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Polymeric Organosilicon Systems. 28. Preparation and Properties of Novel $\sigma-\pi$ Conjugated Polymers with Alternating Disilanylene and 2,5-Diethynylenesilole Units in the Backbone

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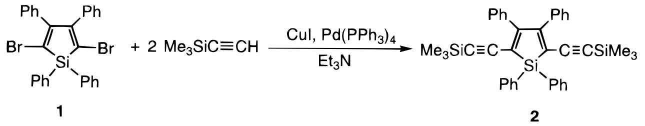
Introduction. Organosilicon polymers composed of an alternating arrangement of a organosilicon unit and π-electron system represent a new class of conjugated polymers.[1] They are potentially useful as functional materials, such as organic semiconductors[1a] and photoresists.[2] In addition, this type of polymer can be used as thermal precursors to silicon carbide.[1d,3]

Recently, silole ring systems have been extensively studied as the new π-electron system with unusual optical properties. The remarkably red-shifted UV absorptions and high electron-transporting properties of the compounds containing the silole ring would result from their low-lying lowest unoccupied molecular orbital (LUMO) due to the $\sigma^*-\pi^*$ interaction between the silole silicon atom and the π-orbitals.[4] Although many papers concerning the synthesis of polymers and oligomers containing the silole ring have been published to date,[5,6] only a few refer to polymers bearing 2,5-linked silole rings in the backbone.[6] In the course of studies concerning the synthesis of silole-containing conjugated polymers,[7,8] we have prepared polymers having repeating organosilicon-2,5-diethynylenesilole units in the backbone, by dehydrobromination of 2,5-dibromosilole and diethynyldi- and monosilanes in the presence of a CuI/Pd$(PPh_3)_4$ catalyst.[9]

Results and Discussion. The starting monomer 2,5-dibromo-1,1,3,4-tetraphenylsilole (**1**) was prepared as reported by Tamao et al.[6b] Tamao et al. have also reported the synthesis of 2,5-bis(phenylethynyl)-1,1,3,4-tetraphenylsilole from the reaction of **1** and phenylacetylene in the presence of a CuI/Pd$(PPh_3)_4$ catalyst in a mixed solvent of THF and triethylamine.[6b] First, we examined a model reaction to confirm that CuI/Pd$(PPh_3)_4$-catalyzed dehydrobromination is applicable to the synthesis of 2,5-bis(silylethynyl)silole. Thus, when **1** was treated with 2 equiv of (trimethylsilyl)acetylene under similar conditions, 2,5-bis(trimethylsilylethynyl)-1,1,3,4-tetraphenylsilole (**2**) was obtained in 94% yield, as the sole volatile product (Scheme 1).

Scheme 1



Scheme 2

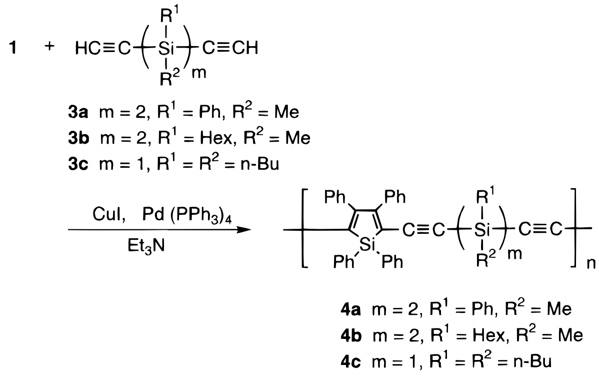


Table 1. Preparation of Polymers 4a−c

polymer	yield (%)	mp (°C)	M_w (M_w/M_n)[a]
4a	38	88−91	8 000 (1.6)
4b	45	78−84	12 000 (1.2)
4c	63	84−88	13 900 (2.4)

[a] Determined by GPC, relative to polystyrene standards.

Table 2. Properties of Polymers 4a−c, 5, and 6

		TGA[b]		CV[e]		
polymer	UV[a] (λ_{max}/nm)	$T_d{}^5$ [c]	weight loss (%)[d]	E_{pa} (V)[f]	E_{pc} (V)[g]	conductivity (S cm^{-1})[h]
4a	412	354	52	0.58	0.44	3.7×10^{-3}
4b	415	401	59	0.62	0.52	1.9×10^{-3}
4c	408	434	67	0.52	0.42	2.1×10^{-4}
5	300	309	76	not observed		$<10^{-10}$
6	310	474	79	0.76	0.52	3.8×10^{-2}

[a] In THF. [b] Measured in a nitrogen atmosphere with a heating rate of 20 °C/min. [c] Temperature resulting in a 5% weight loss. [d] Total weight loss at 1000 °C based on the initial weight. [e] 4 mM solution in THF containing 100 mM of lithium perchlorate as a supporting electrolyte at a scan rate of 50 mV/s in a range of 0.0−1.2 V vs SCE, using glassy carbon and a platinum plate as the working and counter electrode, respectively. [f] Anodic peak potential vs SCE. [g] Cathodic peak potential vs SCE. [h] Doped with $FeCl_3$ vapor, determined by the four-probe method.

Similar treatment of dibromosilole **1** with diethynyldi- and monosilanes (**3a**−**c**), followed by reprecipitation of the organic products from methanol−chloroform, afforded polymers **4a**−**c** in 38−63% yields, as shown in Scheme 2 and Table 1. The rather low yields for the polymers are ascribed to the formation of methanol-soluble oligomers which were separated by reprecipitation. Polymers **4a**−**c** are yellow solids and soluble in common organic solvents, such as hydrocarbons, ethers, and halocarbons, but are insoluble in methanol.

