

## Polymeric organosilicon systems

### XVIII. Synthesis and photochemical properties of poly[2,5-(disilanylene)thienylenes]

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#### Abstract

Poly[2,5-(tetramethyldisilanylene)thienylene] (**Ib**), poly[2,5-(1,2-dimethyldiphenyldisilanylene)thienylene] (**IIb**) and poly(2,5-[1,2-dimethyldi(*p*-tolyl)disilanylene]thienylene) (**IIIb**) were synthesized by sodium condensation reaction of the corresponding 2,5-bis(chlorosilyl)thienylenes in decane. Polymers **Ib–IIIb** reveal characteristic absorptions in the UV region. Irradiation of the thin films of **Ib–IIIb** in air led to disappearance of these absorptions. The photolysis of **Ib–IIIb** in a benzene solution resulted in homolytic scission of silicon–silicon bonds in the polymer backbone. In the photolysis of **Ib**, the cross-linking reaction occurred, while polymers **IIb** and **IIIb** afforded photodegradation products with low molecular weights.

*Key words:* Silicon; Polymer

#### 1. Introduction

Silicon-containing polymers which have a regular alternating arrangement of a disilanylene unit and  $\pi$ -electron system in the polymer backbone are of considerable interest, because these polymers can be used as functional materials [1].

In 1984, we found that poly[*p*-(disilanylene)phenylenes] can be prepared by the sodium condensation of 1,4-bis(chlorosilyl)benzenes and the polymers thus obtained may be used as a top imaging layer of the double-layer photoresist system [2]. Since that time, the synthesis and properties of many types of the alternating copolymers which involve an ethenylene [3], ethynylene [4–8], enyne [9], diyne [10–12] and naphthylene group [13,14], as a  $\pi$ -electron system have been reported. The polymers involving a hetero aromatic unit as the  $\pi$  system, such as thienylene [15–17] and furylene [18,19] have also been synthesized, and some of their photochemical and conducting behavior have been

investigated. In this paper we report the synthesis and photochemical properties of poly[2,5-(disilanylene)thienylenes].

#### 2. Results and discussion

##### 2.1. Synthesis of poly[2,5-(disilanylene)thienylenes]

The starting, 2,5-bis(chlorosilyl)thiophenes were synthesized by the reaction of the di-Grignard reagent prepared from 2,5-dibromothiophene with the corresponding chlorohydrosilanes, followed by treatment of the resulting bis(hydrosilyl)thiophene with carbon tetrachloride in the presence of a catalytic amount of palladium dichloride. Thus the reaction of the di-Grignard reagent of 2,5-dibromothiophene with chlorodimethylsilane gave 2,5-bis(dimethylsilyl)thiophene with a 56% yield. Treatment of 2,5-bis(dimethylsilyl)thiophene with a catalytic amount of palladium dichloride in refluxing carbon tetrachloride for 20 h afforded 2,5-bis(chlorodimethylsilyl)thiophene (**Ia**) in 91% yield. Using this method, 2,5-bis(chloromethylphenylsilyl)thiophene (**IIa**) and 2,5-bis[chloromethyl(*p*-tolyl)

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silyl]thiophene (IIIa) were also prepared in 50% and 52% total yields respectively (Scheme 1).

The reaction of Ia with a slight excess of sodium dispersion in refluxing decane for 3 h afforded a light-yellow solid polymer. Reprecipitation of the polymer from chloroform-ethanol gave poly[2,5-(tetramethyldisilanyl)thienylene] (Ib) with a 64% yield. Similar treatments of IIa and IIIa with sodium dispersion in decane produced poly[2,5-(1,2-dimethyldiphenyldisilanyl)thienylene] (IIb) and poly{2,5-[1,2-dimethyldi(*p*-tolyl)disilanyl]thienylene} (IIIb) with 22% and 24% yields respectively. The low yields of IIb and IIIb are ascribed to the formation of large amounts of insoluble polymers in the sodium condensation reaction of both IIa and IIIa, in contrast to that of Ia. IR spectra of the insoluble polymers are consistent with those of the soluble polymers, indicating that these polymers also have the regular arrangement of a thienylene and disilanyl unit.

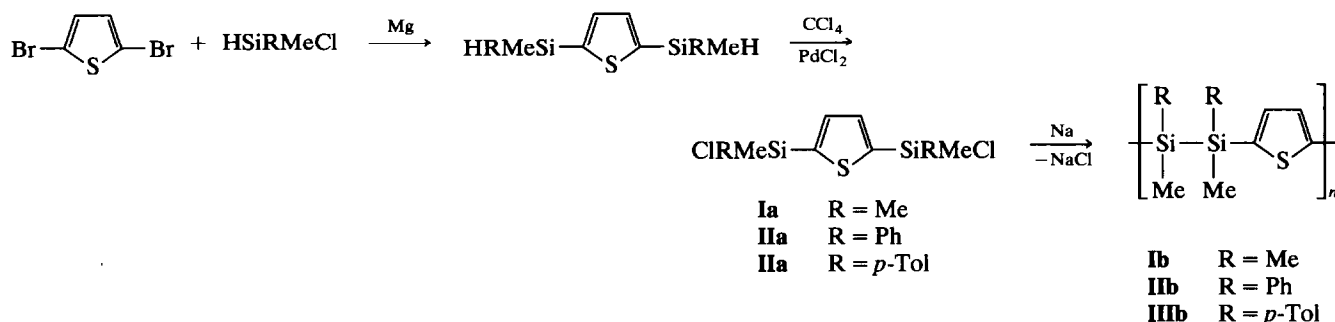
Molecular weights  $M_w$  of Ib, IIb and IIIb which showed broad monomodal distribution were measured to be 20 000, 38 000 and 36 000 respectively. Polydispersities  $M_w/M_n$  of Ib, IIb and IIIb were calculated to be 3.78, 5.43 and 5.14 respectively. The polymer Ib melts at 155–161 °C without decomposition, while polymers IIb and IIIb melt at lower temperature, 68–74 °C for IIb and 92–95 °C for IIIb. These polymers are soluble in common organic solvents, such as benzene, ethers and chlorocarbons, but insoluble in alcohols, such as methanol and ethanol.

