APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 7, 269–277 (1993)

Polymeric organosilicon systems 14. Synthesis and some properties of alternating polymers composed of a dithienylene group and a mono-, di- or tri-silanylene unit

Joji Ohshita, Daisuke Kanaya and Mitsuo Ishikawa*
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 724, Japan

Poly[5,5′-(dimethylsilylene)-2,2′-dithienylene] (4a), poly[5,5′-(methylphenylsilylene)-2,2′-dithienylene] (4b), poly[5,5′-(1,1,2,2-tetramethyldisilanylene)-2,2′-dithienylene] (4c), poly[5,5′-(1,2-dimethyl-1,2-diphenyldisilanylene)-2,2′-dithienylene] (4d), poly[5,5′-(1,2,2,2-tetramethyldisilanylene)-2,2′-dithienylene] (4e), and poly[5,5′-(1,1,2,2,3,3-hexamethyltrisilanylene)-2,2′-dithienylene] were synthesized by dehalogenative coupling of the respective bis(2-bromothienyl)-substituted mono, di- and tri-silanes with magnesium in the presence of a catalytic amount of a nickel(II) complex in 16–99% yields. The polymers thus obtained are light-yellow solids and soluble in common organic solvents. Molecular weights, M_w, of the polymers were measured and found to be 7800–35 000 by gel-permeation chromatography relative to polystyrene standards. The photochemical properties of the polymers (4a–4d) having silylene and disilanylene units were investigated. Only poly[5,5′-(1,2-dimethyl-1,2-diphenyldisilanylene)-2,2′-dithienylene] (4d) was found to be photoactive, but the others were inactive. When the thin solid films prepared from the polymers 4a–4e by spin-coating were exposed to antimony(V) fluoride *in vacuo*, the films became conducting; their conductivities were determined to be 10^{-2}–10^{-3} S cm^{-1} by the four-probe method.

Keywords: Dehalogenative coupling, organosilicon polymer, dithienylene polymer

INTRODUCTION

The polymers in which the regular alternating arrangement of an organosilicon unit and a π-electron system such as phenylene,[1–4] ethenylene,[5] ethynylene,[6–10] diethynylene,[11–13] thienylene,[14–16] furylene[17,18] and butenyne-1,4-diyl[19,20] is found in the polymer backbone are of considerable interest, because they can be used as functional materials such as photoresists, semiconducting materials and precursors of silicon carbide. It is well known that the sodium condensation reactions of bis(chlorosilyl)-substituted compounds or the coupling reactions of dilithio compounds bearing a π-electron system with dichlorosilanes and dichlorodisilanes offer a convenient route to various silicon-containing polymers. The polymers which can be prepared by these methods, however, always involve a small proportion of siloxy units in the polymer backbone, which are probably formed from the hydrolysis of the chlorosilyl units contained in the resulting polymer. The presence of a small number of siloxy units in the polymer backbone would interrupt the electron delocalization through the polymer chain and would therefore result in a significant decrease in the photoactivity and conductivity of the polymers.

Recently, we have reported that poly[(disilanylene)ethynylenes] and poly[(disilanylene)butenyne-1,4-diyls] can be readily synthesized by a method in which no alkali-metal condensation is involved. The former polymers can be obtained by the ring-opening polymerization of 1,2,5,6-tetrasilacycloocta-3,7-diynes in the presence of a catalytic amount of alkyl-lithium,[6,8] while the latter ones can be prepared by the reaction of 1,2-diethynyldisilanes with a catalytic amount of a rhodium(I) complex.[19,20] As expected, these two types of the polymer involve no siloxy unit in the polymer chain.

Very recently, Corriu and his co-workers reported the synthesis and conducting properties of low-molecular-weight poly[5,5′-(dimethylsilylene)-2,2′-dithienylene], together with other thienylene containing polymers.[16]

---

* Author to whom correspondence should be addressed.

0268–2605/93/040269–10 $10.00

Received 11 November 1992
Accepted 9 February 1993

In this paper, we report the synthesis of mono-, di-, and tri-silanylenedithienylene polymers by dehalogenation of di(2-bromothienyl)-substituted mono-, di- and tri-silanes with magnesium in the presence of a nickel(II) catalyst. We also report the photochemical and conducting properties of the resulting polymers.

RESULTS AND DISCUSSION

Dimerization of 5-(2-bromothienyl)-pentamethyldisilane (1)

First, we investigated the reactions of 5-(2-bromothienyl)pentamethyldisilane (**1**) in order to check whether nickel(II)-catalyzed Grignard coupling[21] could be applied to compounds which have a silicon–silicon (Si–Si) bond in the molecule. Thus, when a 1:1 mixture of 5-(2-bromothienyl)pentamethyldisilane (**1**) and 5-(pentamethyldisilanyl)thienylmagnesium bromide prepared from the reaction of **1** with magnesium in THF was heated at 230 °C for 100 h in the presence of a catalytic amount of dichloro(diphenylphosphinoethane)nickel(II) in a sealed glass tube, a coupling product, 5,5′-bis(pentamethyldisilanyl)-2,2′-dithiophene (**2**), was obtained in 79% yield, in addition to 12% of the starting compound **1** and 8% of (2-thienyl)pentamethyldisilane. It is well known that disilanes attached to π-electron systems can react readily with nickel catalyst to produce reactive intermediates such as silene and silylene (for examples, see Refs[22,23]). In this reaction, however, no product arising from the activation of the Si–Si bond by the nickel catalyst was detected by either GLC or spectroscopic analysis. The result clearly indicates that this method can be applied for the synthesis of dithienylene polymers containing di- and tri-silanylene.

