mail addresses: jo@hiroshima-u.ac.jp (J. Ohshita), akunai@hiroshima-u.ac.jp (A. Kunai).
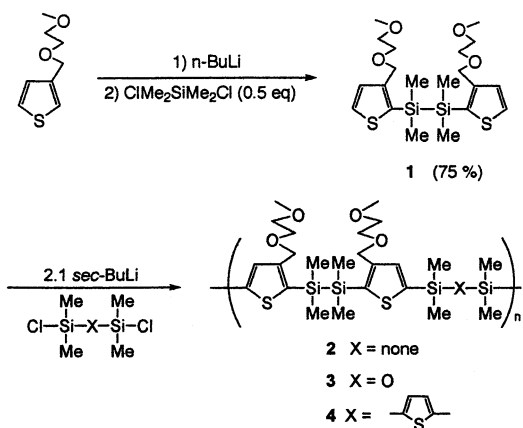
Scheme 1.
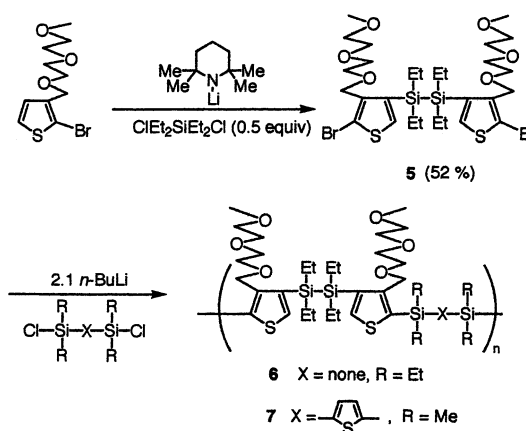
Scheme 2.

tion of the α,α′-dilithiated derivative of **1**, afforded oligomer **4** as pale yellow viscous oil. To obtain oligomers with longer ether side chains, we first prepared monomer **1′** shown in Chart 1 and examined its dilithiation. However, treatment of **1′** with two equivalents of *n*-, *sec*-, and *tert*-butyllithium and LDA always caused Si–C bond cleavage competing the lithiation to give 3-(2,5,8-trioxanonyl)thiophene as the major product. We, therefore, prepared 1,2-bis{4-[5-bromo-4-(2,5,8-trioxanonyl)thienyl]}tetraethyldisilane (**5**) as a monomer by the reaction of lithiated 2-bromo-3-(2,5,8-trioxanonyl)thiophene with 1,2-dichlorotetraethyldisilane as shown in Scheme 2. In this reaction, lithiation occurred at C4-position of the thiophene ring exclusively to give di(3-thienyl)disilane **5**. No products arising from lithiation at C5-position were obtained. Using LDA as the base led to the formation of a complex mixture including a 5% yield of 1,2-bis{2-[5-bromo-4-(2,5,8-trioxanonyl)thienyl]}tetraethyldisilane. In addition, it was necessary to use 1,2-dichlorotetraethyldisilane as the starting disilane to obtain di(3-thienyl)disilane in good yield. In fact, the reaction of lithiated 2-bromo-3-(2,5,8-trioxanonyl)thiophene with 1,2-dichlorotetramethyldisilane gave a 1:3 mixture of the expected 1,2-bis{3-[5-bromo-4-(2,5,8-trioxanonyl)thienyl]}tetramethyldisilane and the corresponding disiloxane that could not be separated from each other by either preparative GPC and silica gel column chromatography. The reaction of monomer **5** with *n*-butyllithium cleanly gave the dilithiated monomer that was then treated with dichlorotetraethyldisilane and
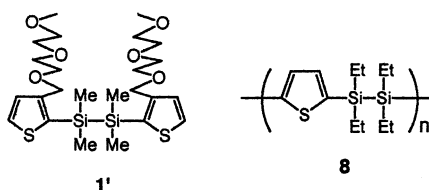
bis(chlorodimethylsilyl)thiophene to afford oligomers **6** and **7**, respectively, as pale yellow viscous oil (Scheme 2).

Table 1 summarizes yields and molecular weights of the oligomers determined by GPC relative to polystyrene standards, after removal of low molecular weight fractions by preparative GPC. The structures of oligomers **4**, **6** and **7** were verified by spectral and elemental analysis. Although some unidentified signals of low intensity, probably due to the end groups, were observed in the NMR spectra, the integral ratios of the oligomer signals in their ¹H-NMR spectra were consistent with the proposed organosilanylene–thienylene repeating structures. In contrast to oligomers **2** and **3** that were soluble even in mixed solvents of water/methanol up to the ratio of 40/1, the present oligomers **4**, **6**, and **7** were insoluble in methanol and ethanol, despite that oligomers **6** and **7** had longer ether side chains than **2** and **3**.