## 2.2. Photochemical reaction

Delocalization of  $\sigma$  electrons of silicon-silicon bonds in the polymer chain of Ib-IIIb is apparent from their UV absorption spectra. They exhibit strong absorption bands at 260, 272 and 271 nm, which are lower in energy than those of 2,5-bis(chlorosilyl)thiophenes Ia-IIIa (see Section 3) and also than that of 1,2-di(2-thienyl)tetramethyldisilane ( $\lambda_{\max} = 244$  nm) [15].

As expected, polymers Ib-IIIb are photoactive, like other alternating polymers composed of a silicon-silicon unit and a  $\pi$ -electron system. In fact, irradiation of thin films prepared from Ib-IIIb with a 6 W low pressure mercury lamp bearing a Vycor filter (254 nm) in air for 1 h led to disappearance of characteristic absorptions at about 265 nm attributed to disilanylenethienylene unit, showing that the scission of the silicon-silicon bonds occurred as observed in the photolysis of the polymers composed of alternating disilanyl units and  $\pi$ -electron systems [2]. IR spectra of polymers Ib-IIIb after 1 h irradiation showed the formation of siloxane and silanol units, arising from a series of reactions involving silylperoxy radicals which would be formed from the reaction of silyl radicals with oxygen.

In solution, irradiation of polymers Ib-IIIb also affords photodegradation products. Thus irradiation of the polymer Ib ( $M_w = 20\,000$ ) with a low pressure mercury lamp in the presence of tert-butyl alcohol in benzene for 2 h resulted in formation of photoproducts with a molecular weight of 4700. However, prolonged irradiation led to a slight increase in the molecular weight of the photodegradation products (Fig. 1, curve d). The photolysis of Ib ( $M_w = 17\,000$ ) in the absence of tert-butyl alcohol, however, led to an increase in the molecular weight with increasing irradiation time, indicating that cross-linking reaction occurred in some extent during the photolysis (Figure 1, curve a). The molecular weight  $M_w$  of the photodegradation product was determined to be 37 000 after 20 h irradiation. The  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of the photoproducts of Ib shows multiplet signals at 2.10–3.00 ppm attributed to methylene protons of 2,3-dihydrothienylene rings, signals of H-Si groups at 4.59 and 4.73 ppm, and broad olefinic signals centered at 5.60, 5.72 and 6.17 ppm and at 6.80–7.62 ppm, in addition to the Me-Si signals as shown in Fig. 2. The COSY experiment on  $^1\text{H}$  NMR shows that the signals due to 2,3-dihydrothienylene rings couple with signals



Scheme 1.