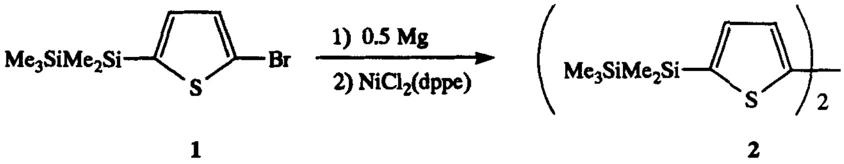
Synthesis of the polymers

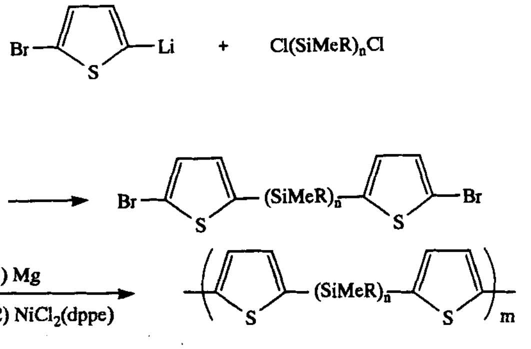
The starting monomers di[5-(2-bromothienyl)]-dimethyl- and di[5-(2-bromothienyl)]methylphenylsilane (**3a** and **3b**), 1,2-di[5-(2-bromothienyl)]tetramethyl-, 1,2-di[5-(2-bromothienyl)]-1,2-dimethyldiphenyl- and 1,1-di[5-(2-bromothienyl)]tetramethyldisilane (**3c**, **3d** and **3e**), and 3-di[5-(2-bromothienyl)]hexamethyltrisilane (**3f**) were synthesized by the reaction of the respective dichlorosilanes, dichlorodisilanes and dichlorotrisilane with 3-bromothienyl-lithium prepared from the reaction of 2,5-dibromothiophene with 1 equiv. of t-butyl-lithium in diethyl ether.

When the monomer **3a** was treated with 1 equiv. of magnesium in THF at room temperature, a mixture consisting of the starting monomer, mono-Grignard reagent, and di-Grignard reagent in the ratio of 1:2:1 was found to be produced by GLC analysis. The resulting solution was heated with a catalytic amount of dichloro(diphenylphosphinoethane)nickel(II) at 230 °C for 100 h to give poly[5,5′-(dimethylsilylene)-2,2′-dithienylene] (**4a**) in 79% yield as light-yellow solids. Similar reaction of monomers **3b**–**3f** proceeded smoothly to afford the corresponding polymers (**4b**–**4f**) in 16–99% yields (Scheme 1).

The structures of the polymers thus obtained were verified by spectroscopic analysis as well as by elemental analysis (see the Experimental section). All resonances observed in the ^{1}H and ^{13}C NMR spectra of **4a**–**4f** were consistent with those of the expected polymers. The chemical shifts of thienylene ring protons in ^{1}H NMR spectra and thienylene ring carbons in ^{13}C NMR spectra of the polymers closely resemble those of **2**, indicating that the polymers must have a regular alternating arrangement of a mono-, di- or tri-silanylene unit and a dithienylene unit in the polymer chain. As a typical example, ^{13}C NMR spectra of **2** and **4c** are shown in Figs 1(a) and 1(b).

In contrast to the similar nickel(II)-catalyzed polymerization of 2,5-dibromothiophene with magnesium, which proceeds readily at 60 °C,[24] the present reaction requires a higher temperature to obtain the high-molecular-weight polymers in high yields. For example, when the reaction of **3c** was carried out at 60 °C for 20 h, polymer **4c** with M_w 5600 (M_n 1900) was obtained only in 11% yield, while the reaction at 230 °C for 23 h gave polymer **4c** (M_w 18 100, M_n 6200) in 25% yield. As





Scheme 1

can be seen in Fig. 1(c), the ^{13}C NMR spectrum of polymer **4c** prepared at 60 °C shows the presence of a terminal thienyl group. Thus, its ^{13}C NMR reveals four resonances at δ 128.3, 130.8, 134.5 and 137.5 ppm due to the terminal thienyl ring carbons, in addition to other sp^2 carbons whose chemical shifts are consistent with those observed for the high-molecular-weight polymer **4c**. The chemical shifts of these four signals are in good agreement with those of 1,2-di(2-thienyl)tetramethyldisilane (**5**) (Fig. 1(d)).

The polymers **4a–4f** are soluble in common organic solvents such as ethers, benzene, toluene and halocarbons, and slightly soluble in aliphatic hydrocarbons, but insoluble in alcohols. The polymer **4c** did not melt even at above 300 °C, while the polymers **4a**, **4b**, **4d** and **4f** melt at 74–172 °C without decomposition. Molecular weights M_w of the polymers were determined to be 7800–35 000 by gel-permeation chromatography (GPC), relative to polystyrene standards. The yields, melting points and molecular weights of the polymers obtained are summarized in Table 1. The low yields of the polymers **4c** and **4f** can be ascribed to the low reactivities of the monomers **3c** and **3f**. In fact, large amounts of oligomers which are soluble in ethanol were found to be formed from the polymerization of **3c** and **3f**. In these cases, it seems likely that the cleavage of the Si–Si bonds in both monomers and polymers by a nickel catalyst gives rise to a large amount of oligomers. ^1H and ^{13}C NMR spectra of polymers **4c** and **4f**, however, are wholly consistent with the (disilanylene)dithienylene structure (see the Experimental section). In conclusion, the introduction of an electron-withdrawing group such as phenyl on the silicon atom would accelerate the oxidative addition of the Br–C bond to a nickel species, which would be involved as a key step in the present reaction.[21]