2.2. Solvatochromic behaviors of organosilanylene–thienylene oligomers with ether side chains in the emission spectra

The UV absorption maximum (λ_{max}) of oligomer **4** in cyclohexane appeared at 256 nm, which is at almost the same energy as that of monomer **1** (250 nm) and at higher energy than that of **2** (274 nm). This seems to indicate that σ-π type conjugation did not take place effectively in **4**, similar to **3**, in which the siloxane bonds interrupt the σ-π type conjugation ($\lambda_{max} = 261$ nm).

Chart 1.

Table 1
Preparation of polymers

Polymer	Yield (%) [a]	M_w (M_w/M_n) [b]	UV λ_{max} (nm) [c]
4	52	3000 (1.1)	256
6	47	4200 (1.1)	280
7	41	4000 (1.1)	262

[a] After purification by preparative GPC.
[b] Determined by GPC, relative to polystyrene standards.
[c] In cyclohexane.

Disilanylene oligomer **6** showed λ_{max} at 280 nm, while λ_{max} of oligomer **7** and monomer **5** were observed at 262 and 269 nm, respectively, again indicating that the efficient σ-π type conjugation was observed only in the disilanylene oligomer **6**. The red-shifted λ_{max} of **6** relative to that of **2** may be due to the substitution effects. Replacement of the methyl groups on the disilanylene unit by more electron-donating ethyl groups would elevate the HOMO energy level. Similar red shifts are also observed when methyl groups on the poly[(tetramethyldisilanylene)bithienylene] are replaced by ethyl groups [5]. The present oligomers showed no evident absorption spectral changes depending on the solvent, similar to **2** and **3**.

Fig. 1 shows the solvent dependence of the emission spectra of oligomer **4**. Oligomers **2** and **3** exhibited quite similar solvatochromic behaviors as illustrated for **2** in Fig. 1 [10]. Disilanylene–thienylene oligomer **8** having no ether chains (Chart 1) also showed similar solvatochromism in the emission spectra. Thus, the spectra of **2**, **3**, and **8** in cyclohexane showed the maxima at about 340 and 350 nm, together with a broad shoulder around 400 nm. In THF, however, the emission maximum at 340–350 nm disappeared and only the shoulder remained. Since no evident solvent dependence was observed in the UV profiles of oligomers **2**, **3** and **8**, we concluded that the solvatochromic behavior was due to the intramolecular interactions of chromophores providing aggregated π-systems that are the origins of the red-shifts in the emission spectra along the solvent polarity.

In contrast to this, oligomer **4** showed the maximum at 389 nm in cyclohexane, which was slightly red-shifted by increasing the solvent polarity as shown in Fig. 1. This seems to indicate that the aggregation of chromophores occurred even in cyclohexane for **4**, which was more preferable in polar solvents leading to low energy shifts of the emission maxima, in the order of cyclohexane < THF < acetonitrile. Oligomers **6** and **7** exhibited solvatochromism similar to **4**, as summarized in Table 2, again indicating the aggregation of chromophores even in nonpolar cyclohexane solution. The favored aggregation of chromophores may be a reason for the less soluble properties of oligomers **4**, **6** and **7**, as compared with oligomers **2** and **3**. The origin of the favored aggregation in oligomers **4**, **6** and **7** is still unclear. However, introduction of a more rigid silylene unit into the oligomer chain in **4**, relative to the disilanylene and disiloxanylene unit in **2**, **3**, and **8**, would lead to a folded and/or helical structure of the oligomer main chain in preference to a linear like structure, in which π-aggregation may be enhanced only in polar solvents. For **6** and **7**, the existence of β-thienylene junction in the backbone seemed to be responsible for the favored aggregation. In fact, MM2 calculations [11] for a tetramethyldisilanylene-2,4-thienylene pentamer suggested that the pentamer would have a loose helical structure, while a tetramethyldisilanylene-2,5-thienylene pentamer was predicted to possess a linear structure (Fig. 2).