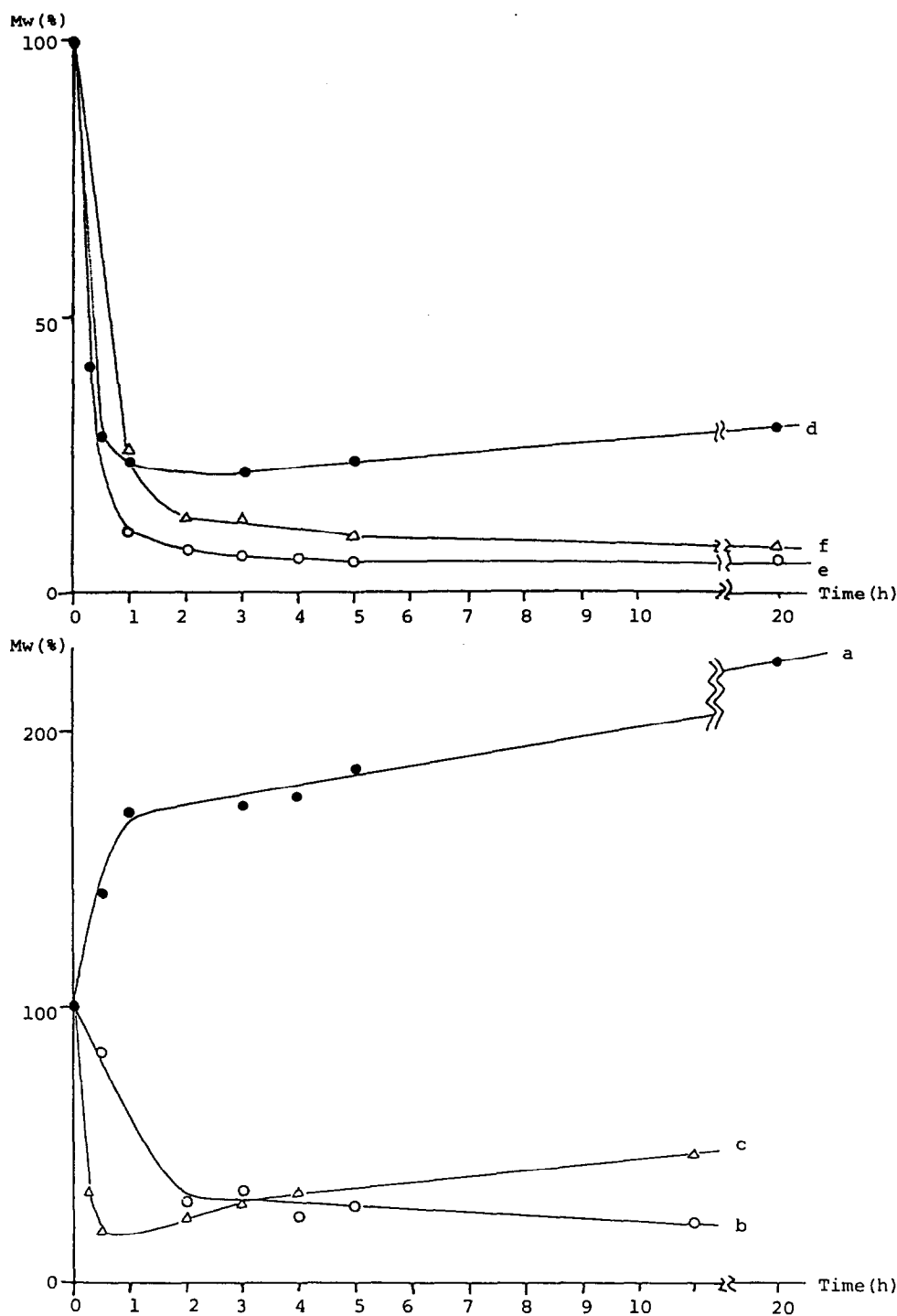


Fig. 1. Plots of the molecular weights  $M_w$  based on the starting molecular weights of the polymers vs. reaction time for the photolysis of **Ib** (curve a), **IIb** (curve b) and **IIIb** (curve c) in the absence of tert-butyl alcohol and of **Ib** (curve d), **IIb** (curve e) and **IIIb** (curve f) in the presence of tert-butyl alcohol.

at 7.2–7.4 ppm and Si–H protons at 4.59 and 4.73 ppm couple with Me–Si signals at 0.20 ppm and 0.38 ppm respectively. In the same experiment, the olefinic signal at 5.60 ppm is found to couple with the signal at 6.17

ppm, while the signal at 5.72 ppm couples with an olefinic signal at 7.25 ppm, indicating that these olefinic signals are assignable to 2,5-dihydrothienylene ring protons. The formation of the dihydrothienylene ring

can be understood in terms of homolytic scission of a silicon-silicon bond, followed by addition of the resulting silyl radical across the thienylene ring (Scheme 2, path a). The formation of Si-H bonds which are indicated by a weak absorption band at  $2150\text{ cm}^{-1}$  observed in the IR spectrum of **Ib**, may be explained by the disproportionation of the silyl radicals produced from the homolytic scission of the Si-Si bond (path b).

The IR spectrum of the photoproducts obtained in the presence of tert-butyl alcohol shows absorption bands at  $2120$  and  $1010\text{ cm}^{-1}$ , due to stretching frequencies of an Si-H and Si-O-<sup>t</sup>Bu bond, respectively. When similar photolysis of **Ib** in the presence of tert-butyl alcohol-*d*<sub>1</sub> was carried out, a photoproduct whose IR spectrum shows absorptions at  $2320\text{ cm}^{-1}$ ,  $2130\text{ cm}^{-1}$ , and  $1080\text{ cm}^{-1}$ , attributed to  $\nu(\text{C-D})$ ,  $\nu(\text{Si-H})$  and  $\nu(\text{Si-O})$  respectively was obtained. Its <sup>2</sup>H NMR spectrum reveals signals at 4.76 ppm and 0.42 ppm, due to an Si-D and a DCSi group respectively. The formation of a C-D bond in the photoproduct may be also understood by path b in Scheme 2. The presence of the Si-D bond clearly indicates that the photolysis of **Ib** in the presence of tert-butyl alcohol involves the direct reaction of photoexcited **Ib** with tert-butyl alcohol, since **Ib** does not react with alcohols in dark (path c). A similar direct reaction of photoexcited naphthyl-

disilanes with methanol has been reported previously [20]. Hu and Weber [15] have reported that the photolysis of **Ib** in the presence of methanol in a benzene solution gave products which have an MeOSi and HSi group [15].

