2000 *Organometallics* **1996,** *15,* 2000−2008

Polymeric Organosilicon Systems. 26. Synthesis and Photochemical and Conducting Properties of Poly[(tetraethyldisilanylene)oligo(2,5-thienylenes)]

Atsutaka Kunai, Takafumi Ueda, Katsuhiro Horata, Eiji Toyoda,
Ikuko Nagamoto, Joji Ohshita, and Mitsuo Ishikawa*

*Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Kagamiyama 1-4-1, Higashi-Hiroshima 739, Japan*

Kazuyoshi Tanaka

*Division of Molecular Engineering, Faculty of Engineering, Kyoto University, Sakyo-ku,
Kyoto 606-01, Japan*

Received July 27, 1995[⊗]

A series of poly[(tetraethyldisilanylene)(2,5-thienylenes)$_n$] (**1**−**5**) with n = 1−5 were synthesized. The $NiCl_2$(dppe)-catalyzed Grignard coupling of 1,2-bis(5-bromothien-2-yl)-tetraethyldisilane (**6**) and 1,2-bis(5′-bromo-2,2′-bithien-5-yl)tetraethyldisilane (**7**) with 1 equiv of Mg afforded polymer **2** (M_w = 53 000, 75% yield) and **4** (M_w = 29 500, 97% yield), respectively, while similar reaction of the di-Grignard reagent obtained from **6** and **7** with 1 equiv of 2,5-dibromothiophene afforded the respective polymers **3** (M_w = 47 000, 77% yield) and **5** (M_w = 17 000, 78% yield). The sodium condensation of 2,5-bis(chlorodiethylsilyl)-thiophene afforded polymer **1** (M_w = 20 000, 32% yield). Irradiation of polymers **1**−**5** with a low-pressure mercury lamp resulted in cleavage of the silicon−silicon bonds, but the reactivity decreased with an increase in the number of thienyl units. When the films of polymers **2**−**5** were doped with $FeCl_3$ vapor, conductivities of doped films were determined to be 10^{-5}−10^{-3} S cm^{-1} (in vacuo).

Introduction

The polymers that have silicon−silicon bonds in the main chain are of considerable interest, because they may be used as functionality materials such as photoresists, semiconducting materials, and precursors of silicon carbide.[1] Previously, we demonstrated that poly[*p*-(disilanylene)phenylenes] prepared by sodium condensation of 1,4-bis(chlorosilyl)benzene are photoactive and may be used as a top imaging layer of the double-layer photoresist system.[2] This polymer also shows conducting properties when the polymer is doped with an oxidizing agent such as antimony pentafluoride. Since that time, the synthesis and properties of many types of alternating disilanylene polymers which involve an ethenylene,[3] ethynylene,[4−8] butenyne-1,4-diyl,[9] or diethynylene[10−12] group as a π-electron system have been reported. Disilanylene copolymers bearing a heteroaromatic unit as the π-system such as the thienylene,[13−17] furylene,[18,19] and (diethynylene)pyridylene[20] groups have been synthesized, and some of their photochemical and conducting behavior has been investigated. These polymers have also been studied from theoretical points of view. For example, the electronic structures of simplified polymers composed of an alternating arrangement of a silicon−silicon unit and a π-electron system such as an ethenylene,[21] ethynylene,[21] phenylene,[21,22] and thienylene[23] group have been reported.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

(1) Zeldin, M.; Wynne, K. J.; Allcock, H. R. Inorganic and Organometallic Polymers. *ACS Symp. Ser.* **1988**, *No. 360*.

(2) Ishikawa, M.; Nate, K. Inorganic and Organometallic Polymers. *ACS Symp. Ser.* **1988**, *No. 360*, 209 and references cited therein.

(3) Ohshita, J.; Kanaya, D.; Ishikawa, M.; Yamanaka, T. *J. Organomet. Chem.* **1989**, *369*, C18.

(4) Ishikawa, M.; Hasegawa, Y.; Kunai, A.; Yamanaka, T. *Organometallics* **1989**, *8*, 2741.

(5) Iwahara, T.; Hayase, S.; West, R. *Macromolecules* **1990**, *23*, 1298.

(6) Ishikawa, M.; Hatano, T.; Hasegawa, Y.; Horio, T.; Kunai, A.; Miyai, Y.; Ishida, T.; Tsukihara, T.; Yamanaka, T.; Koike, T.; Shioya, J. *Organometallics* **1992**, *11*, 1604.

(7) Ijadi-Maghsoodi, S.; Pang, Y.; Barton, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 955.

(8) Hengge, E.; Baumegger, A. *J. Organomet. Chem.* **1989**, *369*, C39.

(9) Ohshita, J.; Matsuguchi, A.; Furumori, K.; Hong, R, Ishikawa, M.; Yamanaka, T.; Koike, T.; Shioya, J. *Macromolecules* **1992**, *25*, 2134.

(10) Ishikawa, M.; Hasegawa, Y.; Kunai, A.; Yamanaka, T. *J. Organomet. Chem.* **1990**, *381*, C57.

(11) Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1990**, *23*, 4485.

(12) Bréfort, J. L.; Corriu, R. J. P.; Gerbier, P.; Guérin, C.; Henner, B. J. L.; Jean, A.; Kuhlmann, T.; Garnier, F.; Yassar, A. *Organometallics* **1992**, *11*, 2500 and references cited therein.

(13) Hu, S.; Weber, W. P. *Polym. Bull.* **1989**, *21*, 133.

(14) Ohshita, J.; Kanaya, D.; Ishikawa, M.; Koike, T.; Yamanaka, T. *Macromolecules* **1991**, *24*, 2106.

(15) Chicart, P.; Corriu, R. J. P.; Moreau, J. J. E.; Garnier, F.; Yassar, A. *Chem. Mater.* **1991**, *3*, 8.

(16) Fang, M. C.; Watanabe, A.; Matsuda, M. *J. Organomet. Chem.* **1995**, *489*, 15.

(17) Chicart, P.; Corriu, R. J. P.; Moreau, J. J. E.; Garnier, F.; Yassar, A. In *Inorganic and Organometallic Polymers with Special Properties*; Laine, R. H., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1992; p 179.

(18) Hong, H. H.; Weber, W. P. *Polym. Bull.* **1989**, *22*, 363.

(19) Ohshita, J.; Kanaya, D.; Ishikawa, M.; Yamanaka, T. *Chem. Express* **1990**, *5*, 489.

(20) Kunai, A.; Toyoda, E.; Horata, K.; Ishikawa, M. *Organometallics* **1995**, *14*, 714.

(21) Tanaka, K.; Nakajima, K.; Okada, M.; Yamabe, T.; Ishikawa, M. *Organometallics* **1991**, *10*, 2679.

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

(23) (a) Tanaka, K.; Ago, H.; Yamabe, T.; Ishikawa, M.; Ueda, T. *Organometallics* **1994**, *13*, 3496. (b) Tanaka, K.; Ago, H.; Yamabe, T. *Synth. Met.* **1995**, *72*, 225.

0276-7333/96/2315-2000$12.00/0

During the course of our studies on the synthesis and properties of organosilicon polymers involving a heteroaromatic unit, we found that, unlike most of the disilanylene polymers, poly[(tetramethyldisilanylene)-bis(2,5-thienylene)] and poly[(hexamethyltrisilanylene)-bis(2,5-thienylene)] are photochemically inactive.[24] On the other hand, the silicon−silicon bonds in poly-[(tetramethyldisilanylene)(2,5-thienylene)] can readily be cleaved homolytically upon irradiation with UV light.[25] It is of interest to us to investigate the photochemical behavior of the alternating polymers composed of a silicon−silicon bond and oligothienylene unit having different numbers of thienylene rings.[23] In this paper, we report the synthesis of a series of poly[(tetraethyldisilanylene)(2,5-thienylenes)$_n$] (**1**−**5**) with $n = 1$−5 and their photochemical and conducting properties.

Results and Discussion

It is well-known that the sodium condensation reaction of bis(chlorosilyl)-substituted compounds or the reaction of dilithio compounds bearing a π-electron system with dichlorosilanes and dichlorodisilanes offers a convenient route to various silicon-containing alternating polymers. The polymers which can be prepared by these methods, however, always involve a small portion of siloxy units in the polymer backbone. The presence of a small amount of siloxy units in the polymer backbone would interrupt the electron delocalization through the polymer chain and therefore result in a significant decrease in the photoactivity and conductivity of the polymers.

Recently, we have reported that Ni(II)-catalyzed Grignard coupling can be applied to the synthesis of the alternating polymers composed of a bithienyl group and mono-, di-, and trisilanylene unit. For example, dehalogenative coupling of the respective bis(5-bromothien-2-yl)-substituted mono-, di-, and trisilanes with magnesium in the presence of a catalytic amount of $NiCl_2$(dppe) afforded the corresponding polymers that involve no siloxy bonds in the polymer backbone.[24]

We extended this method to the synthesis of the disilanylene copolymers involving the oligothiophene moieties with two to five thienyl rings. Thus, the reaction of 1,2-bis(5-bromothien-2-yl)tetraethyldisilane (**6**) with 1 equiv of Mg in refluxing THF gave a mixture[26,27] consisting of the starting compound **6** and the corresponding mono- and di-Grignard reagents (Scheme 1). The mixture was then heated in the presence of 1 mol % of $NiCl_2$(dppe) in a degassed sealed tube at 200 °C for 100 h. After reprecipitation of the resulting product from chloroform−ethanol, poly[(tetraethyldisilanylene)bis(2,5-thienylene)] (**2**), whose molecular weight was determined to be $M_w = 53\,000$ ($M_w/M_n = 4.8$) by GPC was obtained as a light yellow solid in 75% yield (Table 1). Similarly, treatment of the mixture prepared from 1,2-bis(5′-bromo-2,2′-bithien-5-yl)tetraethyldisilane (**7**) and 1 equiv of Mg with the Ni(II) catalyst at 230 °C for 100 h, and reprecipitation of the resulting product from chloroform−ethanol, afforded poly[(tetraethyldisilanylene)tetrakis(2,5-thienylene)] (**4**) with a molecular weight of $M_w = 29\,500$ ($M_w/M_n = 3.8$) as a brownish orange-red solid in 97% yield.