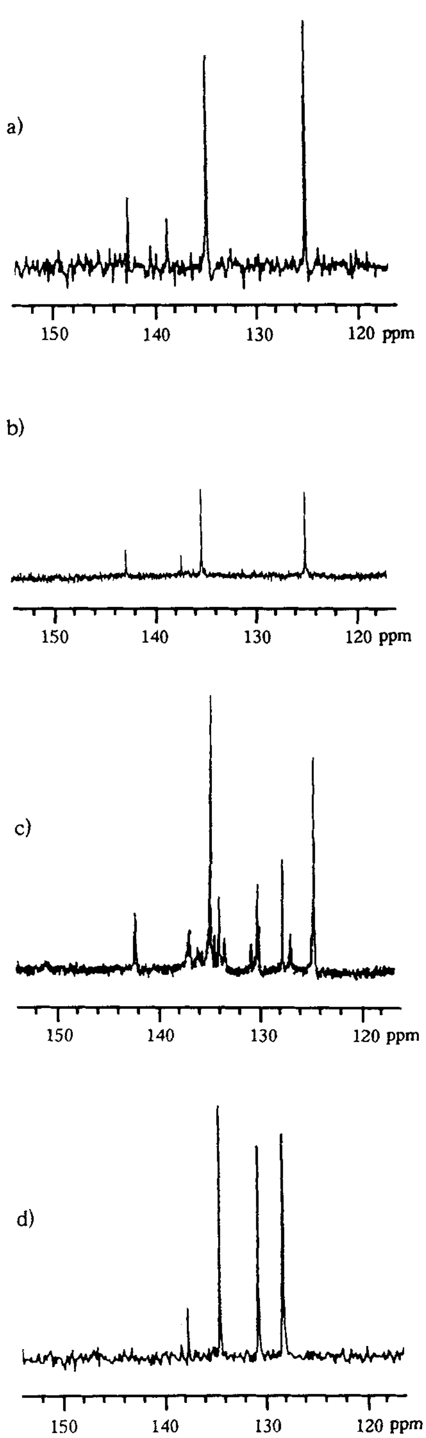


Figure 1 Decoupled ^{13}C NMR spectra in $CDCl_3$: (a) 5,5′-bis(pentamethyldisilanyl)-2,2′-dithiophene (**2**); (b) poly[5,5′-(1,1,2,2-tetramethyldisilanylene)-2,2′-dithienylene] (**4c**) prepared at 230 °C; (c) polymer **4c** prepared at 60 °C; (d) 1,2-di(2-thienyl)tetramethyldisilane (**5**).

Table 1 Properties of polymers **4a–4f**

Polymer	Yield (%)	M.p. (°C)	M_w	M_w/M_n
4a	79	168–172	7800	2.8
4b	99	148–155	30 000	4.0
4c	25	>300	18 100	2.9
4d	94	120–126	27 300	4.6
4e	77	102–107	11 200	5.9
4f	16	74–78	35 000	3.3

Photochemical behaviour of the polymers

The polymers thus obtained show two strong absorption bands in the UV region at about 240 and 350 nm. As in the case of disilanylene-phenylene polymers reported previously,[1–4] the present polymers are also expected to be photoactive. However, to our surprise, when a benzene solution of polymers **4a–4c**, **4e** or **4f** was irradiated with a low-pressure mercury lamp, no change was observed in the molecular weight of the resulting polymer. Furthermore, all spectral data, IR, and ^{1}H and ^{13}C NMR spectra of the polymers obtained from the photolysis were identical with those of the corresponding starting polymers. Only polymer **4d** was found to be photoactive. Thus, irradiation of **4d** in benzene resulted in a decrease in the molecular weights of photoproducts with increasing reaction time, as shown in Fig. 2(a). However, the changes in molecular weight were smaller than those in the photolysis of disilanylenephenylene polymers reported previously.[1–4] The IR spectrum of the photoproducts showed a weak absorption band at 2140 cm^{-1} due to an Si–H bond. Presumably, homolytic scission of the Si–Si bonds in the polymer chain occurred, to form silyl radicals in the solvent cage. The resulting silyl radicals would undergo a disproportionation reaction to give a silene and hydrosilane. ^{1}H and ^{13}C NMR spectra of the photoproducts were almost the same as those of the starting polymer **4d** with one exception, i.e. the presence of weak resonances due to an Si–H bond.

In order to learn much more about the photochemical behavior of **4d**, we carried out the photolysis of **4d** (molecular weight M_w determined to be 27 300; $M_w/M_n = 4.6$) in the presence of methanol, and monitored the progress of the photochemical reaction by GPC. As shown in Fig. 2(b), the molecular weight of the photoproducts gradually decreased with increasing reaction time, and after 4 h of reaction it reached a constant value of $M_w = 4200$ ($M_w/M_n = 18.2$). The spectroscopic analysis of the photoproducts showed the presence of Si–OMe, Si–OH and Si–H groups in the products, indicating that the photodegradation involves the formation of silene and hydrosilane arising from the disproportionation reaction of silyl radicals generated photochemically by the scission of silicon–silicon bonds. Chemical shifts of thienylene ring carbons in the ^{13}C NMR spectrum of the photoproducts were almost the same as those of the starting polymer **4d**. These results indicate that the photoactivity of this polymer is

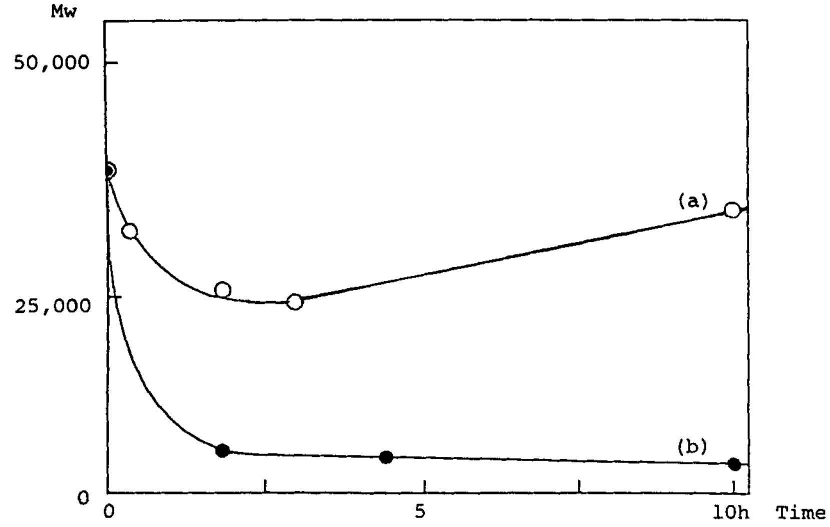


Figure 2 Plot of molecular weights of products vs irradiation time for polymer **4d**: (a) in the absence of methanol and (b) in the presence of methanol in benzene.