The photolysis of polymer **Ib** in the absence of tert-butyl alcohol proceeded considerably in a different fashion from that of **Ib**. Irradiation of a benzene solution of **Ib** resulted in a decrease in the molecular weight of the photoproducts. No increase in the molecular weight of the products with increasing irradiation time was observed (Fig. 1, curve b). Thus the photolysis of a benzene solution of **Ib** with  $M_w = 16000$  for 5 h with a 6 W low pressure mercury lamp led to the formation of a photoproduct with  $M_w = 3400$ , which remained unchanged after 20 h irradiation. The IR spectrum of the photoproduct from **Ib** showed the presence of an Si-H bond. The <sup>1</sup>H NMR spectrum of the product revealed broad signals at 0.00–1.00 ppm, 5.16 ppm and 7.00–8.00 ppm, due to Me-Si, H-Si and Ph-Si groups respectively. No signals assigned to the dihydrothienylene ring which would be formed from path a, were observed in <sup>1</sup>H and <sup>13</sup>C NMR spectra. These results indicate that path b which results in a decrease in the molecular weight is a favourable pathway for **Ib**. Similar irradiation of **Ib** in the presence

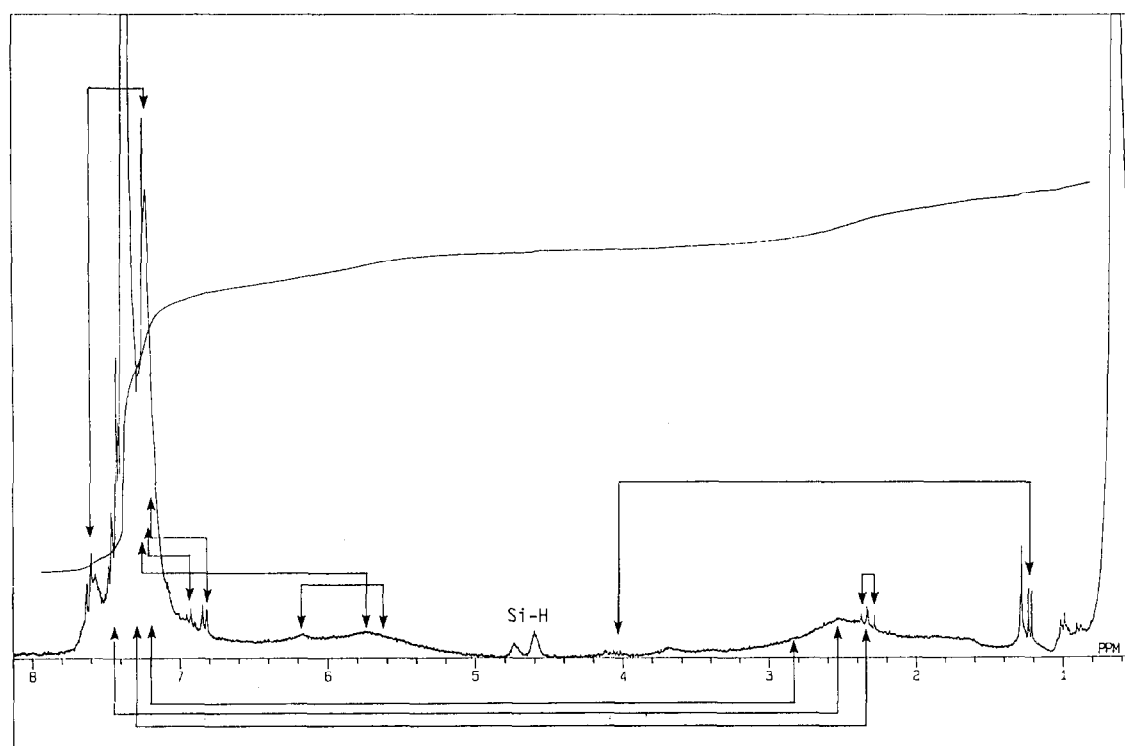
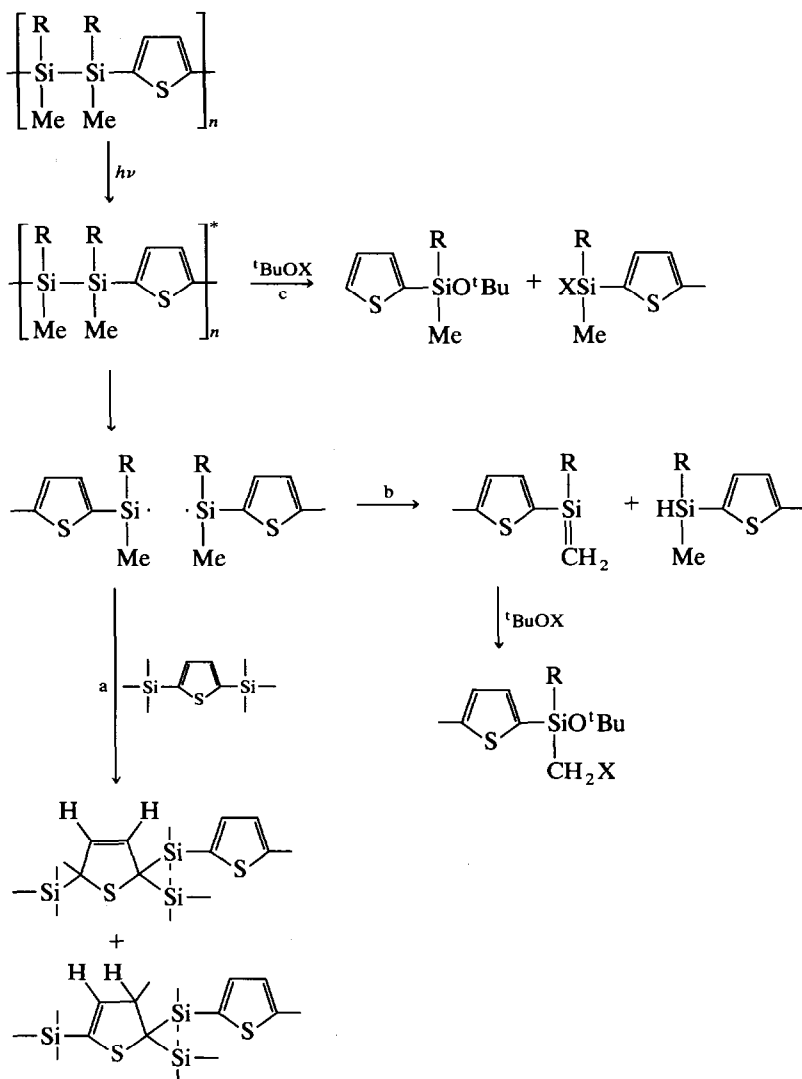