Scheme 1

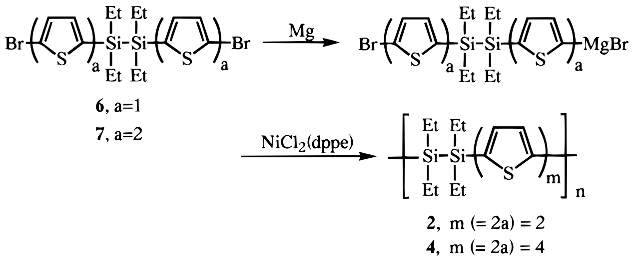
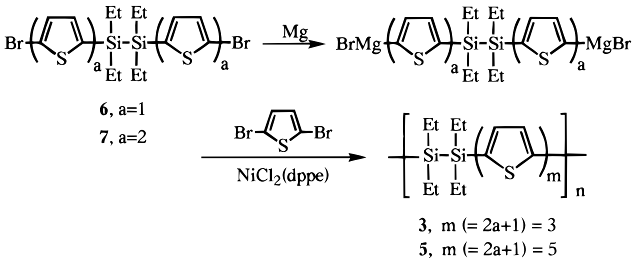


Table 1. Properties of Polymers 1−5

polymer	yield, %	mp, °C	M_w (M_w/M_n)	λ_{max}, nm absorption (ϵ)	 emission
1	32	viscous oil	20 000 (4.0)	270 (12 600)	348 363
2	75	142−148	53 000 (4.8)	221 (9100) 343 (21 200)	383 397
3	77	67−78	47 000 (3.4)	227 (13 300) 389 (26 000)	468 496
4	97	125−134	29 500 (3.8)	224 (12 700) 260 (13 000) 415 (37 900)	472 502
5	78	96−102	17 000 (2.1)	257 (15 000) 308 (10 200) 427 (40 400)	521

Scheme 2



The disilanylene polymers with a terthienyl and quinquethienyl unit were prepared by cross-condensation of the corresponding di-Grignard reagent obtained from **6** and **7** with 2,5-dibromothiophene (Scheme 2). Thus, dibromo compound **6** was treated with 2 equiv of Mg in a similar manner as above, and the resulting di-Grignard reagent was heated with 1 equiv of 2,5-dibromothiophene in the presence of the Ni(II) catalyst at 150 °C for 100 h. The product was reprecipitated from chloroform−ethanol to afford poly[(tetraethyldisilanylene)tris(2,5-thienylene)] (**3**) with a molecular weight of $M_w = 47\,000$ ($M_w/M_n = 3.4$) as a brownish orange solid in 77% yield. Similarly, poly[(tetraethyldisilanylene)pentakis(2,5-thienylene)] (**5**) with a molecular weight of $M_w = 17\,000$ ($M_w/M_n = 2.1$) was obtained as a brownish orange-red solid in 78% yield by the nickel-catalyzed reaction of the di-Grignard reagent prepared from **7** and 2 equiv of Mg with 1 equiv of 2,5-dibromothiophene at 100 °C for 48 h.

Polymers **2**−**5** thus obtained are soluble in common organic solvents such as benzene, ether, and halocarbons, but the solubility decreased markedly with increasing number of the thienyl rings per disilanylene

---

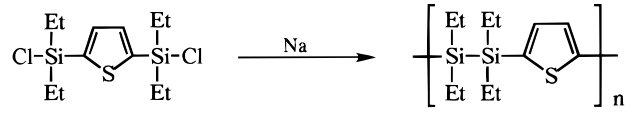
(24) Ohshita, J.; Kanaya, D.; Ishikawa, M. *Appl. Organomet. Chem.* **1993**, *7*, 269.

(25) Ohshita, J.; Kanaya, D.; Ishikawa, M. *J. Organomet. Chem.* **1994**, *468*, 55.

(26) The reagent is actually composed of a 2:1:1 mixture of mono- and di-Grignard reagents and **6**. However, the Ni-catalyzed reaction of the mixture proceeded cleanly to give polymer **2** selectively in high yield. A similar mixture has been reported for the Grignard reagent prepared from 2,5-dibromothiophene and 1 equiv of Mg.[27]

(27) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1497.

Scheme 3



1

unit. For example, the solubility of **5** in benzene is less than 20 mg/100 mL at room temperature. Polymers with an even number of the thienyl rings show higher melting points (142−148 °C for **2** and 125−134 °C for **4**) than those of the polymers with an odd number (liquid for **1** (see below), 67−78 °C for **3**, and 96−102 °C for **5**).

The structures of these polymers[28] were verified by spectroscopic analysis as well as by elemental analysis. IR spectra for all these polymers reveal stretching absorption bands due to the oligothienyl unit at ca. 3050 and 1500−1400 cm^{-1} but no bands due to a siloxy unit. All resonances observed in ^{1}H, ^{13}C, and ^{29}Si NMR spectra are consistent with the structures proposed for these polymers. For example, the ^{13}C NMR spectrum for **2** reveals two resonances due to ethylsilyl carbons at δ 5.2 and 8.2 ppm and four resonances due to thienyl carbons at δ 125.1, 135.3, 135.9, and 142.7 ppm, indicating the regular alternating structure of **2**. Similarly, ^{13}C NMR spectra for **3**−**5** reveal two resonances due to the sp^{3} carbons in the ethylsilyl group, respectively. The sp^{2} carbons in the oligothienyl units resonate as six signals for **3** (terthienyl) and eight signals for **4** (quaterthienyl) in the region 124−143 ppm, while those for **5** (quinquethienyl) appear as eight signals, of which two are overlapping (δ 124.3 and 135.9 ppm). ^{29}Si NMR spectra are also consistent with the structures proposed for **2**−**5**. Polymers **2**−**5** show only a single resonance at δ −18.22, −18.08, −17.99, and −17.94 ppm, respectively.

We also synthesized the disilanylene polymer bearing a mono(thienyl) unit, for the sake of comparison with **2**−**5**. Since the nickel-catalyzed reaction could not be applied to the synthesis of poly[(disilanylene)thienylene], we used the sodium condensation reaction for the synthesis of this type of polymer in a manner similar to that reported previously.[25] Thus, the reaction of 2,5-bis(chlorodiethylsilyl)thiophene with an excess of sodium dispersion in refluxing decane for 1.5 h afforded the crude polymer. Reprecipitation of the polymer from chloroform−ethanol gave poly[(tetraethyldisilanylene)-(2,5-thienylene)] (**1**) with a molecular weight of M_w = 20 000 (M_w/M_n = 4.0)[28] in 32% yield (Scheme 3).

Polymer **1** thus obtained is a light brown viscous oil and is soluble in common organic solvents such as ether, halocarbons, and aromatic solvents. The ^{13}C NMR spectrum for **1** shows resonances due to ethylsilyl carbons at δ 5.3 and 8.2 ppm and resonances due to thienyl ring carbons at δ 135.9 and 141.8 ppm, while the ^{29}Si NMR spectrum reveals a resonance at δ −18.6 ppm. These results unambiguously show that polymer **1** must have the regular alternating structure of a disilanylene unit and thienylene moiety. However, the ^{29}Si NMR spectrum exhibits a weak resonance at near δ −18 ppm. The IR spectrum of polymer **1** also reveals a weak absorption band near 1060 cm^{-1}, ascribable to a silicon−oxygen bond. These facts indicate the presence of a small portion of siloxy unit in the polymer backbone.

Polymers **1**−**5** show strong absorption bands in the UV region in THF solution (Table 1).[29] The absorption maxima for **1**−**5** appear at 270, 343, 389, 415, and 427 nm, respectively, which are significantly red-shifted relative to those of the corresponding 2,5-thienylene oligomers such as thiophene (230 nm), bithiophene (304 nm), terthiophene (353 nm), and quaterthiophene (390 nm in $CHCl_3$). In general, the absorption maxima of α,ω-bis(disilanyl)-substituted oligo(2,5-thiophenes) move to the direction of lower energy, compared to the ordinary oligo(2,5-thiophenes). For example, 2,2′-bithiophene shows an absorption maximum at 304 nm (ϵ = 12 200) in THF, while 5,5′-bis(pentaethyldisilanyl)-2,2′-bithiophene (**8a**) reveals a maximum at 338 nm (ϵ = 25 200), indicating the presence of σ−π conjugation. However, the fact that poly[(tetraethyldisilanylene)bis-(2,5-thienylene)] (**2**) exhibits an absorption maximum at 343 nm (ϵ = 21 200), which shows only a 5-nm shift relative to that of **8a**, suggests that π-electrons on the oligothienyl moieties are hardly delocalized through the polymer chain, but the delocalization of π-electrons is limited only to a disilanylbithiophene segment in the polymer chain.

