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Communications

Synthesis of Organosilanylene–Thienylene Alternating Oligomers Bearing Ether Side Chains. Peculiar Solvatochromic Behavior in Their Fluorescence Spectra

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Summary: Organosilanylene–thienylene alternating oligomers bearing ether side chains were synthesized, and their optical properties were studied. The oligomers exhibited clear solvatochromic shifts in the fluorescence maxima, probably due to the changes in the oligomer conformations, and the emission maxima moved to longer wavelength as the solvent polarity increased.

Polymers composed of π-conjugated units bridged by organosilanylene σ-linkages (σ–π polymers) are of current interest.[1] They may be used as functionality materials, such as photoresists,[2] organic semiconductors,[3] and hole-transporting,[3e,4] photoconducting,[3f,5] and emitting materials.[6] In addition, the highly heat-resistant properties of the polymer materials may be noted.[7] However, the σ–π polymers reported thus far are soluble only in organic solvents of moderate polarity, such as ethers, chlorocarbons, and aromatic compounds.

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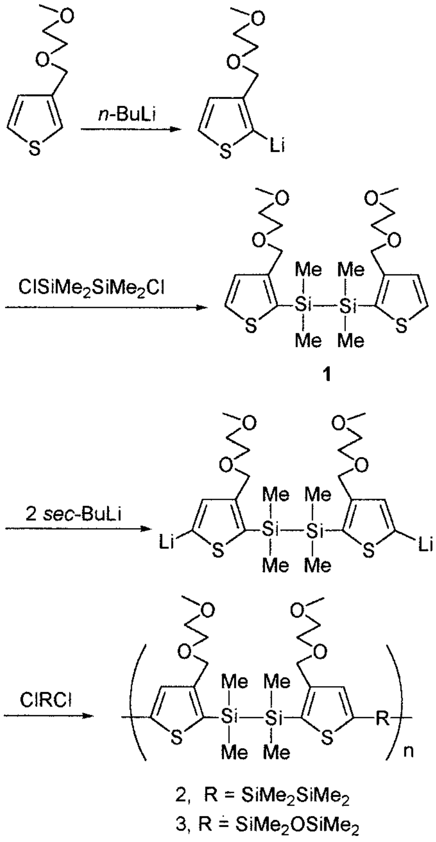
Scheme 1



No $\sigma-\pi$ polymers that are soluble in water and the lower alcohols have been reported, although the solubility in such polar solvents would provide a better chance for their applications in functional materials. Here we report the synthesis of novel organosilanylene−thienylene alternating oligomers bearing ether side chains that are soluble even in methanol/water mixed solvents. Their solvatochromic behavior in the fluorescence spectra is also described.[8]

The monomer 1,2-bis[3-(2,5-dioxahexyl)-2-thienyl]tetramethyldisilane (**1**) was prepared by the reaction of 2-lithio-3-(2,5-dioxahexyl)thiophene with 1,2-dichlorotetramethyldisilane as shown in Scheme 1. Treatment of monomer **1** with 2 equiv of *sec*-butyllithium in THF, followed by addition of 1,2-dichlorotetramethyldisilane or 1,3-dichlorotetramethyldisiloxane to the resulting solution of the α,α'-dilithiated derivative of **1**, afforded the corresponding organosilanylene−thienylene alternating oligomers bearing ether side chains as pale yellow, viscous oils (**2** and **3** in Scheme 1). The molecular weights of the oligomers were determined to be $M_w = 5000$ ($M_w/M_n = 1.5$) for **2** and 4100 ($M_w/M_n = 1.3$) for **3**, by GPC relative to polystyrene standards, after removal of low molecular weight fractions by preparative GPC. The structures of oligomers **2** and **3** were verified by spectral and elemental analysis. Although some unidentified signals of low intensity, probably due to the end groups, were observed in the NMR spectra, the integral ratios of the oligomer signals in their ^{1}H NMR spectra were consistent with the proposed organosilanylene−thienylene repeating structure.[11] For **3**, a small amount of poly(dimethylsiloxane) also was found as a contaminate of the oligomer. This could not be removed even by subjecting the oligomer sample to preparative GPC and silica gel column chromatography. As expected, the oligomers are soluble in almost all of the common organic solvents, from nonpolar hydrocarbons to highly polar ethanol and methanol. They are soluble even in mixed solvents of water/methanol up to the ratio of 40:1, but insoluble in water alone.