Fig. 2. <sup>1</sup>H NMR spectrum of the photoproducts of **Ib**. The arrows indicate the coupling observed in the <sup>1</sup>H-<sup>1</sup>H COSY experiment.



Scheme 2.

of tert-butyl alcohol for 2 h afforded a product with a molecular weight of 2900 which remained almost constant during further irradiation (Fig. 1, curve e).

The photolysis of **IIIb** proceeded in a similar manner to that of **IIb** at the early stage of the reaction (Fig. 1, curve c). Irradiation of **IIIb** ( $M_w = 19000$ ) in the absence of tert-butyl alcohol in benzene resulted in a rapid decrease in the molecular weight. After 2 h irradiation, however, the molecular weight increased slightly and reached  $M_w = 8800$ , indicating that some cross-linking reaction (Scheme 2, path a) occurs during the photolysis.

In conclusion, **Ib–IIIb** show similar photochemical behaviours in the solid state, as well as in a benzene solution which contains tert-butyl alcohol. In the photolysis of **Ib** in the absence of tert-butyl alcohol in the solution, the molecular weight increases with increas-

ing reaction time, while **IIb** and **IIIb** lead to a decrease in the molecular weights. It seems likely that the presence of an aromatic substituent on the silicon atom stabilizes the silyl radical and accelerates the formation of silenes, leading to a decrease in molecular weight.

### 3. Experimental details

#### 3.1. General remarks

All reactions were carried out under an atmosphere of purified argon.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL model JNM-EX-270 spectrometer, a JEOL model JNM-FX-90A spectrometer and a JEOL model JNM-PMX-60 spectrometer, using deuteriochloroform or carbon tetrachloride solution containing tetramethylsilane as an internal standard. IR spectra were recorded on a Perkin-Elmer 1600 Fourier

transform IR spectrometer. Mass spectra were measured on a Shimadzu model GCMS-QP 1000 spectrometer. UV spectra were measured on a Hitachi U-3210 spectrophotometer.

### 3.2. Materials

Benzene and tetrahydrofuran (THF) were dried over lithium aluminum hydride and distilled just before use.

### 3.3. Preparation of 2,5-bis(dimethylsilyl)thiophene

To a 40 ml THF solution of 2,5-thiophenedimagnesium dibromide prepared from 8.4 ml (0.0745 mol) of dibromothiophene and 3.7 g (0.152 mol) of magnesium was added dropwise 15.0 g (0.159 mmol) of chlorodimethylsilane at room temperature. The resulting mixture was heated to reflux for 3 h and then hydrolysed with water. The organic layer was separated and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure to give 8.2 g of 2,5-bis(dimethylsilyl)thiophene (yield, 56%; boiling point (b.p.), 100 °C (16 Torr)). Mass spectroscopy (MS):  $m/z$  200 ( $M^+$ ).  $^1H$  NMR ( $CCl_4$ ): 0.39 (d, 12H,  $J = 4$  Hz, MeSi); 4.55 (sept, 2H,  $J = 4$  Hz, HSi); 7.31 (s, 2H, ring protons) ppm.  $^{13}C$  NMR ( $CDCl_3$ ): -2.7; 136.2; 142.8 ppm. IR:  $\nu$ (Si-H) 2130  $cm^{-1}$ . Anal. Found: C, 47.64; H, 8.00.  $C_8H_{16}SSi_2$  calc.: C, 47.94; H, 8.05%. 2,5-Bis(methylphenylsilyl)thiophene and 2,5-bis[methyl(*p*-tolyl)silyl]thiophene were prepared in a similar manner.