The result obtained by SCF CO calculations[23a] for poly[disilanylene(2,5-thienylenes)$_n$] (PDST-*n*) predicts that the nature of both the highest occupied (HO) and the lowest unoccupied (LU) bands interchanges from σ-type to π-type as the number of thiophene rings increases, due to the development of π-conjugation within the thiophene rings, and that the value of the π−π* gap of PDST-*n* decreases with an increase in *n*, whereas that of the σ−σ* gap does not change much. This obviously signifies that π-conjugation in PDST-*n* becomes strengthened at the thienyl unit. Moreover, the observed λ_{max} values for polymers **1**−**5** are in good agreement with those for the calculated π−π* interband transition for PDST-*n*. This assignment can be supported by the fact that Br-terminated oligothiophenes[30] as well as ordinary oligothiophenes show absorptions similar to those for **1**−**5** and also by the fact that all polymers exhibit strong fluorescence emission.

We examined the photochemical behavior of polymers **1**−**5**. As can be seen in the case of poly[*p*-(disilanylene)-phenylenes] reported previously,[2] when a thin film prepared from **2** was irradiated in air with a 6-W low-pressure mercury lamp bearing a Vycor filter, the absorption maximum near 340 nm disappeared within 40 min, indicating that homolytic scission of the silicon−silicon bonds in the polymer backbone occurs. Profiles of the ultraviolet spectra obtained from irradiation of the film of **2** are shown in Figure 1a. Polymer **1** also exhibited a rapid UV change when its thin film was irradiated. IR spectra of the resulting films reveal strong absorption bands due to Si−O−H and Si−O−Si bonds at 3300 and 1100 cm^{-1}. The formation of the Si−O−H and Si−O−Si bonds can best be explained by the reaction of the silyl radicals generated by homolytic

---

(28) GPC profiles for all polymers **1**−**5** are monomodal, although the values of M_w/M_n are rather high.

(29) The shapes of UV absorption bands of **2**−**5** are exhibited in ref 23a.

(30) The absorption maxima for Br-(2,5-thienylene)$_n$-Br in THF are observed at 252 (n = 1), 320 (n = 2), and 366 (n = 3) nm, and their shapes are quite similar to those for the respective disilanylene polymers **1**−**3**.

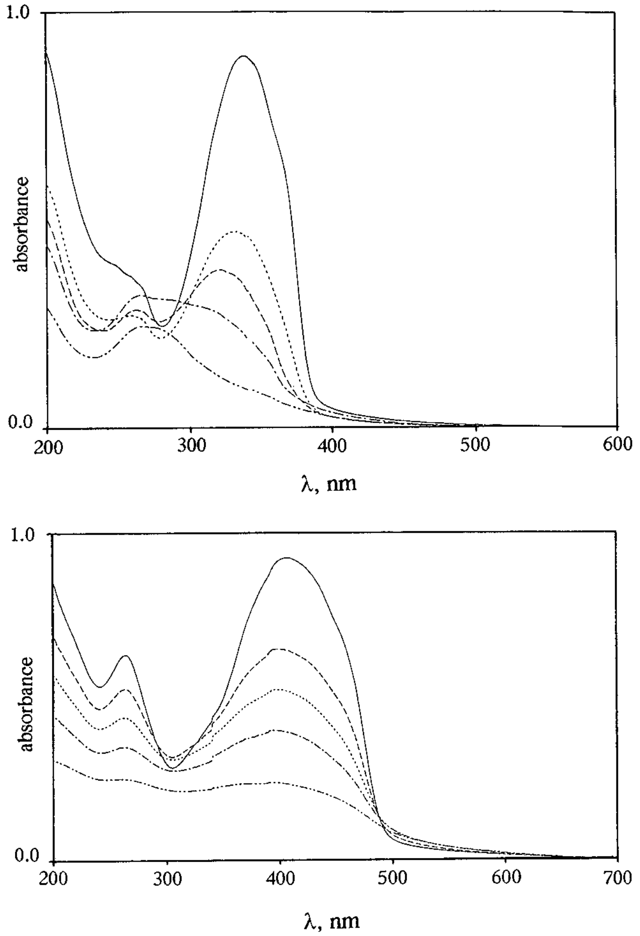


Figure 1. UV spectra of thin solid films of **2** and **4**: (a, top) before irradiation of **2** (—), after irradiation for 5 min (- - -), after irradiation for 10 min (— —), after irradiation for 30 min (— - —), and after irradiation for 40 min (— - - - —), (b, bottom) before irradiation of **4** (—), after irradiation for 1 h (— —), after irradiation for 4 h (- - -), after irradiation for 8 h (— - —), after irradiation for 12 h (— - - —).

scission of the silicon−silicon bonds in the polymer backbone with oxygen in air, as observed previously.[2]

The other polymers **3**−**5** are also photoactive, but they become less sensitive to UV light with expansion of the thienylene π-electron system. For example, disappearance of the absorption band for **3** required 1.5 h upon irradiation of the thin film with a low-pressure lamp in the air, while the absorption bands for **4** and **5** diminished only slowly, and the maxima were still observed even after 8 h of irradiation (see Figure 1b).

Such changes in photochemical reactivity for **1**−**5** can be interpreted by the difference of the natures of the lowest energy excitation in the series of polymers. That is, polymers **1** and **2** have σ−σ^* type band gaps, whereas **3**−**5** have π−π^* type gaps due to an interchange of nature of the optical transition with the lowest energy.[23a] The Si−Si bond cleavage found in **1** and **2** is obviously associated with the nature of their lowest unoccupied crystal orbitals. This cleavage simultaneously shortens the π-conjugation length throughout the polymer backbone, which is responsible for a remarkable decrease in the peak of the π−π^* transition found in Figure 1a. On the other hand, in polymers **3**−**5**, the optical energy by irradiation is rather wasted in the π−π^* transition and makes the Si−Si bond cleavage slow to occur (Figure 1b).

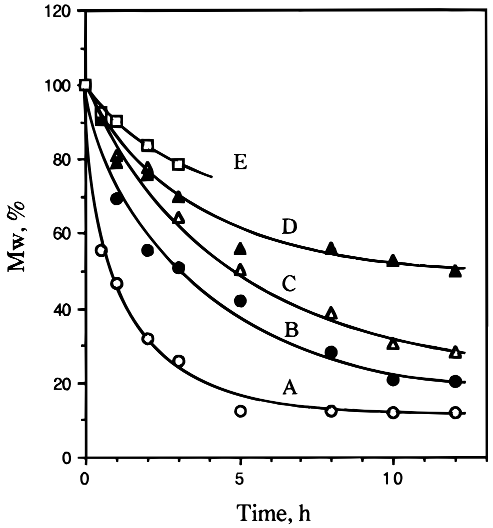


Figure 2. Plot of molecular weights of products vs irradiation time for the photolysis of polymers. Curves stand for the irradiation of **1** (A), **2** (B), **3** (C), **4** (D), and **5** (E) in benzene in the presence of methanol with a low-pressure mercury lamp.

Interestingly, polymer **2** in a benzene solution is less active toward 254 nm light. Thus, when 50 mg of **2** with a molecular weight of 54 000 in 50 mL of benzene was irradiated with a low-pressure mercury lamp bearing a Vycor filter under an argon atmosphere,[31] the molecular weight which was followed by GPC decreased only slowly. After 10 h of irradiation, the molecular weight was found to be 35 000, and all spectral data for the resulting product were identical with those of the starting polymer. The low photosensitivity of **2** seems to be responsible for the previous result obtained for the corresponding permethyl derivative poly[(tetramethyldisilanylene)bis(2,5-thienylene)].[24]

In contrast, when polymer **2** was photolyzed with a 100-W high-pressure mercury lamp through a Pyrex filter, the molecular weight decreased much faster, reaching a level of several thousands after 5 h and then ca. 1000 after 15 h. We therefore reexamined the photoreactivity of polymer **2** toward the light of the low-pressure lamp in a more dilute solution (11 mg in 70 mL of benzene) and found that the molecular weight decreased markedly under these conditions in several hours.[32] When the irradiation was carried out in the presence of methanol, to trap intermediates which would be produced, the decrease in molecular weight was much faster.

We compared the photochemical reactivity of the present polymers toward 254 nm light in dilute benzene solutions in the presence of methanol. Figure 2 shows the relative change in molecular weights for polymers **1**−**5** upon irradiation with the low-pressure mercury lamp. As seen in curve A, the molecular weight for **1** (M_w = 17 300) decreased fastest in the polymer group and reached 47% of its original value after 1 h, 26% after 3 h, and then 13% after 5 h. The photoreactivity of the polymers decreases with an increase in the length of

---

(31) Polymers **1**−**5** and also model compound **8a** are hardly soluble in hexane, and therefore we used benzene as the solvent.