To know more about flexibility around the α- and β-thienylene junction of the oligomer backbone, we

Table 2
Emission maxima (nm) of oligomers in various solvents [a]

Polymer	Cyclohexane	Chloroform	THF	Acetonitrile
4	389	nd [b]	387	407
6	374	387	382	389
7	389	393	391	401

[a] At 1.0×10^{-5} (thienylene unit mol) l^{-1}.
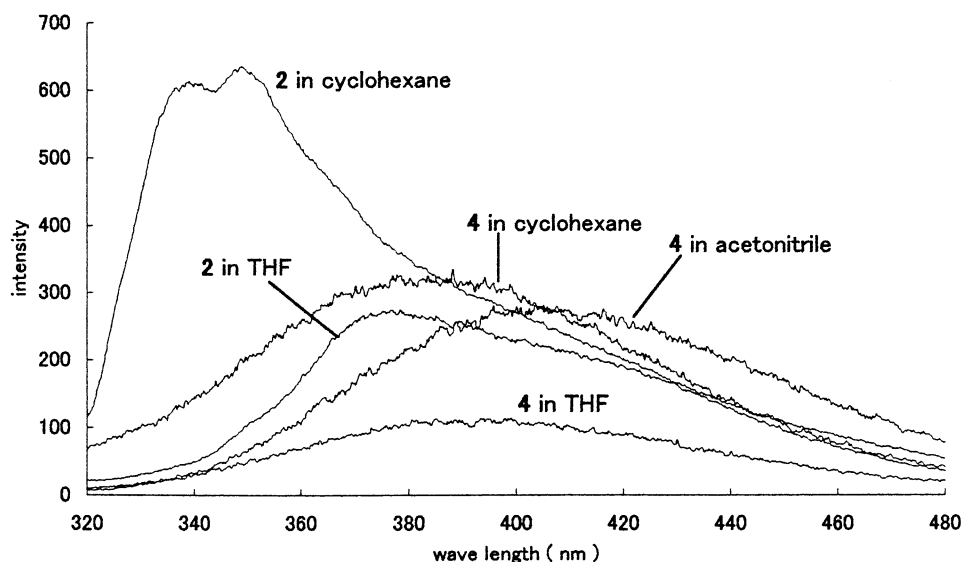[b] Not determined.

Fig. 1. Emission spectra of oligomers **2** and **4**.
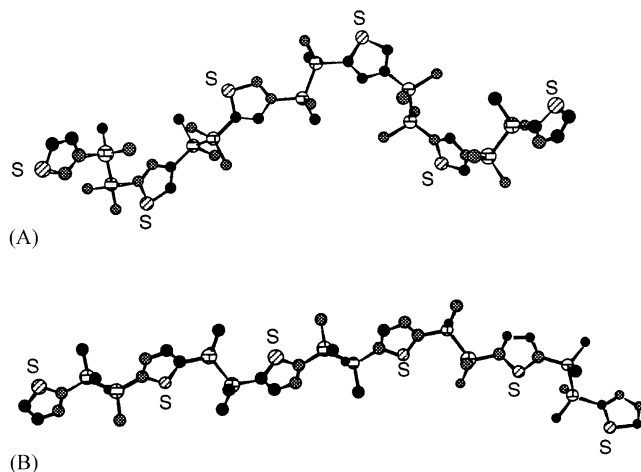
Fig. 2. Optimized geometries for (A) 3-thienyl[-SiMe$_2$SiMe$_2$-(2,4-thienylene)]$_5$H and (B) 2-thienyl[-SiMe$_2$SiMe$_2$-(2,5-thienylene)]$_5$H, derived from MM2 calculations. Protons are omitted for clarity.

carried out molecular orbital calculations on model compounds, 2- and 3-disilanylthiophene, at the level of HF/6-31G [12]. For the calculations, the dihedral angle of C=C–Si–Si was rotated from 0 to 180° and bond lengths, angles, and the other dihedral angles were optimized at this level. Fig. 3 shows the changes of heats of formation as a function of the angle, indicating that the rotation barrier for 2-disilanylthiophene is predicted to be a little smaller than that for 3-disilanylthiophene. The longer ether side chains and bulkier ethyl substituents on the disilanylene units in actual oligomers 6 and 7, which contain β-thienylene junction, may further decrease the flexibility of the oligomer backbone, as compared with oligomers 2, 3 and 8, to prevent the backbone from having a linear-like structure even in non-polar solvents.