#### 3.3.1. 2,5-Bis(methylphenylsilyl)thiophene

Yield, 67%; b.p., 175 °C (0.12 Torr). MS:  $m/z$  324 ( $M^+$ ).  $^1H$  NMR ( $CCl_4$ ): 0.64 (d, 6H,  $J = 4$  Hz, MeSi); 5.01 (sept, 2H,  $J = 4$  Hz, HSi); 7.01–7.64 (m, 12H, ring protons) ppm.  $^{13}C$  NMR ( $CDCl_3$ ): -3.8; 128.0; 129.9; 134.6; 134.8; 137.5; 141.4 ppm. IR:  $\nu$ (Si-H) 2130  $cm^{-1}$ . Anal. Found: C, 66.57; H, 6.18.  $C_{18}H_{20}SSi_2$  calc.: C, 66.61; H, 6.21%.

#### 3.3.2. 2,5-Bis[methyl(*p*-tolyl)silyl]thiophene

Yield, 72%; b.p., 185 °C (0.9 Torr). MS:  $m/z$  352 ( $M^+$ ).  $^1H$  NMR ( $CCl_4$ ): 0.63 (d, 6H,  $J = 4$  Hz, MeSi); 2.30 (s, 6H, tolyl Me); 4.96 (sept, 2H,  $J = 4$  Hz, HSi); 6.96 (d, 4H,  $J = 8$  Hz, tolyl ring protons); 7.22 (s, 2H, thienylene ring protons); 7.29 (d, 4H,  $J = 8$  Hz, tolyl ring protons) ppm.  $^{13}C$  NMR ( $CDCl_3$ ): -3.7; 21.5; 128.9; 131.2; 134.6; 137.4; 139.8; 141.6 ppm. IR:  $\nu$ (Si-H) 2130  $cm^{-1}$ . Anal. Found: C, 68.02; H, 6.79.  $C_{20}H_{24}SSi_2$  calc.: C, 68.12; H, 6.86%.

### 3.4. Preparation of bis(chlorodimethylsilyl)thiophene (Ia)

A mixture of 3.2 g (16.0 mmol) of 2,5-bis(dimethylsilyl)thiophene and about 5 mg of palladium dichloride

in 70 ml of  $CCl_4$  was heated to reflux for 3 h. After evaporation of the solvent, the residue was distilled under reduced pressure to give 3.3 g of **Ia** (yield, 91%; b.p., 125 °C (15 Torr)). MS:  $m/z$  268 ( $M^+$ ).  $^1H$  NMR ( $CCl_4$ ): 0.70 (s, 12H, MeSi); 7.23 (s, 2H, ring protons) ppm.  $^{13}C$  NMR ( $CDCl_3$ ): 3.3; 136.7; 143.5 ppm. UV (THF):  $\lambda_{max}$  241 nm ( $\epsilon = 17500 M^{-1} cm^{-1}$ ). Anal. Found: C, 35.45; H, 5.20.  $C_8H_{14}Cl_2SSi_2$  calc.: C, 35.68; H, 5.24%. Compounds **IIa** and **IIIa** were prepared in a similar manner.

#### 3.4.1. 2,5-Bis(chloromethylphenylsilyl)thiophene (IIa)

Yield, 75%; b.p., 190 °C (0.8 Torr). MS:  $m/z$  392 ( $M^+$ ).  $^1H$  NMR ( $CCl_4$ ): 0.94 (s, 6H, MeSi); 7.20–7.87 (m, 12H, ring protons) ppm.  $^{13}C$  NMR ( $CDCl_3$ ): 2.1; 128.2; 130.9; 133.8; 142.5 ppm. UV (THF):  $\lambda_{max}$  234 nm ( $\epsilon = 20600 M^{-1} cm^{-1}$ ). Anal. Found: C, 54.95; H, 4.57.  $C_{18}H_{18}Cl_2SSi_2$  calc.: C, 54.95; H, 4.61%.

#### 3.4.2. 2,5-Bis[chloromethyl(*p*-tolyl)]thiophene (IIIa)

Yield, 72%; b.p., 190 °C (0.3 Torr). MS:  $m/z$  420 ( $M^+$ ).  $^1H$  NMR ( $CCl_4$ ): 0.93 (s, 6H, MeSi); 2.35 (s, 6H, tolyl Me); 7.20 (d, 4H,  $J = 8$  Hz, tolyl ring protons); 7.29 (s, 2H, thienylene ring protons); 7.39 (d, 4H,  $J = 8$  Hz, tolyl ring protons) ppm.  $^{13}C$  NMR ( $CDCl_3$ ): 2.2; 21.6; 129.0; 130.5; 133.9; 137.8; 141.1; 142.7 ppm. UV (THF):  $\lambda_{max}$  247 nm ( $\epsilon = 9100 M^{-1} cm^{-1}$ ), 227 nm ( $\epsilon = 11500 M^{-1} cm^{-1}$ ). Anal. Found: C, 56.92; H, 5.17.  $C_{20}H_{22}Cl_2SSi_2$  calc.: C, 57.00; H, 5.26%.