(32) Consequently, the photochemical insensitivity observed previously for poly[(tetramethyldisilanylene)bis(2,5-thienylene)][24] might also depend on the wavelength of light (254 nm) and the concentration of the polymer (100 mg in 25 mL in this case).

the oligothienyl unit. At the point of 3 h of irradiation, for example, the molecular weights for **2** fell to 51% of the initial value (curve B), while the molecular weights for **3** and **4** dropped to 64% and 71% (curves C and D), respectively. Although the photoreactivity for **5** was found to be the lowest (curve E), insoluble products were formed after 3 h of irradiation, and therefore, GPC measurement became impossible thereafter. On the other hand, photolysis of polymers **1**−**4** with a high-pressure mercury lamp with a Pyrex filter resulted in a rapid decrease in molecular weights in all cases of **1**−**4**, and the correlation between the length of the oligothienyl unit and the photoreactivity to $\lambda > 300$ nm light was not clear.[33]

In order to learn more about the photochemical degradation of the polymers, we examined the reaction of 5,5′-bis(pentaethyldisilanyl)-2,2′-bithiophene (**8a**) chosen as a model compound of polymer **2**. Thus, **8a** was irradiated in benzene with a high-pressure mercury lamp through a Pyrex filter, and the progress of the reaction was monitored by GLC. As the starting compound **8a** decreased, new GLC peaks due to two products increased gradually. After 77 h of irradiation, these two products were isolated by liquid chromatography on silica gel and confirmed by spectrometric analysis as 5-(pentaethyldisilanyl)-2,2′-bithiophene (**9**; 23% GLC yield) and triethylphenylsilane (46% GLC yield). Similar photolysis of **8a** in benzene in the presence of methanol resulted in a mixture consisting of several products. In the mixture, small amounts of 5-(pentaethyldisilanyl)-5′-(diethylphenylsilyl)-2,2′-bithiophene (**10**), 5-(pentaethyldisilanyl)-5′-(diethylmethoxysilyl)-2,2′-bithiophene (**11**), 5,5′-bis(diethylmethoxysilyl)-2,2′-bithiophene (**12**), and triethylmethoxysilane were detected by GC-mass spectrometric analysis, besides **9** and triethylphenylsilane.

Interestingly, the corresponding permethyl derivative 5,5′-bis(pentamethyldisilanyl)-2,2′-bithiophene[24] (**8b**) was found to be photochemically inert. When **8b** was irradiated with the high-pressure mercury lamp under the same conditions as above, no reaction was observed, and starting compound **8b** was recovered quantitatively after 15 h of irradiation. The inactivity of permethyl derivative **8b** is similar to the low photosensitivity of the permethyl polymer, as previously observed.[24]

Scheme 4

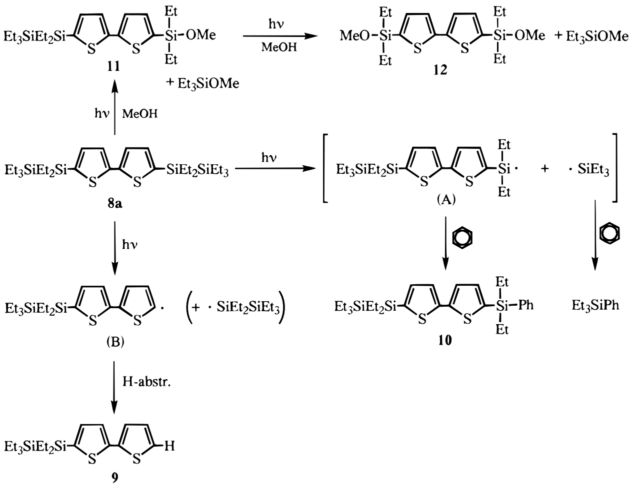


Table 2. Conductivities of Polymers 2−5 Doped with I_2 and $FeCl_3$ Vapors

	conductivity, S cm^{-1} (in vacuo)	
polymer	with I_2 (period, h)	with $FeCl_3$ (period, h)
2	1.6×10^{-5} (10)	4.1×10^{-5} (4)
3	1.0×10^{-5} (13)	9.3×10^{-4} (3.5)
4	5.7×10^{-4} (12)	8.6×10^{-4} (4)
5	1.8×10^{-4} (12)	7.5×10^{-3} (4.5)

The reaction pathway of **8a** leading to **9**−**12**, Et_3SiPh, and Et_3SiOMe is shown in Scheme 4. The formation of **10** and Et_3SiPh is understood in terms of homolytic scission of a silicon−silicon bond of **8a**, followed by homolytic aromatic substitution of the resulting silyl radical (A) and triethylsilyl radical onto solvent benzene. Products **11**, **12**, and Et_3SiOMe may be formed competitively by methanolysis of the photoexcited Si−Si bonds. The formation of **9** may be explained by the scission of a silicon−sp^2 carbon bond in **8a** followed by hydrogen abstraction of the resulting thienyl radical (B), though no products derived from its counterpart, pentaethyldisilanyl radical, were detected in the mixture. There might be an alternative possibility that radical B is formed from radical A. Since no products arising from extrusion of silylene were detected in the reaction mixture in the presence of triethylsilane or diethylphenylsilane used as a trapping agent, we propose that radical B is formed directly from the excited state of **8a**. On the basis of the reaction of model compound **8a**, the photodegradation of polymers **1**−**5** seems to involve the homolytic scission of the silicon−silicon and silicon−sp^2 carbon bonds in the polymer backbone.

In general, polymers composed of an alternating disilanylene unit and π-electron system are insulators. However, when the polymers are treated with an oxidizing agent, they become conducting. Thus, when cast thin films of **2**−**5** were exposed to iodine vapor under reduced pressure (1 mmHg), the conductivity of the films increased steadily and reached almost constant values after 10−13 h of doping (Table 2). The conductivity at this point was determined to be 1.6×10^{-5} (**2**), 1.0×10^{-5} (**3**), 5.7×10^{-4} (**4**), and 1.8×10^{-4} S cm^{-1} (**5**) by the two-probe method. When the polymer films were exposed to $FeCl_3$ vapor supplied by heating the salt at 150 °C under reduced pressure (1 mmHg) for 3.5−4.5 h, conducting films whose conductivities were found to be 4.1×10^{-5} (**2**), 9.3×10^{-4} (**3**), 8.6×10^{-4} (**4**), and 7.5×10^{-3} S cm^{-1} (**5**) in vacuo were obtained.

Experimental Section

General. All reactions were carried out under an atmosphere of dry nitrogen. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on JEOL Model JNM-EX 270 and Bruker AMX-400 spectrometers. Mass spectra were measured with a Shimadzu GCMS QP-1000 instrument. Molecular weights of polymers were determined by gel-permeation chromatography using Shodex 806 and 804 as the column and using THF as the eluent, relative to polystyrene standards. IR and UV spectra were measured on Hitachi U-3210 and Perkin-Elmer FTIR Model 1600 spectrometers, respectively. Emission spectra were measured with a Hitachi F-2000 spectrometer.

---

(33) It is worth noting that upon irradiation with a low-pressure lamp, a novel GPC profile of molecular weight distribution was observed for polymers **2**−**5**. Thus, a GPC peak due to the original polymer decreased in its position, and instead, a new peak grew in a lower molecular weight region with increasing time of irradiation. On the other hand, an initial monomodal peak shifted gradually to the lower direction, when polymer **1** was photolyzed with the low-pressure lamp, or when all polymers were photolyzed with a high-pressure mercury lamp.

Materials. Tetrahydrofuran (THF) and ether used for the preparation of monomers were dried over sodium−benzophenone ketyl and distilled. THF used for polymerization was dried over Na−K alloy and distilled into a reaction vessel. Benzene used for photolysis was dried over lithium aluminum hydride and distilled before use.

Preparation of 2,5-Bis(diethylsilyl)thiophene. In a 500 mL four-necked flask, a di-Grignard reagent was prepared by the reaction of 48.4 g (0.2 mol) of 2,5-dibromothiophene and 9.72 g (0.4 mol) of magnesium in 250 mL of THF. To this was added 51.72 g (0.4 mol) of chlorodiethylsilane, and the mixture was stirred at room temperature for 15 h. After hydrolysis of the mixture, the organic layer was separated and distilled under reduced pressure to give 26.86 g (52% yield) of 2,5-bis(diethylsilyl)thiophene as a colorless liquid: bp 95−97 °C (2 mmHg); IR (neat) 3063, 2955, 2874, 2117 (Si−H), 1488, 1458, 1412, 1267, 1232, 1202, 1078, 1011, 970, 800, 743, 690, 613, 507 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.81−0.92 (m, 8H, $SiCH_2$), 1.02−1.09 (m, 12H, CH_3), 4.40 (quint, 2H, J = 3.0 Hz, SiH), 7.38 (s, 2H, thienyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) 4.14, 8.02 (EtSi), 136.60, 140.30 (thienyl ring carbons); MS m/z 256 (M^+).

Preparation of 2,5-Bis(chlorodiethylsilyl)thiophene. A solution of 28.9 g (0.113 mol) of 2,5-bis(diethylsilyl)thiophene and 10 mg of palladium dichloride in 200 mL of carbon tetrachloride was stirred at 40−50 °C for 60 h. The solvent was evaporated, and the residue was distilled under reduced pressure to give 33.89 g (92% yield) of 2,5-bis(chlorodiethylsilyl)thiophene as a colorless liquid: bp 130−132 °C (2 mmHg); IR (neat) 3058, 2962, 2937, 2913, 2879, 1784, 1616, 1487, 1459, 1411, 1380, 1268, 1235, 1204, 1085, 1012, 961, 810, 733, 636, 521, 507 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 1.09 (s, 20H, SiEt), 7.50 (s, 2H, thienyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) 6.58, 9.20 (EtSi), 136.93, 140.92 (thienyl ring carbons); ^{29}Si NMR (δ, in $CDCl_3$) 19.26; MS m/z 324 (M^+ as ^{35}Cl). Anal. Calcd for $C_{12}H_{22}SSi_2Cl_2$: C, 44.29; H, 6.81. Found: C, 44.11; H, 6.90.