The UV absorption maximum of oligomer **2** in cyclohexane appeared at 274 nm, which is at almost the same energy as those of simple poly[disilanylene(2,5-thienylene)]s having no ether side chains (ca. 270 nm), reported previously,[12] and red-shifted from that of monomer **1** (251 nm) in similar nonpolar solvents. This was indicative that the delocalization of π-electrons through the Si−Si σ-orbital ($\sigma-\pi$ conjugation) took place in oligomer **2**, as other $\sigma-\pi$ oligomers and polymers.[1a] Thus the presence of ether chains did not affect the degree of the conjugation. In contrast, the absorption maximum of oligomer **3** was observed at 261 nm in the middle of the maxima of **1** and **2**. Presumably, in oligomer **3**, the $\sigma-\pi$ conjugation along the oligomer backbone is interrupted by the siloxane bond. The siloxanylene units likely act only as the electron-donating substituents of the thienylene units, elevating the HOMO energy level to some extent, resulting in a slight red-shift in the absorption maximum from that of monomer **1**.

Figure 1 shows the solvent dependence of the fluorescence spectra of oligomers **2**, **3**, and **4**. As can be seen in Figure 1a, the fluorescence spectrum of **2** in cyclohexane shows its maxima at 340 and 350 nm, together with a broad shoulder around 400 nm. In THF, however, the fluorescence maximum disappears and only the shoulder remains, which has moved to longer wavelength in methanol. Oligomer **3** also exhibits similar solvatochromism, and the maxima were red-shifted along with the solvent polarity (Figure 1b). This is in contrast to the fact that no evident solvent dependence was observed in the UV profiles of oligomers **2** and **3**, although the absorption coefficiencies were a little affected by the solvent polarity. A similar solvent-dependent red-shift of the fluorescence maximum was observed for oligomer **4** when the solvent was changed from cyclohexane to THF. However, as can be seen in Figure 1, the degree of the red-shift was much smaller than that observed for oligomers **2** and **3**. Oligomer **4** is

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(8) Solvatochromic behavior of polysilanes (ref 9) and polythiophenes (ref 10) that are substituted with ether side chains has been reported.

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(11) Oligomer **2** was obtained in 66% yield, after removal of the low molecular weight fractions by recycling GPC using Shodex columns KF-801 and KF-802 (600 mm × 30 mm ϕ) with benzene as the eluent. Data for **2**: ^{1}H NMR (δ in CDCl$_3$) 0.26 (s, 12H), 0.35 (s, 12H), 3.35 (s, 6H), 3.50 (br s, 8H), 4.34 (s, 4H), 7.27 (s, 2H); ^{13}C NMR (δ in CDCl$_3$) −2.5, −1.9, 59.0, 68.5, 69.3, 72.0, 137.9, 140.9, 143.6, 147.6; ^{29}Si NMR (δ in CDCl$_3$) −25.3, −25.1; GPC (THF) $M_n = 3400$, $M_w = 5000$. Anal. Calcd for $(C_{24}H_{44}Si_4S_2O_4)_n$: C, 50.30; H, 7.74. Found: C, 50.06; H, 7.75. Oligomer **3** was obtained in 59% yield after purification by preparative GPC as above. Data for **3**: ^{1}H NMR (δ in CDCl$_3$) 0.34 (s, 6H), 0.37 (s, 6H), 0.42 (s, 12H), 3.35 (s, 6H), 3.51 (s, 8H), 4.34 (s, 4H), 7.37 (s, 2H); ^{13}C NMR (δ in CDCl$_3$) −2.0, 1.8, 58.9, 68.5, 69.4, 71.9, 137.7, 140.7, 144.9, 147.3; ^{29}Si NMR (δ in CDCl$_3$) −5.6, −25.2; GPC $M_n = 3200$, $M_w = 4100$. Anal. Calcd for $(C_{24}H_{44}Si_4S_2O_5)_n$: C, 49.10; H, 7.55. Found: C, 49.15; H, 7.88.

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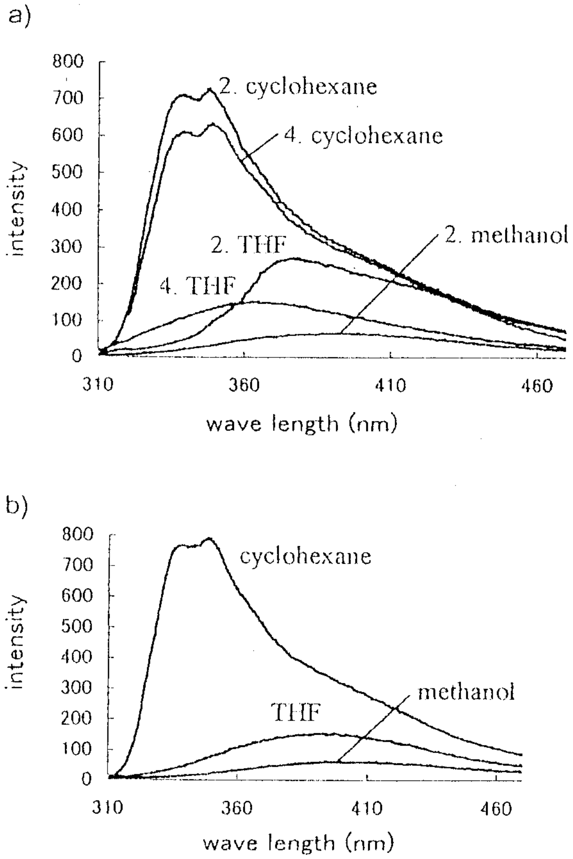
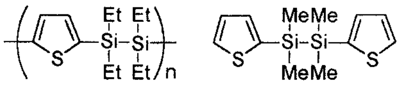