Table 2 Conductivity of polymers **4a**–**4e** doped with SbF_5 vapor

Polymer	Film thickness (μm)	Conductivity ($S\,cm^{-1}$)
4a	1.0	1.2×10^{-2}
4b	1.5	1.6×10^{-3}
4c	1.0	2.1×10^{-2}
4d	1.5	9.2×10^{-2}
4e	1.0	2.3×10^{-3}

considerably lower than that of disilanylene polymers reported previously. The low reactivity of the present polymers may be ascribed to the presence of the (disilanylene)thienylene group. In fact, the model compound **2** was found to be inert towards UV irradiation. Thus, when **2** was irradiated in the presence of methanol under the same conditions for 10 h, the starting compound **2** was recovered unchanged.

Conducting properties of the polymers

The conducting properties of the polymers **4a**–**4e** were also investigated. The polymers **4a**–**4e** can be cast as thin solid films with a thickness of 1–1.5 μm by spin coating. These films were treated with antimony(V) fluoride (SbF_5) vapor under reduced pressure (1 mm Hg) and the changes in conductivity were measured simultaneously by the four-probe method. The conductivities of the films increased immediately after contact with SbF_5 vapor up to maximum values of 10^{-2}–$10^{-3}\,S\,cm^{-1}$. The doped films prepared from polymers **4a**, **4b** and **4e** exhibited stable conducting properties during treatment with SbF_5 vapor; their conductivity did not decrease for 30 h. However, the conductivity of the films from **4c** and **4d** decreased after about 40 min, when it had reached the maximum value. After five days, the conductivity of the films reached a constant value of $4.1\times10^{-4}\,S\,cm^{-1}$ for **4c** and $1.0\times10^{-4}\,S\,cm^{-1}$ for **4d**, even in the SbF_5 vapor. Instability in the conducting properties of the doped films of **4c** and **4d** is presumably due to the cleavage of Si–Si bonds in the polymer chain by the reaction with SbF_5. The thickness of the films and maximum conductivity of the doped films are summarized in Table 2.

Interestingly, when the SbF_5-doped films from **4a** and **4c** are exposed to air, the conductivity suddenly increases to 2.1 and $0.3\,S\,cm^{-1}$ for **4a** and **4c**, respectively. Similar increases in the conductivity of the SbF_5 doped films prepared from the copolymer composed of silylene and disilanylene units and a π-electron system have been reported previously.[20,25] A trace of moisture in the air might play an important role in the increase in the conductivity. Presumably, hydrolysis of SbF_5 takes place to give ion species on the surface of the film.

Corriu and his coworkers have reported the conductivity of the BF_4^--doped film prepared from poly[5,5′-(dimethylsilylene)-2,2′-dithienylene to be $3\times10^{-5}\,S\,cm^{-1}$.[16] The relative low conductivity of this film may be ascribed to the low molecular weight of the polymer ($M_w = 2550$; $M_w/M_n = 1.2$).

On the basis of the conductivity data obtained in this experiment, the number of silicon atoms which are present between two dithienylene groups exerts no significant influence on conductivities.

EXPERIMENTAL

General

All reactions were carried out under an atmosphere of purified argon. ^1H and ^{13}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. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR spectrometer. Mass spectra were measured on a Shimadzu model GCMS-QP 1000 spectrometer.

Materials

1,1-Dichlorotetramethyldisilane,[26] 1,2-dichlorotetramethyldisilane,[27] 1,2-dichloro-1,2-dimethyldiphenyldisilane,[20] and 1,3-dichlorohexamethyltrisilane[28] were prepared as reported in the literature. Diethyl ether was dried over lithium aluminum hydride and distilled just before use. THF was dried over sodium–potassium alloy and distilled under reduced pressure by means of the vacuum line just before use.

Preparation of 2-(5-bromothienyl)pentamethyldisilane (1)

A solution of 6.44 g (26.7 mmol) 2,5-dibromothiophene in 25 cm^3 diethyl ether was placed in a 50 cm^3 two-necked flask and the flask was cooled to −80 °C. To this was added 16.8 cm^3 (26.7 mmol) 1.59 M n-butyl-lithium–hexane solution through a dropping funnel. The resulting mixture was allowed to warm to room temperature and to stand for 12 h, and then 4.4 g (26.4 mmol) chloropentamethyldisilane was added. After the mixture had been heated under reflux for 2 h, it was hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with hexane. The organic layer and the extracts were combined and washed with water, and then dried over anhydrous magnesium sulfate. The solvents were evaporated and the residue was distilled under reduced pressure to give 4.4 g (yield 56%) of **1**: b.p. 114 °C; MS *m/z* 292 (M^+); 60 MHz ^{1}H NMR (δ in CCl_4) 0.12 (s, 9H, Me_3Si), 0.35 (s, 6H, Me_2Si), 6.78 (d, 1H, $J = 4$ Hz, ring proton), 6.90 (d, 1H, $J = 4$ Hz, ring proton); ^{13}C NMR (δ in $CDCl_3$) −2.9, −2.5, 116.3, 131.2, 134.4, 142.2. Analysis: Calcd for $C_9H_{17}BrSSi_2$: C, 36.85; H, 5.84. Found: C, 36.61; H, 5.85%.