### 3.5. Synthesis of poly[2,5-(tetramethyldisilanyl-ene)thienylene] (Ib)

In a 200 ml three-necked flask fitted with a dropping funnel and reflux condenser was placed 1.1 g (47.8 mmol) of sodium and 70 ml of decane, and the mixture was heated to reflux with vigorous stirring. To this was added dropwise 4.7 g (17.5 mmol) of **Ia** dissolved in 5 ml of toluene. After additional heating for 3 h, the mixture was cooled to 0 °C and hydrolyzed with ethanol and water. The organic layer was separated and the aqueous layer was extracted with  $CHCl_3$ . The organic layer and the extracts were combined and dried over anhydrous magnesium sulphate. After evaporation of the solvent, the residue was reprecipitated from benzene-ethanol to give 2.2 g of **Ib** (yield, 64%; melting point (m.p.), 155–161 °C;  $M_w = 20000$ ;  $M_n = 5300$ ).  $^1H$  NMR ( $CCl_4$ ): 0.34 (s, 12H, MeSi); 7.14 (s, 2H, ring protons) ppm.  $^{13}C$  NMR ( $CDCl_3$ ): -2.5; 135.6; 143.9 ppm. UV (THF):  $\lambda_{max}$  260 nm ( $\epsilon = 41000 M^{-1} cm^{-1}$ ). Anal. Found: C, 48.23; H, 7.41.  $(C_8H_{14}SSi_2)_n$  calc.: C, 48.42; H, 7.11%.

Polymers **IIb** and **IIIb** were synthesized as a similar manner.

### 3.5.1. Poly[2,5-(1,2-dimethyldiphenyldisilanyl)thienylene] (**IIb**)

Yield, 22%; m.p., 68–74 °C;  $M_w = 38\,000$ ;  $M_n = 7\,000$ .  $^1\text{H NMR}$  ( $\text{CCl}_4$ ): 0.65 (s, 6H, MeSi); 7.13–7.34 (m, 12H, ring protons) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): –3.3; 127.8; 129.1; 134.7; 135.8; 137.5; 142.0 ppm. UV (THF):  $\lambda_{\text{max}}$  272 nm ( $\epsilon = 8\,500\ \text{M}^{-1}\ \text{cm}^{-1}$ ). Anal. Found: C, 67.28; H, 5.67.  $(\text{C}_{18}\text{H}_{18}\text{SSi}_2)_n$  calc.: C, 67.02; H, 5.62%. Chloroform-insoluble polymer was also obtained in 45% yield.

### 3.5.2. Poly[2,5-(1,2-dimethyldi(p-tolyl)disilanyl)thienylene] (**IIIb**)

Yield, 24%; m.p., 92–95 °C;  $M_w = 36\,000$ ;  $M_n = 7\,000$ .  $^1\text{H NMR}$  ( $\text{CCl}_4$ ): 0.69 (s, 6H, MeSi); 2.27 (s, 6H, tolyl Me); 6.72–7.55 (m, 10H, ring protons) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): –3.1; 21.5; 128.7; 132.4; 134.9; 137.4; 138.9; 142.1 ppm. UV (THF):  $\lambda_{\text{max}}$  271 nm ( $\epsilon = 24\,000\ \text{M}^{-1}\ \text{cm}^{-1}$ ). Anal. Found: C, 68.48; H, 6.84.  $(\text{C}_{20}\text{H}_{22}\text{SSi}_2)_n$  calc.: C, 68.51; H, 6.32%. Chloroform-insoluble polymer was also obtained with a 55% yield.

### 3.6. Photolysis of thin solid films of polymers **Ib**–**IIIb**

A 10% chloroform solution of polymers was coated on a quartz plate or an NaCl plate and dried under reduced pressure to give solid films with a thickness of 0.05–0.1 mm. The films were irradiated with a low pressure mercury lamp bearing a Vycor filter in air. After 1 h irradiation, UV spectra of the films showed the disappearance of absorption bands at 260–270 nm, and their IR spectra revealed strong absorptions at 3000–3500 and 1100  $\text{cm}^{-1}$  for **Ib**, 3000–3500 and 1040  $\text{cm}^{-1}$  for **IIb**, and 3113 and 1010  $\text{cm}^{-1}$  for **IIIb**.

### 3.7. Photolysis of poly[2,5-(tetramethyldisilanyl)thienylene] (**Ib**) in benzene

In a 25 ml reaction vessel fitted with a low pressure mercury lamp (254 nm) containing a Vycor filter was placed 25 ml benzene solution of 99.7 mg of polymer **Ib** ( $M_w = 17\,000$ ;  $M_n = 2\,400$ ). The solution was irradiated, and the progress of the reaction was monitored by gel-permeation chromatography (GPC) whose results are shown in Fig. 1, curve a. After 20 h irradiation, the solvent was evaporated to give a photodegradation product:  $M_w = 37\,000$ ;  $M_n = 3\,700$ . IR:  $\nu(\text{Si-H})$  2150  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 0.20, 0.38 and 0.58 (br s, MeSi); 2.10–3.00 (m, HCS); 4.59 and 4.73 (m, H-Si); 5.60, 5.72 and 6.17 (br. s, olefinic protons); 6.80–7.62 (m, olefinic protons) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): –2.6; 0.2; 1.1; 1.9; 135.6 (br); 135.6 (br); 169.7 (br) ppm.