In conclusion, we prepared three new organosilanylene–thienylene oligomers having ether side chains and found that the conformation of the
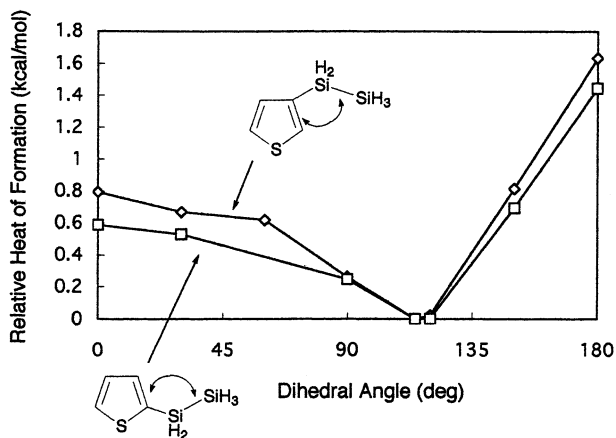

Fig. 3. Plots of dihedral angles of C=C–Si–Si vs. heats of formation for 2- and 3-disilanylthiophene, derived from MO calculations at the level of HF/6-31G.

backbone was significantly affected by the oligomer structures, leading to the obvious changes in the emission spectral profiles.

3. Experimental

3.1. General

All reactions were carried out under an inert atmosphere. THF and ether used as the solvents were dried over sodium-potassium alloy and distilled just before use. 2-Bromo-3-(2,5,8-trioxanonyl)thiophene [13], and monomers 1 [10] and 2,5-bis(chlorodimethylsilyl)thiophene [6] were prepared as reported in the literature. Work up procedure for the following experiments involved hydrolysis of the reaction mixture with water, separation of the organic layer, extraction of the aqueous layer with chloroform, drying the combined organic layer and the extracts over anhydrous magnesium sulfate, and evaporation of the solvent.

3.2. Preparation of oligomer 4

In a 50 ml two-necked flask fitted with a dropping funnel was placed 0.50 g (1.1 mmol) of monomer 1 and 25 ml of THF. The flask was cooled at −80 °C and 2.5 ml (2.4 mmol) of a 0.96 M hexane–cyclohexane solution of sec-BuLi was added to the mixture through the dropping funnel and the mixture was stirred at this temperature for 4 h. To this was added 0.30 g (1.1 mmol) of 2,5-bis(chlorodimethylsilyl)thiophene then the mixture was stirred at room temperature (r.t.) over night. After work up of the reaction mixture, the residue was subjected to preparative GPC to remove the low molecular weight fractions giving 0.37 g (52% yield) of 4: ^{1}H-NMR (CDCl$_3$) δ 0.43 (s, 12H, SiMe$_2$), 0.61 (s, 12H, SiMe$_2$), 3.35 (s, 6H, OCH$_3$), 3.48 (s, 4H, CH$_2$), 3.51 (s, 4H, CH$_2$), 4.29 (s, 4H, CH$_2$), 7.36 (s, 2H, β-H) 7.39 (s, 2H, β-H). ^{13}C-NMR (CDCl$_3$) δ −2.05 (SiMe$_2$), 0.09 (SiMe$_2$), 58.96 (OCH$_3$), 68.40 (CH$_2$), 69.24 (CH$_2$), 71.87 (CH$_2$), 130.30, 130.50, 136.50, 138.74, 146.47, 147.45 (ring carbons). GPC (THF) $M_w = 3000$, $M_w/M_n = 1.1$. Anal. Found: C, 51.54; H, 7.30. Calc. for C$_{28}$H$_{46}$Si$_4$S$_3$O$_4$: C, 51.33; H, 7.08%.

3.3. Preparation of monomer 5

In a 50 ml two-necked flask fitted with a dropping funnel was placed 1.8 g (13 mmol) of tetramethylpyperidine and 15 ml of THF. The flask was cooled at 0 °C and 6.3 ml (10 mmol) of a 1.59 M hexane solution of n-BuLi was added to the mixture through the dropping funnel and the mixture was stirred at this temperature for 1 h. The mixture was slowly added to a solution of 3.0 g (10 mmol) of 2-bromo-3-(2,5,8-trioxanonyl)thio-