Synthesis of 5,5′-bis(pentamethyldisilanyl)-2,2′-dithiophene (2)

A mixture of 200 mg (0.68 mmol) **1** and 83 mg (0.34 mmol) of magnesium in 2 cm^3 THF was placed in a Pyrex tube, i.d. 10 mm, and the mixture was warmed at 50 °C with stirring until all the magnesium was consumed (2–3 h). To this was added 20 mg (5.5 mol %) dichloro(diphenylphosphinoethane)nickel(II), and then the tube was degassed under reduced pressure (0.1 mm Hg) and sealed. The sealed glass tube was heated at 230 °C for 100 h. The resulting mixture was hydrolyzed and analyzed by GLC using 19.5 mg (0.0690 mmol) eicosane as an internal standard; it was found to comprise **2** (79%), **1** (12%), and 2-thienylpentamethyldisilane (8%). Mass spectra and the GLC retention time for compounds **1** and 2-thienylpentamethyldisilane were identical with those of authentic samples. The solvent was evaporated and the residue was recrystallized from ethanol to give **2**: m.p. 56 °C; ^{1}H NMR (δ in $CDCl_3$) 0.11 (s, 18H, Me_3Si), 0.37 (s, 12H, Me_2Si), 6.94 (d, 2H, $J = 4$ Hz, ring protons), 7.12 (d, 2H, $J = 4$ Hz, ring protons); ^{13}C NMR (δ in $CDCl_3$) −2.8, −2.4, 125.1, 134.8, 138.7, 142.5. Analysis: Calcd for $C_{18}H_{34}S_2Si_4$: C, 50.64; H, 8.03. Found: C, 50.40; H, 7.87%.

Preparation of 2-thienylpentamethyldisilane

In a 25 cm^3 two-necked flask fitted with a reflux condenser and a dropping funnel were placed 50.0 mg (2.06 mmol) magnesium and 5 mL THF. To this mixture was added a solution of 0.525 g (1.87 mmol) of **1** in 5 cm^3 THF; the resulting mixture was stirred at room temperature until almost all the magnesium had been consumed. The Grignard agent thus formed was hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and washed with water, and then dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was chlomatographed on a silica-gel column eluting with hexane to give 0.243 g 2-thienylpentamethyldisilane (yield 57%): MS *m/z* 214 (M^+); 270 MHz ^{1}H NMR (δ in $CDCl_3$) 0.15 (s, 9H, Me_3Si), 0.42 (s, 6H, Me_2Si), 7.22–7.27 (m, 2H, ring protons), 7.63 (dd, 1H, $J = 4.3$ Hz, 1.3 Hz, ring proton); ^{13}C NMR (δ in $CDCl_3$) −2.7, −2.4, 128.2, 130.3, 134.0, 138.9. Analysis: Calcd for $C_9H_{18}SSi_2$: C, 50.40; H, 8.46. Found: C, 50.13; H, 8.44%.

Preparation of 1,2-di[2-(5-bromothienyl)]dimethylsilane (3a)

In a 50 cm^3 two-necked flask fitted with a dropping funnel was placed 10.0 g (41.3 mmol) 2,5-dibromothiophene in 20 cm^3 diethyl ether, and the flask was cooled to −80 °C. To this mixture was added 25.0 cm^3 (42.5 mmol) 1.70 M t-butyllithium–pentane solution through the dropping funnel over a period of 1 h. The resulting solution was allowed to warm to room temperature and to stand for 12 h, and then 2.6 g (20.0 mmol) dichlorodimethylsilane was added. After the mixture had been heated under reflux for 3 h, the resulting solution was hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and washed with water, and then dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure to give crude **3a** (b.p. 115 °C/0.1 mm Hg). Crude **3a** was then chromatographed on silica gel, eluting with hexane to give 5.5 g (yield 72%) of pure **3a**: MS *m/z* 380 (M^+); 270 MHz ^{1}H NMR (δ in

$CDCl_3$) 0.49 (s, 6H, Me_2Si), 6.94 (d, 2H, $J = 4$ Hz, ring protons), 6.99 (d, 2H, $J = 4$ Hz, ring protons); ^{13}C NMR (δ in $CDCl_3$) −0.6, 118.2, 131.4, 135.9, 139.6. Analysis: Calcd for $C_{10}H_{10}Br_2S_2Si$: C, 31.43; H, 2.64. Found: C, 31.24; H, 2.70%.

Monomers **3b–3f** were synthesized similarly to **3a**.

Di[2-(5-bromothienyl)]methylphenylsilane (3b)

Compound **3b** was purified directly by silica-gel column chromatography, eluting with hexane, without distillation: 69% yield; MS *m/z* 442 (M^+); 60 MHz ^1H NMR (δ in CCl_4) 0.75 (s, 3H, MeSi), 6.95–7.45 (m, 9H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.4, 124.7, 128.1, 129.9, 131.2, 134.5, 134.9, 135.2, 136.8. Analysis: Calcd for $C_{15}H_{12}Br_2S_2Si$: C, 40.55; H, 2.72. Found: C, 40.66; H, 2.90%.

1,2-Di[2-(5-bromothienyl)]tetramethyldisilane (3c)

Yield 84%; b.p. 125 °C (0.1 mm Hg); MS *m/z* 438 (M^+); 60 MHz ^1H NMR (δ in CCl_4) 0.39 (s, 12H MeSi), 6.75 (d, 2H, $J = 4$ Hz, ring protons), 6.96 (d, 2H, $J = 4$ Hz, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.0, 117.0, 131.4, 135.0, 140.6. Analysis: Calcd for $C_{12}H_{16}Br_2S_2Si_2$: C, 32.73; H, 3.66. Found: C, 32.70; H, 3.66%.