Preparation of 1,2-Bis(5-bromothien-2-yl)tetraethyldisilane (6). Into a 500 mL four-necked flask was placed 39.1 g (0.162 mol) of 2,5-dibromothiophene in 200 mL of ether. To this was added 96 mL (0.162 mol) of a 1.7 M hexane solution of *tert*-butyllithium at −80 °C over 1.5 h. The mixture was stirred at −80 °C for 1 h, and then 18.87 g (0.078 mol) of 1,2-dichlorotetraethyldisilane was added to the mixture at −80 °C over 1 h. The mixture was warmed to room temperature, stirred for 12 h, and then hydrolyzed with 150 mL of dilute aqueous hydrochloric acid. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on silica gel using hexane as the eluent to give 16.2 g (42% yield) of 1,2-bis(5-bromothien-2-yl)tetraethyldisilane (**6**) as a colorless viscous liquid: IR (neat) 3060, 2954, 2873, 1749, 1587, 1502, 1459, 1402, 1286, 1232, 1203, 1067, 1007, 947, 793, 707, 663, 609, 484 cm^{-1}; UV (λ_{max} in THF) 264 nm (ϵ = 23 000); ^{1}H NMR (δ, in $CDCl_3$) 0.89−1.03 (m, 20H, SiEt), 6.89 (d, 2H, J = 3.7 Hz, thienyl ring protons), 7.06 (d, 2H, J = 3.7 Hz, thienyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) 5.05, 8.09 (EtSi), 116.84, 131.27, 135.54, 138.58 (thienyl ring carbons); ^{29}Si NMR (δ, in $CDCl_3$) −17.79; MS m/z 496 (M^+ as $^{79}Br^{81}Br$). Anal. Calcd for $C_{16}H_{24}S_2Si_2Br_2$: C, 38.71; H, 4.87. Found: C, 38.64; H, 4.81.

Preparation of 1,2-Bis(5′-bromo-2,2′-bithien-5-yl)tetraethyldisilane (7). Into a 500 mL four-necked flask was placed 43.17 g (0.133 mol) of 5,5′-dibromo-2,2′-bithiophene in 250 mL of ether. To this was added 78 mL (0.133 mol) of a 1.7 M hexane solution of *tert*-butyllithium at −80 °C over 2 h. The mixture was warmed to room temperature with stirring, and 15.65 g (0.064 mol) of 1,2-dichlorotetraethyldisilane was added to the mixture over 1 h. This mixture was stirred for 12 h and hydrolyzed with 150 mL of dilute aqueous hydrochloric acid. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on silica gel using hexane as the eluent to give 13.1 g (31% yield) of 1,2-bis(5′-bromo-2,2′-bithien-5-yl)tetraethyldisilane (**7**) as a light yellow viscous liquid: IR (neat) 3058, 2954, 2873, 1732, 1550, 1498, 1439, 1417, 1377, 1304, 1224, 1210, 1195, 1068, 1006, 968, 900, 868, 787, 705, 664 cm^{-1}; UV (λ_{max} in THF) 333 (ϵ = 47 000), 240 (ϵ = 19 000) nm; ^{1}H NMR (δ, in $CDCl_3$) 0.88−1.07 (m, 20H, SiEt), 6.88 (d, 2H, J = 3.8 Hz, thienyl ring protons), 6.92 (d, 2H, J = 3.8 Hz, thienyl ring protons), 7.02 (d, 2H, J = 3.5 Hz, thienyl ring protons), 7.13 (d, 2H, J = 3.5 Hz, thienyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) 5.12, 8.21 (EtSi), 110.89, 123.72, 125.25, 130.57, 135.87, 135.94, 138.94, 141.69 (thienyl ring carbons); ^{29}Si NMR (δ, in $CDCl_3$) −17.97; MS m/z 660 (M^+ as $^{79}Br^{81}Br$). Anal. Calcd for $C_{24}H_{28}S_4Si_2Br_2$: C, 43.63; H, 4.27. Found: C, 43.53; H, 4.25.

Preparation of 5,5′-Bis(pentaethyldisilanyl)-2,2′-bithiophene (8a). Into a 500 mL four-necked flask was placed 7.60 g (23.45 mmol) of 5,5′-dibromo-2,2′-bithiophene in 200 mL of THF. To this was added 29 mL (49.3 mmol) of a 1.7 M hexane solution of *tert*-butyllithium at −80 °C over 1 h. The mixture was stirred at −80 °C for 4 h, and then 11.07 g (46.7 mmol) of chloropentaethyldisilane was added to the mixture at −80 °C over 2 h. The mixture was warmed to room temperature, stirred for 12 h, and then hydrolyzed with 150 mL of dilute aqueous hydrochloric acid. The organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was chromatographed on silica gel using hexane as the eluent to give 7.39 g (56% yield) of 5,5′-bis(pentaethyldisilanyl)-2,2′-bithiophene (**8a**) as a colorless viscous liquid: IR (neat) 3057, 2954, 2906, 2873, 2730, 1748, 1592, 1462, 1418, 1376, 1308, 1260, 1233, 1207, 1196, 1071, 1004, 983, 902, 870, 795, 704, 665, 583, 496 cm^{-1}; UV (λ_{max} in THF) 338 (ϵ = 25 200) nm; ^{1}H NMR (δ, in $CDCl_3$) 0.65−1.11 (m, 50H, EtSi), 7.07 (d, 2H, J = 3.6 Hz, thienyl ring protons), 7.24 (d, 2H, J = 3.6 Hz, thienyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) 3.79, 5.59, 8.27, 8.32 (EtSi), 124.85, 135.26, 136.68, 142.44 (thienyl ring carbons); ^{29}Si NMR (δ, in $CDCl_3$) −9.46, −17.40; MS m/z 566 (M^+). Anal. Calcd for $C_{28}H_{54}S_2Si_4$: C, 59.29; H, 9.60. Found: C, 59.14; H, 9.60.

Preparation of Polymer 2. A mixture of 35 mg (1.44 mmol) of magnesium and 0.709 g (1.43 mmol) of 1,2-bis(5-bromothien-2-yl)tetraethyldisilane (**6**) in 3 mL of THF was stirred in a Pyrex tube (10 mm × 150 mm) at 50 °C, until all magnesium was consumed. To the resulting mono-Grignard reagent was added 7 mg (1 mol %) of dichloro[bis(diphenylphosphino)ethane]nickel(II), and the reaction tube was degassed under reduced pressure and sealed. The tube was heated at 200 °C for 100 h, and then the reaction mixture was hydrolyzed and filtered. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layer and extracts were dried over anhydrous magnesium sulfate. After the solvent was evaporated off, the residue was reprecipitated from ethanol−chloroform to give 0.360 g (75% yield) of **2** as a light yellow solid: mp 142−148 °C; M_w = 53 000 (M_w/M_n = 4.8); IR (film) 3054, 2954, 2906, 2873, 1461, 1418, 1195, 1072, 1006, 984, 870, 794, 704, 666, 559 cm^{-1}; UV (λ_{max} in THF) 343 (ϵ = 21 200), 221 (ϵ = 9100) nm; ^{1}H NMR (δ, in $CDCl_3$) 0.97−1.04 (m, 20H, SiEt), 7.06 (d, 2H, J = 3.4 Hz, thienyl ring protons), 7.25 (d, 2H, J = 3.4 Hz, thienyl ring protons); ^{13}C NMR (δ, in $CDCl_3$) 5.21, 8.22 (EtSi), 125.12, 135.34, 135.94, 142.67 (thienyl ring carbons); ^{29}Si NMR (δ, in $CDCl_3$) −18.22. Anal. Calcd for $(C_{16}H_{24}S_2Si_2)_n$: C, 57.08; H, 7.19. Found: C, 57.00; H, 7.35.

Preparation of Polymer 4. To a mono-Grignard reagent, prepared from 47 mg (1.93 mmol) of Mg and 1.278 g (1.93 mmol) of 1,2-bis(5′-bromo-2,2′-bithien-5-yl)tetraethyldisilane (**7**) in 3 mL of THF in a manner similar to that above, was added 12 mg (2 mol %) of dichloro[bis(diphenylphosphino)ethane]nickel(II), and the mixture was heated in a degassed sealed tube at 230 °C for 100 h. After the same workup as above, the products were reprecipitated from ethanol−chloroform to give 0.942 g (97% yield) of polymer **4** as a brownish orange-red solid: mp 125−134 °C; M_w = 29 500 (M_w/

M_n = 3.8); IR (film) 3063, 2954, 2906, 2873, 1750, 1634, 1490, 1456, 1423, 1377, 1308, 1212, 1196, 1070, 1007, 982, 914, 847, 790, 666, 608 cm^{-1}; UV (λ_{max} in THF) 415 (ϵ = 37 900), 260 (ϵ = 13 000), 224 (ϵ = 12 700) nm; ^{1}H NMR (δ, in CDCl$_3$) 1.03 (br s, 20H, SiEt), 7.04 (br s, 6H, thienyl ring protons), 7.20 (br s, 2H, thienyl ring protons); ^{13}C NMR (δ, in CDCl$_3$) 5.14, 8.23 (EtSi), 124.21, 124.37, 125.00, 135.74, 135.90, 135.96, 136.28, 142.37 (thienyl ring carbons); ^{29}Si NMR (δ, in CDCl$_3$) −17.99. Anal. Calcd for $(C_{24}H_{28}S_4Si_2)_n$: C, 57.55; H, 5.63. Found: C, 57.25; H, 5.60.

