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Polymeric Organosilicon Systems. 10. Synthesis and Conducting Properties of Poly[2,5-(disilanylene)thienylenes]

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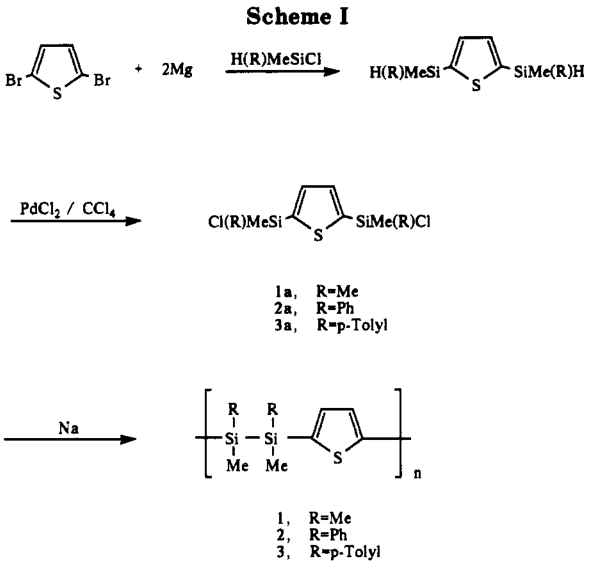
We have demonstrated that the sodium condensation reaction of compounds involving two chlorosilyl groups attached to a π-electron system offers a convenient route to silicon-containing polymers in which a regular alternating arrangement of a disilanyl unit and a π-electron system is found in the polymer backbone.[2,3] As part of our continuing studies concerning the design and synthesis of silicon-containing functional materials, we have prepared a new type of polymer containing both disilanylene units and thienylene groups in the polymer backbone, and have investigated their conducting properties. We have also carried out calculations of the electronic structures of the poly[2,5-(disilanylene)thienylenes]. In the course of our studies, the synthesis and photodegradation of one of the polymers described here, poly[(tetramethyldisilanylene)thienylene], have been reported by Hu and Weber.[4]

The starting monomers, 2,5-bis(chlorodimethylsilyl)-, 2,5-bis(chloromethylphenylsilyl)-, and 2,5-bis[chloromethyl(p-tolyl)silyl]thiophene (**1a**, **2a**, and **3a**), were synthesized in 51, 57, and 51% yields, respectively, by the reaction of Grignard reagent, prepared from 2,5-dibromothiophene and magnesium, with the corresponding chlorohydrosilanes, followed by treatment of the resulting 2,5-bis(hydrosilyl)thiophene with a catalytic amount of palladium dichloride in carbon tetrachloride. Treatment of **1a** with a slight excess of sodium dispersion in decane at 130 °C for 10 h gave a solid polymer. Reprecipitation of the resulting polymer from benzene–ethanol afforded a light yellow solid polymer, poly[2,5-(tetramethyldisilanylene)thienylene][5] (**1**), in 63% yield (Scheme I). Polymer **1** thus obtained melts at 155–161 °C without decomposition and is soluble in THF and chlorocarbons. The molecular weight (M_w) of **1** determined by GPC was found to be 17 000, relative to polystyrene standards (M_w/M_n = 2.93).

The structure of **1** was verified by spectroscopic analysis, as well as by elemental analysis. The ^{1}H NMR spectrum of **1** shows two sharp resonances at δ 0.34 and 7.14 ppm, due to the dimethylsilyl protons and olefinic protons of the thienylene ring, respectively. The ^{13}C NMR spectrum reveals three signals at δ −2.5, 135.6, and 143.9 ppm, attributed to the dimethylsilyl carbons and two different kinds of carbons in the thienylene ring. These results clearly indicate that **1** must have the regular alternating arrangement of both groups in the polymer backbone.

The reaction of **2a** with a sodium dispersion in decane at refluxing temperature for 10 h gave poly[2,5-(1,2-dimethyldiphenyldisilanylene)thienylene] (**2**) in 22% yield, after reprecipitation of the resulting polymer from chloroform–ethanol and chloroform–isopropyl alcohol, respectively. In this reaction, insoluble substances were obtained in 45% yield. A similar reaction of **3a** with sodium in decane afforded poly[2,5-(1,2-dimethyldi(p-tolyl)disilanylene)thienylene] (**3**) in 24% yield, along with 55% insoluble polymers. Polymer **2** melts at 68–74 °C, while polymer **3** melts at 92–95 °C without decomposition. Both are soluble in benzene, toluene, ethers, and chlorocarbons. The molecular weights were determined to be 38 000 (M_w/M_n = 5.33) for **2** and 36 000 (M_w/M_n = 5.10) for **3**, relative to polystyrene standards. All spectral data obtained for **5** and **6** are consistent with the proposed structures.[6,7]