1,2-Di[2-(5-bromothienyl)]-1,2-dimethyldiphenyldisilane (3d)

Compound **3d** was purified by treatment with silica-gel column chromatography, eluting with hexane: yield 32%; white solid; m.p. 75 °C; MS *m/z* 562 (M^+); 60 MHz ^1H NMR (δ in CCl_4) 0.70 (s, 6H MeSi), 6.85 (d, 2H, $J = 4$ Hz, thienyl ring protons), 7.05 (d, 2H, $J = 4$ Hz, thienyl ring protons), 7.32 (br s, 10H, Ph); ^{13}C NMR (δ in $CDCl_3$) −3.5, 118.1, 128.1, 129.6, 131.5, 134.7 (two carbons), 136.9, 137.9. Analysis: Calcd for $C_{22}H_{20}Br_2S_2Si_2$: C, 46.81; H, 3.57. Found: C, 46.81; H, 3.57%.

1,1-Di[2-(5-bromothienyl)]-1,2,2,2-tetramethyldisilane (3e)

Compound **3e** was purified by treatment with silica-gel column chromatography, eluting with hexane: MS *m/z* 423 ($M^+ - Me$); 270 MHz ^1H NMR (δ in $CDCl_3$) 0.20 (s, 9H, Me_3Si), 0.63 (s, 3H, MeSi), 7.02 (d, 2H, $J = 4$ Hz, ring protons), 7.11 (d, 2H, $J = 4$ Hz, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.1, −2.2, 117.8, 131.5, 136.0, 138.7. Analysis: Calcd for $C_{12}H_{16}Br_2S_2Si_2$: C, 32.73; H, 3.66. Found: C, 32.70; H, 3.66%.

1,3-Di[2-(5-bromothienyl)]hexamethyltrisilane (3f)

Yield 23%; b.p. 140 °C (0.1 mm Hg); MS *m/z* 496 (M^+); 270 MHz ^1H NMR (δ in $CDCl_3$) 0.17 (s, 6H Me_2Si), 0.35 (s, 12H, Me_2Si), 6.87 (d, 2H, $J = 4$ Hz, ring protons), 7.09 (d, 2H, $J = 4$ Hz, ring protons); ^{13}C NMR (δ in $CDCl_3$) −2.1, −1.4, 116.6, 131.3, 134.5, 141.8. Analysis: Calcd for $C_{14}H_{22}Br_2S_2Si_3$: C, 33.73; H, 4.45. Found: C, 33.69; H, 4.41%.

Synthesis of poly[5,5′-(dimethylsilylene)-2,2′-dithienylene] (4a) at 230 °C

Magnesium (24.3 mg; 1.00 mmol) in a Pyrex tube, i.d. 10 mm was carefully dried *in vacuo*. Purified argon was introduced into the tube, and then a solution of 382 mg (1.00 mmol) **3a** in 2 cm^3 THF was added. The mixture was warmed at 50 °C with stirring until all the magnesium had been consumed (2–3 h). To this was added 6.9 mg (1.3 mol %) dichloro(diphenylphosphinoethane)-nickel(II), and then the tube was degassed under reduced pressure (0.1 mm Hg) and sealed. The sealed glass tube was heated at 230 °C for 100 h, and the resulting mixture was hydrolyzed. The organic layer was separated and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After the solvent had been evaporated, the residue was reprecipitated from chloroform–ethanol to give 175 mg of **4a** (79% yield): m.p. 168–172 °C; M_w 7800; M_n 2800; 270 MHz ^1H NMR (δ in $CDCl_3$) 0.63 (s, 6H, MeSi), 7.20 (br s, 4H, ring protons); 67.8 MHz ^{13}C NMR (δ in $CDCl_3$) −0.3, 125.4, 136.3, 136.8, 143.2. Analysis: Calcd for $(C_{10}H_{10}SiS_2)_m$: C, 53.06; H, 4.45. Found: C, 53.00; H, 4.45%.

Polymers **4b–4f** were synthesized similarly to **4a** at 230 °C for 100 h.

Poly[5,5′-(methylphenylsilylene)-2,2′-dithienylene] (4b)

Yield 99%; m.p. 148–155 °C; M_w 30 000; M_n 7400; 270 MHz ^1H NMR (δ in $CDCl_3$) 0.87 (s, 3H, MeSi), 7.18–7.61 (m, 9H, ring protons);

67.8 MHz ^{13}C NMR (δ in $CDCl_3$) −1.4, 125.6, 128.1, 130.1, 134.7, 134.9, 135.0, 137.8, 143.9. Analysis: Calcd for $(C_{15}H_{12}S_2Si)_m$: C, 63.33; H, 4.25. Found: C, 63.24; H, 4.38%.

Poly[5,5′-(1,1,2,2-tetramethyldisilanylene)-2,2′-dithienylene] (4c)

Yield 25%; m.p. >300 °C; M_w 18 100; M_n 6200; 270 MHz ^{1}H NMR (δ in $CDCl_3$) 0.41 (s, 12H, MeSi), 7.04 (d, 2H, ring protons, $J = 3.3$ Hz), 7.22 (d, 2H, ring protons, $J = 3.3$ Hz); 67.8 MHz ^{13}C NMR (δ in $CDCl_3$) −2.8, 125.3, 135.4, 137.4, 142.7. Analysis: Calcd for $(C_{12}H_{16}S_2Si_2)_m$: C, 51.37; H, 5.75. Found: C, 50.28; H, 5.63%.