Preparation of Polymer 3. A mixture of 59 mg (2.43 mmol) of Mg and 0.610 g (1.23 mmol) of 1,2-bis(5-bromothien-2-yl)tetraethyldisilane (**6**) in 3 mL of THF in a Pyrex tube was stirred at 50°C in a manner similar to that above. To the resulting di-Grignard reagent was added 0.288 g (1.19 mmol) of 2,5-dibromothiophene and 14 mg (2 mol %) of dichloro[bis(diphenylphosphino)ethane]nickel(II), and the mixture was heated in a degassed sealed tube at 150 °C for 80 h. After the same workup as above, the products were reprecipitated from ethanol−chloroform to give 0.385 g (77% yield) of polymer **3** as a brownish orange solid: mp 67−78 °C; M_w = 47 000 (M_w/M_n = 3.4); IR (film) 3059, 2952, 2873, 1456, 1424, 1195, 1068, 1006, 983, 911, 892, 792, 705, 518 cm^{-1}; UV (λ_{max} in THF) 389 (ϵ = 26 000), 227 (ϵ = 13 300) nm; ^{1}H NMR (δ, in CDCl$_3$) 1.01−1.05 (m, 20H, SiEt), 7.05−7.22 (m, 6H, thienyl ring protons); ^{13}C NMR (δ, in CDCl$_3$) 5.18, 8.23 (EtSi), 124.35, 124.92, 135.58, 135.96, 136.15, 142.44 (thienyl ring carbons); ^{29}Si NMR (δ, in CDCl$_3$) −18.08. Anal. Calcd for $(C_{20}H_{26}S_3Si_2)_n$: C, 57.36; H, 6.26. Found: C, 57.36; H, 6.16.

Preparation of Polymer 5. To a di-Grignard reagent, prepared from 74 mg (3.04 mmol) of Mg and 1.03 g (1.56 mmol) of 1,2-bis(5′-bromo-2,2′-bithien-5-yl)tetraethyldisilane (**7**) in 3 mL of THF in a manner similar to that above, was added 9 mg (1 mol %) of dichloro[bis(diphenylphosphino)ethane]nickel(II) and 0.356 g (1.47 mmol) of 2,5-dibromothiophene, and the mixture was heated in a degassed sealed tube at 100 °C for 48 h. After the same workup as above, the products were reprecipitated from ethanol−chloroform to give 0.668 g (78% yield) of polymer **5** as a brownish orange-red solid: mp 96−102 °C; M_w = 17 000 (M_w/M_n = 2.1); IR (film) 3063, 2954, 2873, 1490, 1454, 1423, 1211, 1069, 1006, 982, 843, 790, 704, 666, 508, 497 cm^{-1}; UV (λ_{max} in THF) 427 (ϵ = 40 400), 308 (ϵ = 10 200), 257 (ϵ = 15 000) nm; ^{1}H NMR (δ, in CDCl$_3$) 1.04 (br s, 20H, SiEt), 7.04 (br s, 8H, thienyl ring protons), 7.20 (br s, 2H, thienyl ring protons); ^{13}C NMR (δ, in CDCl$_3$) 5.13, 8.24 (EtSi), 124.26 (2 peaks), 124.38, 125.27, 135.76, 135.94 (2 peaks), 136.28, 136.38, 142.38 (thienyl ring carbons); ^{29}Si NMR (δ, in CDCl$_3$) −17.94. Anal. Calcd for $(C_{28}H_{30}S_5Si_2)_n$: C, 57.68; H, 5.19. Found: C, 57.57; H, 5.17.

Preparation of Polymer 1. Into a 150 mL three-necked flask fitted with a reflux condenser and dropping funnel were placed 1.08 g (46.9 mmol) of sodium dispersion and 40 mL of decane. To this was added dropwise a solution of 5.39 g (16.6 mmol) of 2,5-bis(chlorodiethylsilyl)thiophene in 20 mL of decane at room temperature. The mixture was heated at 150 °C for 4 h and hydrolyzed with ethanol and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layer and extracts were washed with water and dried over anhydrous magnesium sulfate. After the solvent was evaporated off, the residue was reprecipitated from ethanol−chloroform to give 1.35 g (32% yield) of **1** as a light orange viscous oil: M_w = 20 000 (M_w/M_n = 4.0); IR (film) 2954, 2874, 1482, 1456, 1413, 1261, 1232, 1200, 1001, 801, 706, 514 cm^{-1}; UV (λ_{max} in THF) 270 (ϵ = 12 600) nm; ^{1}H NMR (δ, in CDCl$_3$) 1.03 (br s, 20H, SiEt), 7.19 (br s, 2H, thienyl ring protons); ^{13}C NMR (δ, in CDCl$_3$) 5.30, 8.20 (EtSi), 135.90, 141.80 (thienyl ring carbons); ^{29}Si NMR (δ, in CDCl$_3$) −18.58. Anal. Calcd for $(C_{12}H_{22}SSi_2)_n$: C, 56.62; H, 8.71. Found: C, 56.56; H, 8.79.

Photolysis of Thin Films of Polymers. A polymer was dissolved in benzene and cast onto a quartz or NaCl plate. The film was irradiated with a 6-W low-pressure mercury lamp in air, and the progress of the reaction was monitored by IR and UV spectroscopy. IR spectra of the resulting films showed strong absorptions at 3200 (SiO−H) and 1060 (Si−O−Si) cm^{-1}, at the point of 1.5 h for **2**, 4 h for **3**, 10 h for **4**, and 12 h for **5**. UV spectra of the resulting films showed disappearance of λ_{max} bands in the region 270−430 nm, at the point of 40 min for **1**, 40 min for **2**, 1.5 h for **3**, 12 h for **4**, and 12 h for **5**.

General Procedure for the Photolysis of Polymers in Benzene with a Low-Pressure Mercury Lamp. A solution of 0.03 mmol (for **1**−**3**) or 0.015 mmol (for **4** and **5**) of a polymer (per unit) in 70 mL of benzene was irradiated with a 6-W low-pressure mercury lamp bearing a Vycor filter either in the absence (runs a−e) or in the presence (runs f−j) of methanol at room temperature under a nitrogen atmosphere. Changes in molecular weight of the reaction mixture were monitored by GPC. After irradiation for 12 h, the solvent was removed to leave a photoproduct, which was characterized by IR and NMR spectra.

(a) Photolysis of 1. A solution of 9 mg (35 μmol per unit) of **1** (M_w = 20 000, M_w/M_n = 3.3) in 70 mL of benzene was irradiated. The molecular weight of the products became M_w = 16 000 (80% of initial value) after irradiation for 1 h, M_w = 15 000 (75%) after 2 h, M_w = 11 600 (58%) after 3 h, M_w = 8200 (41%) after 5 h, M_w = 7500 (38%) after 8 h, M_w = 6500 (33%) after 10 h, and M_w = 4300 (22%) after 12 h. For the photoproduct: IR (film) 2240, 2115 cm^{-1}; ^{1}H NMR (δ, in CDCl$_3$) 0.30 (s), 0.33 (s), 0.80−1.10 (br m), 7.15−7.55 (br m); ^{13}C NMR (δ, in CDCl$_3$) 1.53, 4.50, 5.02, 5.37, 6.67, 7.42, 8.00, 8.16, 8.43, 9.10, 128.03, 131.79.

(b) Photolysis of 2. A solution of 11 mg (33 μmol per unit) of **2** (M_w = 43 000, M_w/M_n = 6.1) in 70 mL of benzene was irradiated. The molecular weight of the products became M_w = 40 400 (94% of initial value) after irradiation for 1 h, M_w = 39 000 (91%) after 2 h, M_w = 28 600 (67%) after 3 h, M_w = 26 600 (62%) after 5 h, M_w = 25 800 (60%) after 8 h, M_w = 24 500 (57%) after 10 h, and M_w = 20 700 (48%) after 12 h. For the photoproduct: IR (film) 2249 cm^{-1}; ^{1}H NMR (δ, in CDCl$_3$) 0.95−1.06 (br s), 7.04 (s), 7.23 (s); ^{13}C NMR (δ, in CDCl$_3$) 5.12, 8.23, 125.12, 127.15, 128.73, 135.34, 135.94, 142.66.

(c) Photolysis of 3. A solution of 14 mg (33 μmol per unit) of **3** (M_w = 31 000, M_w/M_n = 3.5) in 70 mL of benzene was irradiated. The molecular weight of the products became M_w = 25 000 (81% of initial value) after irradiation for 1 h, M_w = 26 000 (84%) after 2 h, M_w = 26 000 (84%) after 3 h, M_w = 22 000 (71%) after 5 h, M_w = 20 000 (65%) after 8 h, M_w = 18 000 (58%) after 10 h, and M_w = 15 000 (48%) after 12 h. For the photoproduct: IR (film) 2246 cm^{-1}; ^{1}H NMR (δ, in CDCl$_3$) 0.26−0.36 (m), 0.84−0.88 (m), 0.90−1.25 (br m), 7.00−7.28 (br m); ^{13}C NMR (δ, in CDCl$_3$) 1.55, 3.74, 5.16, 5.54, 8.21, 124.35, 124.91, 135.26, 135.58, 135.96, 136.14, 142.43.

(d) Photolysis of 4. A solution of 7 mg (14 μmol per unit) of **4** (M_w = 24 700, M_w/M_n = 4.2) in 70 mL of benzene was irradiated. The molecular weight of the products became M_w = 22 700 (92% of initial value) after irradiation for 1 h, M_w = 21 400 (87%) after 2 h, M_w = 21 000 (85%) after 3 h, M_w = 19 800 (80%) after 5 h, M_w = 16 900 (68%) after 8 h, M_w = 16 900 (68%) after 10 h, and M_w = 16 800 (68%) after 12 h. For the photoproduct: IR (film) 2253 cm^{-1}; ^{1}H NMR (δ, in CDCl$_3$) 0.95−1.20 (br m), 7.08−7.35 (m); ^{13}C NMR (δ, in CDCl$_3$) 5.12, 8.23, 29.69, 124.21, 124.39, 125.00, 135.76, 135.89, 135.96, 136.26, 142.35.