Figure 1. Fluorescence spectra of (a) oligomers **2** and **4** and (b) oligomer **3**, excited at 280 nm.

Chart 1



4 **5**

insoluble in methanol, and further studies on the solvatochromism could not be carried out.

Since the concentration did not affect the fluorescence profiles of **2** and **3**, the solvatochromic behavior was not due to the intermolecular interactions of chromophores but to intramolecular ones. To know more about the solvatochromism of **2**−**4**, we carried out molecular orbital calculations on a model compound, 1,1,2,2-tetramethyl-1,2-di(2-thienyl)disilane (**5** in Chart 1), by the MOPAC/PM3 method.[13] For the calculations, the dihedral angle of C(α)−Si−Si−C(α) was rotated from −60° to 60° and bond lengths, angles, and the other dihedral angles were optimized at this level. Figure 2 represents the changes of heats of formation as a function of the C(α)−Si−Si−C(α) angles, as derived from the calculations. As can be seen in Figure 2a, the heats of formation in vacuo increased along the dihedral angle from −60° passing through the maximum value at 0°, at which **5** has the eclipsed conformation with respect to the Si−Si bond, then decreased monotonically. In contrast, similar calculations for **5** in water by applying COSMO approximation led to a lowering of the total energy, or even an energy minimum at the dihedral angle of 10°. This clearly suggests the existence of an eclipsed form as a more stable conformer than that in vacuo, which may allow the $\pi-\pi$ aggregation (Figure 2b). This is probably due to the favored solvation of the eclipsed form with its larger dipole moment than the others. For the present oligomers, the thiophene ring would interact not only with the neighboring thiophene rings but also with any other thiophene rings in the oligomer main chain, to provide aggregated π-systems that are the origins of the red-shifts in the fluorescence spectra along the solvent polarity.

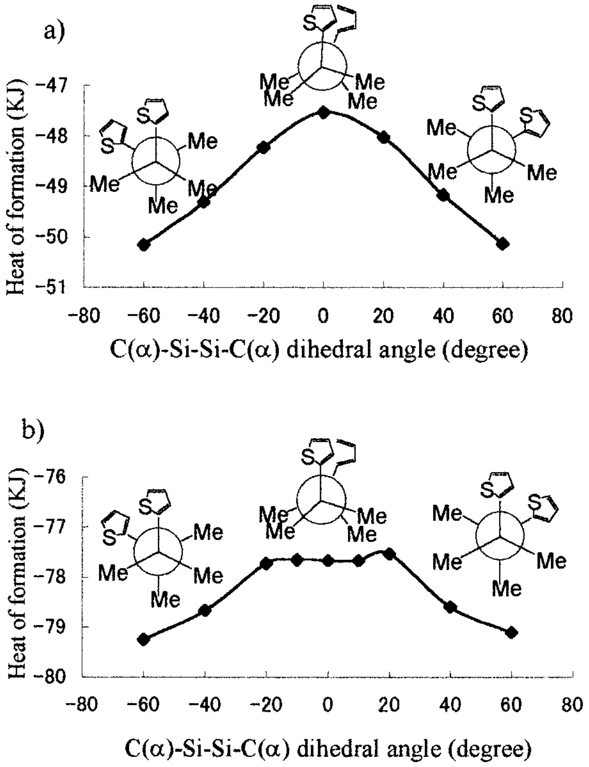


Figure 2. Plots of dihedral angles of C(α)−Si−Si−C(α) vs heats of formation for compound **5** (a) in vacuo and (b) in water, derived from MOPAC/PM3 calculations. Calculations in water were performed by applying COSMO approximations with the dielectric constant of 78.4.

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Supporting Information Available: Experimental details for the preparation of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) *Win MOPAC 3.0 Pro*; Fujitsu Co., Japan, 2000.