Poly[5,5′-(1,2-dimethyl-1,2-diphenyldisilanylene)-2,2′-dithienylene] (4d)

Yield 94%; m.p. 120–126 °C; M_w 27 300; M_n 6000; 270 MHz ^{1} NMR (δ in $CDCl_3$) 0.79 (s, 6H, MeSi), 7.08–7.47 (m, 14H, ring protons); 67.8 MHz ^{13}C NMR (δ in $CDCl_3$) −3.3, 125.5, 127.9, 129.4, 134.8, 135.4, 137.3 (two carbons), 143.4. Analysis: Calcd for $(C_{22}H_{20}S_2Si_2)_m$: C, 65.29; H, 4.98. Found: C, 65.07; H, 4.80%.

Poly[5,5′-(1,2,2,2-tetramethyldisilanylene)-2,2′-dithienylene] (4e)

Yield 77%; m.p. 102–107 °C; M_w 11 200; M_n 3900; 270 MHz ^{1}H NMR (δ in $CDCl_3$) 0.20 (s, 9H, Me_3Si), 0.67 (s, 3H, MeSi), 7.17 (d, 2H, $J = 3.0$ Hz, ring protons), 7.26 (d, 2H, $J = 3.0$ Hz, ring protons); 67.8 MHz ^{13}C NMR (δ in $CDCl_3$) −2.9, −2.2, 125.4, 135.7, 136.3, 143.2.

Poly[5,5′-(1,1,2,2,3,3-hexamethyltrisilanylene)-2,2′-dithienylene] (4f)

Yield 16%; m.p. 74–78 °C; M_w 35 000; M_n 10 500; 270 MHz ^{1}H NMR (δ in $CDCl_3$) 0.16 (s, 6H, Me_2Si), 0.35 (s, 12H, Me_2Si), 6.99 (d, 2H, $J = 3.3$ Hz, ring protons), 7.19 (d, 2H, $J = 3.3$ Hz, ring protons); 67.8 MHz ^{13}C NMR (δ in $CDCl_3$) −6.7, −2.0, 125.1 (two carbons), 134.9, 142.6. Analysis: Calcd for $(C_{14}H_{22}S_2Si_3)_m$: C, 49.65; H, 6.55. Found: C, 48.49; H, 6.58%.

Synthesis of poly[5,5′-(1,1,2,2-tetramethyldisilanylene)-2,2′-dithienylene] (4c) at 60 °C

To 0.193 g (7.95 mmol) magnesium in 5 cm^3 of THF in a 30 cm^3 flask was added a solution of 3.50 g (7.95 mmol) of **3a** in 5 cm^3 THF at room temperature. The resulting mixture was stirred at 50 °C for 2 h until all the magnesium had been consumed. Then 12.3 mg (0.5 mol %) dichloro(diphenylphosphinoethane)nickel (II) was added, and the mixture was warmed at 60 °C for 15 h. The resulting mixture was hydrolyzed with water. The organic layer was separated and the aqueous layer was extracted with chloroform. The organic layer and the extracts were combined and washed with water, and then dried over anhydrous magnesium sulfate. Ater the solvent had been evaporated, the residue was reprecipitated from chloroform–ethanol to give 246.5 mg **4c** (yield 11%): m.p. >300 °C; M_w 5600; M_n 1900; 270 MHz ^{1}H NMR (δ in $CDCl_3$) 0.41 (s, 12H, MeSi), 7.04 (d, 2H, ring protons, $J = 3.3$ Hz), 7.22 (d, 2H, ring protons, $J = 3.3$ Hz); 67.8 MHz ^{13}C NMR (δ in $CDCl_3$) −2.8, −2.7, 125.2, 127.5, 128.3, 130.8, 131.4, 134.0, 134.5, 135.4, 137.5, 142.7.

Synthesis of 1,2-di(2-thienyl)tetramethyldisilane (5)

To a solution of 12.3 mmol 2-thienylmagnesium bromide prepared from 2.00 g 2-bromothiophene and 300 mg magnesium in 20 cm^3 THF was added dropwise 1.15 g 1,2-dichlorotetramethyldisilane in 5 cm^3 THF with ice cooling. The resulting mixture was stirred overnight at room temperature. After hydrolysis with water, the organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and washed with water, and then dried over anhydrous magnesium sulfate. After the solvent had been evaporated, the residue was distilled under reduced pressure to give 1.42 g (yield 82%) of **5**: b.p. 155 °C (15 mm Hg); 60 MHz ^{1}H NMR (δ in CCl_4) 0.39 (s, 12H, Me_2Si), 6.96–7.16 (m, 2H, ring protons), 7.34–7.54 (m, 1H, ring proton); 22.5 MHz ^{13}C NMR (δ in $CDCl_3$) −2.6, 128.3, 130.7, 134.5, 137.7. Analysis: Calcd for $C_{12}H_{18}S_2Si_2$: C, 51.01; H, 6.42. Found: C, 51.01; H, 6.40%.

Photolysis of polymers 4a–4f in benzene

In a 25 cm^3 reaction vessel, fitted with a low-pressure immersion mercury lamp (254 nm), was placed a benzene solution of *ca* 100 mg of polymer **4a**. The solution was irradiated and the progress of the reaction was monitored by GPC. The procedure was repeated for each of the polymers **4b–4f**. No changes were observed for **4a–4c**, **4e** or **4f** after 10 h of irradiation. For **4d**, The IR spectrum showed an absorption band due to $\nu_{\text{Si–H}}$ at 2132 cm^{-1}.