(e) Photolysis of 5. A solution of 8 mg (14 μmol per unit) of **5** (M_w = 12 300, M_w/M_n = 2.9) in 70 mL of benzene was irradiated. After the irradiation for 1 h, insoluble products were formed.

(f) Photolysis of 1 in the Presence of MeOH. A solution of 7 mg (28 μmol per unit) of **1** (M_w = 17 300, M_w/M_n = 4.2) and 1 mL of methanol in 70 mL of benzene was irradiated. The molecular weight of the products became M_w = 8100 (47% of initial value) after irradiation for 1 h, M_w = 5500 (32%) after 2 h, M_w = 4500 (26%) after 3 h, M_w = 2200 (13%) after 5 h,

M_w = 2200 (13%) after 8 h, M_w = 2100 (12%) after 10 h, and M_w = 2100 (12%) after 12 h. For the photoproduct: IR (film) 2247, 2117, 1100 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.32 (s), 0.37 (s), 0.45–1.14 (br m), 1.56–1.90 (br s), 3.15–3.64 (br m, SiOMe), 7.18–7.56 (br m); ^{13}C NMR (δ, in $CDCl_3$) 1.55, 3.18, 5.30, 5.56, 6.27, 6.60, 7.42, 8.02, 8.21, 127.67, 128.14, 129.22, 132.97, 133.71.

(g) Photolysis of 2 in the Presence of MeOH. A solution of 11 mg (33 μmol per unit) of **2** (M_w = 43 000, $M_\mathrm{w}/M_\mathrm{n}$ = 6.2) and 1 mL of methanol in 70 mL of benzene was irradiated. The molecular weight of the products became M_w = 30 000 (70% of initial value) after irradiation for 1 h, M_w = 24 000 (56%) after 2 h, M_w = 21 800 (51%) after 3 h, M_w = 18 100 (42%) after 5 h, M_w = 12 100 (28%) after 8 h, M_w = 9000 (21%) after 10 h, and M_w = 8700 (20%) after 12 h. For the photoproduct: IR (film) 2249, 1100 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.23 (s), 0.92 (br s), 3.08–3.52 (br m, SiOMe), 6.95 (br s), 7.14 (br s), 7.44 (br s); ^{13}C NMR (δ, in $CDCl_3$) 5.21, 8.23, 125.12, 127.57, 128.25, 129.11, 132.90, 135.34, 135.96, 142.68.

(h) Photolysis of 3 in the Presence of MeOH. A solution of 14 mg (33 μmol per unit) of **3** (M_w = 31 000, $M_\mathrm{w}/M_\mathrm{n}$ = 5.0) and 1 mL of methanol in 70 mL of benzene was irradiated. The molecular weight of the products became M_w = 25 000 (81% of initial value) after irradiation for 1 h, M_w = 24 400 (78%) after 2 h, M_w = 20 100 (64%) after 3 h, M_w = 16 000 (52%) after 5 h, M_w = 12 100 (39%) after 8 h, M_w = 9600 (31%) after 10 h, and M_w = 9000 (29%) after 12 h. For the photoproduct: IR (film) 2248, 1100 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.33 (br s), 1.04 (br s), 3.20–3.54 (br m, SiOMe), 7.07 (br s), 7.22 (br s), 7.36 (br s), 7.54 (br s); ^{13}C NMR (δ, in $CDCl_3$) 5.14, 8.20, 124.33, 124.89, 127.64, 128.27, 129.18, 132.94, 135.54, 135.92, 136.10, 139.75, 142.41.

(i) Photolysis of 4 in the Presence of MeOH. A solution of 7 mg (14 μmol per unit) of **4** (M_w = 34 000, $M_\mathrm{w}/M_\mathrm{n}$ = 3.6) and 1 mL of methanol in 70 mL of benzene was irradiated. The molecular weight of the products became M_w = 27 000 (79% of initial value) after irradiation for 1 h, M_w = 26 000 (76%) after 2 h, M_w = 24 000 (71%) after 3 h, M_w = 19 100 (56%) after 5 h, M_w = 19 000 (56%) after 8 h, M_w = 18 000 (53%) after 10 h, and M_w = 17 000 (50%) after 12 h. For the photoproduct: IR (film) 2250, 1100 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.58–0.73 (m), 0.80–1.86 (br m), 3.10–4.60 (br m, SiOMe), 7.02–7.44 (br m); ^{13}C NMR (δ, in $CDCl_3$) 6.18, 6.34, 6.44, 6.53, 6.69, 7.35, 8.20, 29.66, 123.72, 124.21, 124.35, 124.55, 127.89, 135.81, 136.28, 137.00.

(j) Photolysis of 5 in the Presence of MeOH. A solution of 8 mg (14 μmol per unit) of **5** (M_w = 12 300, $M_\mathrm{w}/M_\mathrm{n}$ = 2.9) and 1 mL of methanol in 70 mL of benzene was irradiated. The molecular weight of the products became M_w = 11 100 (90%) after irradiation for 1 h, M_w = 10 300 (84%) after 2 h, and M_w = 9700 (79%) after 3 h. After irradiation for 3 h, insoluble products were formed.

General Procedure for the Photolysis of Polymers in Benzene with a High-Pressure Mercury Lamp. A solution of 0.03 mmol (for **1**–**3**) or 0.015 mmol (for **4**–**5**) of a polymer (per unit) in 60 mL of benzene was irradiated with a 100-W high-pressure mercury lamp through a Pyrex filter either in the absence (runs a–e) or in the presence (runs f–j) of methanol at room temperature under nitrogen atmosphere. The change in molecular weight of the reaction mixture was monitored by GPC. After irradiation for 12 h, the solvent was removed to leave a photoproduct, which was characterized by IR and NMR spectra.

(a) Photolysis of 1. A solution of 8 mg (31 μmol per unit) of **1** (M_w = 21 300, $M_\mathrm{w}/M_\mathrm{n}$ = 5.5) in 60 mL of benzene was irradiated. The molecular weight of the products became M_w = 14 800 (69%) after irradiation for 1 h, M_w = 13 400 (63%) after 2 h, M_w = 9100 (43%) after 3 h, M_w = 6200 (29%) after 5 h, M_w = 4800 (23%) after 8 h, M_w = 4800 (23%) after 10 h, and M_w = 4700 (22%) after 12 h. For the photoproduct: IR (film) 2251, 2116 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.45–1.35 (br m), 7.15–7.68 (br m); ^{13}C NMR (δ, in $CDCl_3$) 4.28, 5.28, 6.54, 6.68, 7.41, 8.01, 8.17, 29.69, 127.75, 134.63, 135.32, 136.90.

(b) Photolysis of 2. A solution of 11 mg (33 μmol per unit) of **2** (M_w = 36 000, $M_\mathrm{w}/M_\mathrm{n}$ = 5.2) in 60 mL of benzene was irradiated. The molecular weight of the products became M_w = 24 000 (67% of initial value) after irradiation for 1 h, M_w = 16 000 (44%) after 2 h, M_w = 10 000 (28%) after 3 h, M_w = 4700 (13%) after 5 h, M_w = 3200 (9%) after 8 h, M_w = 2700 (8%) after 10 h, and M_w = 1900 (5%) after 12 h. For the photoproduct: IR (film) 2247, 2120 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.44–1.56 (br m), 6.84–7.86 (br m); ^{13}C NMR (δ, in $CDCl_3$) 4.94, 5.14, 6.40, 6.49, 6.60, 7.19, 7.24, 7.28, 7.37, 8.20, 127.82, 129.40, 134.57, 134.63, 134.75, 135.76, 135.81, 135.90, 136.69, 136.73.

(c) Photolysis of 3. A solution of 14 mg (33 μmol per unit) of **3** (M_w = 47 000, $M_\mathrm{w}/M_\mathrm{n}$ = 5.0) in 60 mL of benzene was irradiated. The molecular weight of the products became M_w = 33 000 (70% of initial value) after irradiation for 1 h, M_w = 30 000 (64%) after 2 h, M_w = 22 000 (47%) after 3 h, M_w = 20 000 (43%) after 5 h, M_w = 11 000 (23%) after 8 h, M_w = 7500 (16%) after 10 h, and M_w = 5000 (10%) after 12 h. For the photoproduct: IR (film) 2246 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.30–1.22 (br m), 3.64 (m, SiH), 6.85–7.49 (br m); ^{13}C NMR (δ, in $CDCl_3$) 4.96, 5.18, 6.71, 7.37, 8.21, 8.32, 124.37, 124.46, 124.92, 127.84, 134.73, 135.96, 136.17.

(d) Photolysis of 4. A solution of 7 mg (14 μmol per unit) of **4** (M_w = 33 000, $M_\mathrm{w}/M_\mathrm{n}$ = 4.3) in 60 mL of benzene was irradiated. The molecular weight of the products became M_w = 23 000 (70% of initial value) after irradiation for 1 h, M_w = 14 000 (42%) after 2 h, M_w = 13 000 (39%) after 3 h, M_w = 6000 (18%) after 5 h, M_w = 3000 (9%) after 8 h, M_w = 2000 (6%) after 10 h, and M_w = 1200 (4%) after 12 h. For the photoproduct: IR (film) 2249 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.26–1.27 (br m), 7.27–7.47 (br m); ^{13}C NMR (δ, in $CDCl_3$) 1.55, 5.07, 8.23, 124.26, 125.00, 135.92.

(e) Photolysis of 5. A solution of 8 mg (14 μmol per unit) of **5** (M_w = 12 300, $M_\mathrm{w}/M_\mathrm{n}$ = 2.9) in 60 mL of benzene was irradiated. After irradiation for 1 h, insoluble products were formed.