phene in 30 ml of ether at $-80\,^{\circ}$C and the mixture was stirred at this temperature for 4 h. To the resulting mixture containing β-lithiated 2-bromo-3-(2,5,8-trioxa-nonyl)thiophene was added 1.2 g (5.0 mmol) of 1,2-dichlorotetraethyldisilane and the mixture was stirred at $-80\,^{\circ}$C for 4 h. After work up of the reaction mixture, the residue was subjected to silica gel chromatography eluting with hexane/ethyl acetate $= 3/1$ to give 2.0 g (52% yield) of **5**: MS m/z 379 [M^+/2]. ^{1}H-NMR (CDCl$_3$) δ 0.98 (br s, 20H, SiEt$_2$), 3.39 (s, 6H, OCH$_3$), 3.51–3.65 (m, 16H, CH$_2$), 4.08 (s, 4H, CH$_2$), 7.14 (s, 2H, α-H). ^{13}C-NMR (CDCl$_3$) δ 4.71, 7.89 (SiEt$_2$), 59.03 (OCH$_3$), 68.52, 69.74, 70.51, 70.55, 71.93 (CH$_2$), 116.41, 133.10, 134.30, 147.78 (ring carbons); ^{29}Si-NMR (δ in CDCl$_3$) -18.81. Anal. Found: C, 44.41; H, 6.31. Calc. for C$_{28}$H$_{48}$Si$_2$S$_2$O$_6$Br$_2$: C, 44.20; H, 6.36%.

3.4. Preparation of oligomer 6

In a 50 ml two-necked flask fitted with a dropping funnel was placed 0.50 g (0.60 mmol) of monomer **5** and 10 ml of THF. The flask was cooled at $-80\,^{\circ}$C and 0.82 ml (1.3 mmol) of a 1.59 M hexane solution of *n*-BuLi was added to the mixture through the dropping funnel and the resulting mixture was stirred at this temperature for 2 h. To this was added 1.7 g (0.69 mmol) of 1,2-dichlorotetraethyldisilane and the mixture was stirred at r.t. over night. After work up of the reaction mixture, the residue was subjected to preparative GPC to remove the low molecular weight fractions giving 0.22 g (47% yield) of **6**: ^{1}H-NMR (CDCl$_3$) δ 0.96 (brs, 40H, SiEt$_2$), 3.37 (s, 6H, OCH$_3$), 3.53–3.56 (m, 8H, CH$_2$), 3.63–3.64 (m, 8H, CH$_2$), 4.34 (s, 4H, CH$_2$), 7.30 (s, 2H, α-H). ^{13}C-NMR (CDCl$_3$) δ 4.91, 5.23 (Si*C*H$_2$CH$_3$), 7.93, 8.20 (SiCH$_2$*C*H$_3$), 59.00 (OCH$_3$), 68.60, 69.45, 70.59, 71.72, 71.95 (CH$_2$), 138.15, 138.15, 141.92, 147.71 (ring carbons). ^{29}Si-NMR (δ in CDCl$_3$) -19.35, -19.04. GPC (THF) $M_w = 4200$, $M_w/M_n = 1.1$. Anal. Found: C, 55.68; H, 9.09. Calc. for C$_{36}$H$_{68}$Si$_4$S$_2$O$_6$: C, 55.91; H, 8.86%.

3.5. Preparation of oligomer 7

Oligomer **7** was prepared in a fashion similar to that of **6** using 2,5-bis(chlorodimethylsilyl)thiophene as a monomer instead of 1,2-dichlorotetraethyldisilane. For **7**: 41% yield. ^{1}H-NMR (CDCl$_3$) δ 0.65 (s, 12H, SiMe$_2$), 0.96 (br s, 20H, SiEt$_2$), 3.36 (s, 6H, CH$_3$), 3.41–3.53 (m, 8H, CH$_2$), 3.60–3.62 (m, 8H, CH$_2$), 4.17 (s, 4H, CH$_2$),

7.34 (s, 2H, α-H), 7.37 (s, 2H, β-H). ^{13}C-NMR (CDCl$_3$) δ 0.13 (SiMe$_2$), 4.67, 7.93 (SiCH$_2$CH$_3$), 58.95 (OCH$_3$), 68.30, 69.48, 69.57, 70.42, 71.82 (CH$_2$), 136.42, 138.67, 139.49. 142.77, 143.89, 147.54 (ring carbons). ^{29}Si-NMR (δ in CDCl$_3$) -18.94, -16.14. GPC (THF) $M_w = 4000$, $M_w/M_n = 1.1$. Anal. Found: C, 54.26; H, 7.94. Calc. for C$_{36}$H$_{62}$Si$_4$S$_3$O$_6$: C, 54.09; H, 7.81%.

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