### 3.8. Photolysis of **IIb**

A solution of 99.0 mg of **IIb** ( $M_w = 16\,000$ ;  $M_n = 3\,800$ ) in 25 ml of benzene was irradiated in a similar manner to that of **Ib** and the progress of the reaction

was monitored by GPC (Fig. 1, curve b). After 10 h irradiation, the molecular weight of the photoproducts was found to be  $M_w = 3\,400$  and  $M_n = 660$ . After evaporation of the solvent, the residue was analysed by spectroscopy. IR:  $\nu(\text{Si-H})$  2130  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 0.00–1.00 (m, MeSi); 5.16 (br m, H-Si); 7.00–8.00 (m, ring protons) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): –0.4; 1.0; 127.8–134.7 (m) ppm.

### 3.9. Photolysis of **IIIb**

A solution of 101.1 mg of **IIIb** ( $M_w = 19\,000$ ;  $M_n = 5\,200$ ) in 25 ml of benzene was irradiated in a similar manner to that of **Ib** and the progress of the reaction was monitored by GPC (Fig. 1, curve c). After 10 h irradiation, the molecular weight of the photoproducts was found to be  $M_w = 8\,800$  and  $M_n = 2\,400$ . After evaporation of the solvent, the residue was analysed by spectroscopy. IR:  $\nu(\text{Si-H})$  2130  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 0.25–0.75 (m, MeSi); 2.25 (s, tolyl Me); 7.08–7.35 (m, ring protons) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): –1.7–0.76 (m); 21.5; 127.8–139.7 (m) ppm.

### 3.10. Photolysis of polymer **Ib** in the presence of $^t\text{BuOH}$ in benzene

A mixture of 100 mg of polymer **Ib** ( $M_w = 20\,000$ ;  $M_n = 5\,800$ ) and 4 ml of tert-BuOH in 20 ml of benzene was irradiated with a low pressure mercury lamp and the progress of the reaction was monitored by GPC (Fig. 1, curve d). After 10 h irradiation, the molecular weight of the photoproducts was found to be  $M_w = 5\,700$  and  $M_n = 770$ . After evaporation of the solvent, the residue was analysed by spectroscopy. IR:  $\nu(\text{Si-H})$  2120,  $\nu(\text{Si-O})$  1010  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 0.41 and 0.67 (br s, MeSi); 1.26 (br s,  $^t\text{Bu}$ ); 4.59 (m, H-Si); 7.15–7.45 (m, ring protons) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): –2.56; 0.18 (w); 1.87; 2.54; 28.6; 31.2; 72.6; 135.6 (br); 136.5 (br.) ppm.

### 3.11. Photolysis of **Ib** in the presence of $^t\text{BuOD}$

A 5 ml benzene solution of 18 mg of **Ib** ( $M_w = 37\,000$ ;  $M_n = 5\,300$ ) and 0.5 ml of  $^t\text{BuOD}$  was externally irradiated for 10 h. The solvent and  $^t\text{BuOD}$  were evaporated to give a photoproduct:  $M_w = 2\,100$ ;  $M_n = 1\,300$ . IR:  $\nu(\text{C-D})$  2320,  $\nu(\text{Si-H})$  2130 w,  $\nu(\text{Si-O})$  1080  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 0.41 and 0.65 (MeSi); 1.28 ( $^t\text{Bu}$ ); 4.60 (w, H-Si); 7.13–7.48 (ring protons) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): –2.55; 0.47–1.85 (m); 1.57; 1.76; 27.9; 31.2; 135.3 (br); 136.4 (br) ppm.

### 3.12. Photolysis of **IIb** in the presence of $^t\text{BuOH}$

A solution of 99 mg of polymer **IIb** ( $M_w = 19\,000$ ;  $M_n = 5\,200$ ) and 4 ml of  $^t\text{BuOH}$  in 20 ml of benzene was irradiated and the progress of the reaction was monitored by GPC (Fig. 1, curve e). After 20 h irradiation, the solvent and  $^t\text{BuOH}$  were evaporated to give a

photoproduct:  $M_w = 2900$ ;  $M_n = 520$ . IR:  $\nu(\text{Si-H})$  2130,  $\nu(\text{Si-O})$  1110  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 0.35–0.65 (m, MeSi); 1.22 (br s,  $^t\text{Bu}$ ); 5.02–6.14 (br, H–Si); 6.37–7.77 (m, ring protons) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): –3.8–0.65 (m); 31.4; 32.0, 66.0; 127.1–138.1 (m) ppm.

### 3.13. Photolysis of **IIIb** in the presence of $^t\text{BuOH}$

A solution of 102 mg of **IIIb** and 4 ml of  $^t\text{BuOH}$  in 20 ml of benzene was irradiated and the progress of the reaction was monitored by GPC (Fig. 1, curve f). After 20 h irradiation, the solvent was evaporated to give a photoproduct:  $M_w = 2700$ ;  $M_n = 1200$ . IR:  $\nu(\text{Si-H})$  2130,  $\nu(\text{Si-O})$  1110  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 0.23–0.79 (m, MeSi); 1.15 (s); 1.17 (m); 1.20 (s); 1.26 (s,  $^t\text{Bu}$ ); 2.25 (br s, tolyl Me); 4.98 (weak m, HSi); 6.85–7.48 (m, ring protons) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ ): –1.6–1.6 (m); 21.5; 28.5; 31.1; 31.4; 32.0; 73.8; 127.8–139.9 (m) ppm.

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