(f) Photolysis of 1 in the Presence of MeOH. A solution of 7 mg (28 μmol per unit) of **1** (M_w = 18 000, $M_\mathrm{w}/M_\mathrm{n}$ = 4.0) and 1 mL of methanol in 60 mL of benzene was irradiated. The molecular weight of the products became M_w = 6600 (37% of initial value) after irradiation for 1 h, M_w = 4300 (24%) after 2 h, M_w = 3700 (21%) after 3 h, M_w = 2500 (14%) after 5 h, M_w = 1800 (10%) after 8 h, M_w = 1300 (7%) after 10 h, and M_w = 1600 (9%) after 12 h. For the photoproduct: IR (film) 2116, 1100 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.19–1.40 (br m), 3.00–3.20 (br m, SiOMe), 3.25–3.86 (br m, SiOMe), 4.33–4.48 (br m, SiOMe), 5.04–5.23 (br m, SiOMe), 7.06–7.68 (br m); ^{13}C NMR (δ, in $CDCl_3$) 6.56, 6.67, 7.33, 7.42, 8.57, 46.08, 127.78, 127.93, 127.97, 133.24, 133.33.

(g) Photolysis of 2 in the Presence of MeOH. A solution of 11 mg (33 μmol per unit) of **2** (M_w = 36 000, $M_\mathrm{w}/M_\mathrm{n}$ = 5.2) and 1 mL of methanol in 60 mL of benzene was irradiated. The molecular weight of the products became M_w = 20 000 (56% of initial value) after irradiation for 1 h, M_w = 14 000 (39%) after 2 h, M_w = 7000 (19%) after 3 h, M_w = 4400 (12%) after 5 h, M_w = 2700 (8%) after 8 h, M_w = 2700 (8%) after 10 h, and M_w = 2000 (6%) after 12 h. For the photoproduct: IR (film) 2245, 1100 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.80–1.24 (br m), 3.60 (br m, SiOMe), 6.93–7.77 (br m); ^{13}C NMR (δ, in $CDCl_3$) 4.93, 5.12, 5.35, 6.53, 7.18, 7.36, 51.07, 124.95, 125.09, 125.24, 127.83, 129.39, 134.63, 135.91, 136.13, 136.74.

(h) Photolysis of 3 in the Presence of MeOH. A solution of 14 mg (33 μmol per unit) of **3** (M_w = 31 000, $M_\mathrm{w}/M_\mathrm{n}$ = 3.5) and 1 mL of methanol in 60 mL of benzene was irradiated. The molecular weight of the products became M_w = 23 000 (74% of initial value) after irradiation for 1 h, M_w = 14 000 (45%) after 2 h, M_w = 6000 (19%) after 3 h, M_w = 2800 (9%) after 5 h, M_w = 1700 (5%) after 8 h, M_w = 1500 (5%) after 10 h, and M_w = 1500 (5%) after 12 h. For the photoproduct: IR (film) 2242, 1100 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.48−1.43 (br m), 3.14−4.05 (br m, SiOMe), 7.04−7.67 (br m); ^{13}C NMR (δ, in $CDCl_3$) 6.62, 6.76, 7.01, 7.12, 7.48, 7.59, 123.68, 124.30, 124.46, 127.51, 127.85, 129.04, 133.53.

(i) Photolysis of 4 in the Presence of MeOH. A solution of 7 mg (14 μmol per unit) of **4** ($M_w = 28\,500$, $M_w/M_n = 4.2$) and 1 mL of methanol in 60 mL of benzene was irradiated. The molecular weight of the products became $M_w = 17\,000$ (60% of initial value) after irradiation for 1 h, $M_w = 10\,600$ (37%) after 2 h, $M_w = 6200$ (22%) after 3 h, $M_w = 1500$ (5%) after 5 h, $M_w = 850$ (3%) after 8 h, $M_w = 830$ (3%) after 10 h, and $M_w = 830$ (3%) after 12 h. For the photoproduct: IR (film) 2253, 1100 cm^{-1}; ^{1}H NMR (δ, in $CDCl_3$) 0.62−2.35 (br m), 3.05−4.35 (br m, SiOMe), 7.00−7.72 (br m); ^{13}C NMR (δ, in $CDCl_3$) 4.48, 5.29, 6.47, 7.30, 8.74, 14.04, 22.59, 22.95, 24.21, 24.75, 27.12, 29.02, 29.22, 29.26, 29.38, 29.60, 31.83, 32.51, 33.82, 33.93, 46.35, 62.00, 70.44, 124.24, 124.62, 124.87, 127.42, 127.78, 129.60, 129.92, 134.12, 134.54, 136.10.

(j) Photolysis of 5 in the Presence of MeOH. A solution of 7 mg (12 μmol per unit) of **5** ($M_w = 12\,300$, $M_w/M_n = 2.9$) and 1 mL of methanol in 60 mL of benzene was irradiated. After the irradiation for 1 h, insoluble products were formed.

Photolysis of 5,5′-Bis(pentaethyldisilanyl)-2,2′-bithiophene (8a) in Benzene. A solution of 533 mg (0.94 mmol) of 5,5′-bis(pentaethyldisilanyl)-2,2′-bithiophene (**8a**) in 50 mL of benzene was irradiated with a 100-W high-pressure mercury lamp through a Pyrex filter at room temperature under a nitrogen atmosphere. After irradiation for 77 h, 5-(pentaethyldisilanyl)-2,2′-bithiophene (**9**) (23% GLC yield) and Et_3SiPh (46% GLC yield) were isolated from the reaction mixture by liquid chromatography on silica gel. For **9**: IR (film) 3066, 2952, 2906, 2872, 1458, 1418, 1375, 1212, 1198, 1067, 1004, 982, 909, 885, 838, 819, 797, 690, 662, 580, 531 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.66−1.11 (m, 25H, SiEt), 6.98−7.25 (m, 5H, thienyl ring protons); ^{13}C NMR (δ in $CDCl_3$) 3.78, 5.56, 8.27, 8.32 ($SiEt_3$), 123.56, 124.10, 124.96, 127.73, 135.24, 137.07, 137.61, 142.21 (thienyl ring carbons); MS *m/z* 366 (M^+), 337 ($M^+ - Et$). Anal. Calcd for $C_{18}H_{30}S_2Si_2$: C, 58.95; H, 8.25. Found: C, 59.08; H, 8.22. For Et_3SiPh: IR (film) 3068, 2954, 2910, 2875, 1458, 1427, 1377, 1237, 1110, 1011, 969, 721, 699, 671, 580, 518 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) 0.79 (q, 6H, $J = 7.5$ Hz, $SiCH_2CH_3$), 0.96 (t, 9H, $J = 7.5$ Hz, $SiCH_2CH_3$), 7.31−7.50 (m, 5H, phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) 3.36, 7.39 ($SiEt_3$), 127.66, 128.70, 134.20, 137.41 (phenyl ring carbons); MS *m/z* 192 (M^+), 163 ($M^+ - Et$). All spectral data for Et_3SiPh were identical with those of an authentic sample.

Photolysis of 8a in Benzene in the Presence of Methanol. A solution of 85 mg (0.15 mmol) of **8a** and 1 mL of methanol in 60 mL of benzene was irradiated with a 100-W high-pressure mercury lamp through a Pyrex filter at room temperature under nitrogen atmosphere. After irradiation for 14 h, GC-MS spectrometric analysis of the reaction mixture revealed the existence of **9**, Et_3SiPh, 5-(pentaethyldisilanyl)-5′-(diethylphenylsilyl)-2,2′-bithiophene (**10**), 5-(pentadisilanyl)-5′-(diethylmethoxysilyl)-2,2′-bithiophene (**11**), 5,5′-bis(diethylmethoxysilyl)-2,2′-bithiophene (**12**), and Et_3SiOMe as the products. For **10**: MS *m/z* 528(M^+). For **11**: MS *m/z* 482(M^+). For **12**: MS *m/z* 398(M^+). For Et_3SiOMe: MS *m/z* 146(M^+).

Conductivity Measurement for Polymer Films Doped with I_2. A benzene solution of a polymer was cast into a thin film on a glass plate. After the solvent was evaporated, the film was dried in vacuo overnight and then exposed to saturated I_2 vapor under reduced pressure (1 mmHg) in a glass vessel. The conductivity of the films increased steadily with increasing time of doping and reached almost constant values after 10−13 h. The conductivities at this point were determined by the two-probe method to be 1.6×10^{-5} (**2**), 1.0×10^{-5} (**3**), 5.7×10^{-4} (**4**), and 1.8×10^{-4} S cm^{-1} (**5**).

Conductivity Measurement for Polymer Films Doped with $FeCl_3$. A thin film of a polymer was prepared in the same manner as described above. The film was held over ferric chloride powder which was placed in a glass vessel. Doping was performed under reduced pressure (1 mmHg) by heating the bottom of the glass vessel at 150 °C for 3−4.5 h. The conductivities in vacuo were determined by the two-probe method to be 4.1×10^{-5} (**2**), 9.3×10^{-4} (**3**), 8.6×10^{-4} (**4**), and 7.5×10^{-3} S cm^{-1} (**5**).

Acknowledgment. This research was supported in part by a Grant-in-Aid for Developmental Scientific Research (No. 06555274) from the Ministry of Education, Science and Culture, to which our thanks are due. We also express our appreciation to Shin-Etsu Chemical Co. Ltd., Nitto Electric Industrial Co. Ltd., Dow Corning Asia Ltd., Toshiba Silicone Co. Ltd., Sumitomo Electric Co. Ltd., Kaneka Corp., and the Japan High Polymer Center for financial support.

OM950585J