Photolysis of polymer 4d in the presence of methanol in benzene

In a 25 cm^3 reaction vessel, fitted with a low-pressure mercury lamp, (254 nm), was placed in a mixture of 100 mg polymer **4d** and 2 cm^3 methanol in 25 cm^3 benzene. The solution was irradiated and the progress of the reaction was monitored by GPC: After 10 h of irradiation, the reaction mixture was analyzed by GPC: M_w 4200; IR $\nu_{\text{O–H}}$ 3400 cm^{-1}, $\nu_{\text{Si–H}}$ 2140 cm^{-1}, $\nu_{\text{Si–O}}$ 1100 cm^{-1}; ^{1}H NMR (δ in $CDCl_3$) −0.02, 0.62 (s, MeSi), 3.24 (m, MeO), 5.50–5.60 (b, SiH), 6.91–7.50 (m, ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.43, 0.94, 57.0–59.5 (MeO), 125.4, 127.9, 128.2, 129.3, 129.5, 134.1, 134.6, 134.7, 135.3, 137.2, 143.3.

Photolysis of 2 in the presence of methanol

In a 25 cm^3 reaction vessel bearing a vicor filter, fitted internally with a low-pressure mercury lamp, was placed a mixture of 264.0 mg (2.93 mmol) of **2** and 3 cm^3 methanol in 20 cm^3 benzene. The mixture was irradiated for 10 h, and the resulting mixture was analyzed by GLC and ^{1}H NMR spectroscopy, which indicated that all the starting compound **2** remained unchanged.

Doping experiments

Doping experiments on thin solid films of polymer **4a–4e** were carried out as described in a previous paper.[20] The results are shown in Table 2.

Acknowledgement This research was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials, Design, Preparation, and Control, from the Ministry of Education, Science and Culture, to which our thanks are due. We thank Sumitomo Electric Industry Ltd for doping experiments and determination of the conductivity of doped polymers. We also express our appreciation to Shin-Etsu Chemical Co. Ltd, Nitto Electric Industrial Co. Ltd, Dow Corning Japan Ltd and Toshiba Silicone Co. Ltd for financial support.

REFERENCES

1. Ishikawa, M, Ni, H, Matsuzaki, K, Nate, K, Inoue, T and Yokono, H *J. Polym. Sci., Polym. Lett. Ed.*, 1984, 22: 669
2. Nate, K, Ishikawa, M, Ni, H, Watanabe, H and Saheki, Y *Organometallics*, 1987, 6: 1673
3. Ishikawa, M and Nate, K *Inorganic and Organometallic Polymers*, American Chemical Society, ACS Symp. Ser. No. 360 Washington, DC, 1988 p. 209
4. Shiina, K *J. Organomet. Chem.*, 1986, 310: C57
5. Ohshita, J, Kanya, D, Ishikawa, M and Yamanaka, T *J. Organomet. Chem.*, 1989, 369: C18
6. Ishikawa, M, Hasegawa, Y, Kunai, A and Yamanaka, T *Organometallics*, 1989, 8: 2741.
7. Iwahara, T, Hayase, S and West, R *Macromolecules*, 1990, 23: 1298
8. Ishikawa, M, Hatano, T, Hasegawa, Y, Horio, T, Kunai, A, Miyai, Y, Ishida, T, Tsukihara, T, Yamanaka, T, Koike, T and Shioya, J *Organometallics*, 1992, 11: 1604
9. Maghsoodi, S-I, Pang, Y and Barton, T J *J. Polym. Sci., Polym. Chem.*, 1990, 28: 955
10. Hengge, E and Baumegger, A *J. Organomet. Chem.*, 1989, 369: C39
11. Ishikawa, M, Hasegawa, Y, Kunai, A and Yamanaka, T *J. Organomet. Chem.*, 1990, 381: C57.
12. Ijadi-Maghsoodi, S and Barton, T J *Macromolecules*, 1990, 23: 4485
13. Bréfort, J L, Corriu, R J P, Gerbier, P, Guérin, C, Henner, B J L, Jean, A, Kuhlmann, T, Garnier, F and Yassar, A *Organometallics*, 1992, 11: 2500 and references therein
14. Hu, S and Weber, W P *Polym. Bull.*, 1989, 21: 133
15. Ohshita, J, Kanaya, D, Ishikawa, M, Koike, T and Yamanaka, T *Macromolecules*, 1991, 24: 2106
16. Chicart, P, Corriu, R J P, Moreau, J J E, Garnier, F and Yassar, A *Chem. Mater.*, 1991, 3: 8
17. Hong, H H and Weber, W P *Polym. Bull.*, 1989, 22: 363
18. Ohshita, J, Kanaya, D, Ishikawa, M and Yanamaka, T *Chem. Express*, 1990, 5: 489
19. Ohshita, J, Furumori, K, Ishikawa, M and Yamanaka, T *Organometallics*, 1989, 8: 2084
20. Ohshita, J, Matsuguchi, A, Furumori, K, Hong, R, Ishikawa, M, Yamanaka, T, Koike, T and Shioya, J *Macromolecules*, 1992, 25: 2134
21. Tamao, K, Kodama, S, Nishimura, I, Kumada, M and Minato, A *Tetrahedron*, 1982, 38: 3347
22. Ishikawa, M, Nishimura, Y, Tozaki, E, Kunai, A and Ohshita, J *Organometallics*, 1992, 11: 483
23. Ohshita, J, Naka, A and Ishikawa, M *Organometallics*, 1992, 11: 602
24. Yamamoto, T, Sanechika, K and Yamamoto, A *Bull. Chem. Soc. Jpn.*, 1983, 56: 1947
25. Hayashi, T, Uchimaru, Y, Reddy, N P and Tanaka, M *Chem. Lett.*, 1992, 647
26. Ishikawa, M, Fuchikami, T and Kumada, M *J. Organomet. Chem.*, 1976, 118: 139
27. Kumada, M, Yamaguchi, M, Yamamoto, Y, Nakajima, J and Shiina, K *J. Org. Chem.*, 1956, 21: 1264
28. Sakurai, H, Tominaga, K, Watanabe, T and Kumada, M *Tetrahedron Lett.*, 1966, 45: 5493