Scheme I



Characteristic of the polymers reported here is a strong absorption in the ultraviolet region. Polymer **1** exhibits an absorption at 260 nm, while **2** and **3** absorb at 270 and 287 nm, respectively. As expected, these polymers are highly photoactive, and irradiation of the films prepared from **1**–**3** in air with a 6-W low-pressure mercury lamp leads to the disappearance of the absorption at 260 nm for **1**, at 270 nm for **2**, and at 287 nm for **3**, indicating that homolytic scission of silicon–silicon bonds in the polymer backbone occurs, as observed in the photolyses of the polymers involving disilanylene units and π-electron systems.[2,3]

Like poly[(disilanylene)ethenylenes],[3] poly[(disilanylene)butenyne-1,4-diyls],[8] and poly[(disilanylene)ethynylenes],[9] thin films of polymers **1**–**3** treated with antimony pentafluoride vapor gave conducting films, in which conductivities are in the range 1–10 S/cm. Thus, the conductivity determined by the four-probe method was shown to be 5.47 S/cm for **1**, 2.33 S/cm for **2**, and 1.80 S/cm for **3**.

We have calculated the electronic structures of polymer **1** and poly[(tetrahydrodisilanylene)thienylene] (**4**). All calculations were performed on the basis of the tight-binding SCF-CO (self-consistent-field crystal orbital) method at the level of the CNDO/2 approximation, including all the valence electrons.[10] In the present calculations, silicon 3d atomic orbitals were not used in the basic functions, since they give no discrepancy in the electronic structure of the present polymers including cationic silicons.[11] The optimized structure of each polymer was obtained by using the energy gradient method.

The structures of polymers **1** and **4** are shown in Figure 1 with the bond lengths and angles in the optimized geometries. The calculated electronic properties are listed in Table I. Considering that the Hartree–Fock-type SCF-CO method[12] always leads to the overestimation of the value for the band gap (3–4 times), both polymers show a relatively small value of the band gap, which is calculated to be 7.4 eV for **1** and 7.6 eV for **4**. These values are similar

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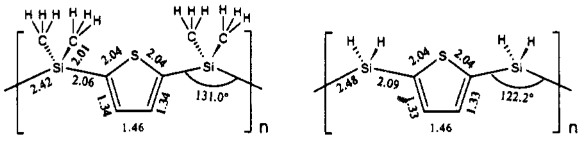

1 **4**

Figure 1.

Table I
Electronic Properties of Polymers 1 and 4[a]

	1	4
HO bandwidth	1.601	1.153
LU bandwidth	0.005	0.228
band gap	7.472	7.624
ionization potential[b]	7.688	7.752
electron affinity	−0.216	−0.128

[a] All values are in eV. [b] Values are uncorrected for the polarization energy of the lattice.

to the calculated value for *trans*-polyacetylene (7.455 eV).[13] Therefore, the results obtained here show that these polymers could be candidates for conductive polymers.

As can be seen in Table I, it is suggested that the introduction of methyl groups does not play an effective role of suppression of the plus charge on the silicon atom.[11]

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(5) Polymer **1**: mp 155–161 °C; M_w 17 000 (M_w/M_n = 2.93); ^{1}H NMR (δ in $CDCl_3$) 0.34 (s, 12 H, Me_2Si), 7.14 (s, 2 H, thienyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −2.5 (Me_2Si), 135.6, 143.9 (thienylene ring carbons). Anal. Calcd for $(C_8H_{14}Si_2S)_n$: C, 48.42; H, 7.11. Found: C, 48.23; H, 7.41.

(6) Polymer **2**: mp 68–74 °C; M_w 38 000 (M_w/M_n = 5.33); ^{1}H NMR (δ in $CDCl_3$) 0.65 (s, 6 H, MeSi), 7.12–7.34 (m, 12 H, thienylene and phenyl ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.3 (MeSi), 127.8, 129.1, 134.7, 135.8 (two peaks) (phenyl ring carbons), 137.5, 142.0 (two peaks) (thienylene ring carbons). Anal. Calcd for $(C_{18}H_{18}Si_2S)_n$: C, 67.02, H, 5.62. Found: C, 67.28; H, 5.67.

(7) Polymer **3**: mp 92–95 °C; M_w 36 000 (M_w/M_n = 5.10); ^{1}H NMR (δ in $CDCl_3$) 0.69 (s, 6 H, MeSi), 2.29 (s, 6 H, *p*-Me), 6.72–7.55 (m, phenyl and thienylene ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.1 (MeSi), 21.5 (*p*-Me), 128.7, 132.3, 132.4, 134.9, 137.4 (phenyl ring carbons), 138.9, 142.1 (two peaks) (thienylene ring carbons). Anal. Calcd for $(C_{20}H_{22}Si_2S)_n$: C, 68.51; H, 6.32. Found: C, 68.48; H, 6.84.

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