Table 2 summarizes some properties of polymers **4a**−**c**, together with those of analogous ethynylene polymers **5**[7] and **6**, which have a 3,4-linked silole and 1,4-phenylene ring, respectively, for comparison (Chart 1). As listed in Table 2, polymers **4a**−**c** show strong UV absorptions at about 410 nm, which are red-shifted by about 20 nm from the model compound **2** ($\lambda_{max} = 390$ nm). This is probably due to the intramolecular interaction between diethynylenesilole units. Similar enhancement of intramolecular interaction between π-conjugated units by a silicon spacer has been previously reported.[10] The absorptions of disilanylene polymers **4a**,**b** are only slightly red-shifted from that of silylene polymer **4c**, indicating that $\sigma-\pi$ conjugation between

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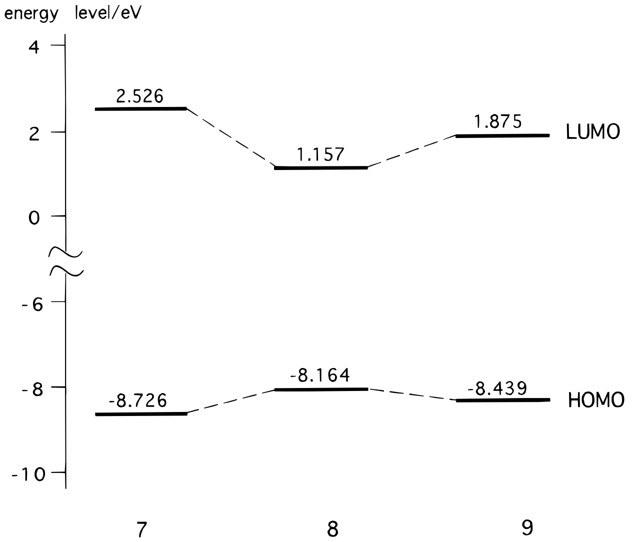
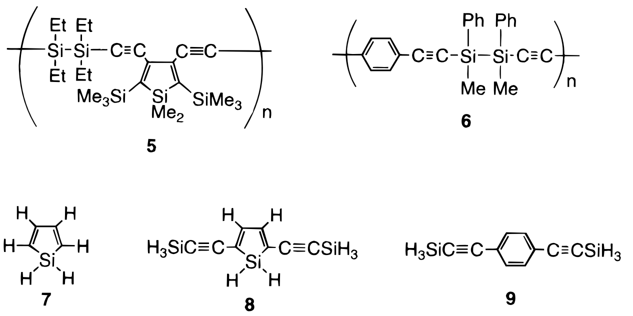


Figure 1. Relative HOMO and LUMO energy levels for compounds **7**−**9**, derived from RHF/6-31G calculations.

Chart 1



the π-electron system and disilanylene unit is not significantly operative in the present disilanylene polymers. This is in accordance with recent findings of the reduced σ−π conjugation[1d] in poly[(disilanylene)oligo(2,5-thienylenes)][11] ($[\mathrm{SiR_2SiR_2{-}(C_4H_2S)_m}]_n$, $m = 1-5$) and poly[(disilanylene)oligophenylenes][12] ($[\mathrm{SiR_2SiR_2{-}(C_6H_4)_m}]_n$, $m = 1-4$) along the expansion of the π-conjugated carbon units. The σ−π conjugation is no longer important for the disilanylene polymers having terthiophene and terphenylene or longer units ($m \geq 3$). Interestingly, the absorptions of polymers **5** and **6** are blue-shifted, relative to **4a**−**c**. For polymer **5**, cross conjugation in the 3,4-diethynylenesilole system may be the reason for the blue shift.

To clarify the origin of red-shifted UV absorption maxima for polymers **4a**−**c**, relative to that of polymer **6**, we carried out molecular orbital (MO) calculations on model compounds (**7**−**9**, Chart 1). The results are shown in Figure 1. As can be seen in Figure 1, the HOMO(highest occupied molecular orbital)−LUMO energy gap of **8** is calculated to be the smallest of the model compounds. The smaller band gap of **8** relative to **7** suggests the existence of favored orbital interactions between the silole ring system and ethynyl π-orbitals in **8**. The difference in LUMO levels (ca. 0.72 eV) for **8** and **9** is calculated to be much greater than that of the respective HOMOs (ca. 0.28 eV), and hence is primarily responsible for the smaller HOMO−LUMO gap for **8**. Tamao et al. have previously reported similar results of MO calculations for some heterocycles including silole **7**, pyrrole, furan, and thiophene, for which **7** has the smallest HOMO−LUMO gap arising primarily from its lower-lying LUMO.[4c]

Thermal properties of polymers **4a**−**c** were examined by the thermogravimetric analysis (TGA) in a temperature range of 20−1000 °C under an atmosphere of nitrogen. The results are also summarized in Table 2. The TGA profiles for the polymers are essentially the same, showing continuous weight loss from 300 to 500 °C. When compared with polymers **5** and **6**, the thermal decomposition of polymers **4a**−**c** occurs at higher temperatures and gives higher char yields at 1000 °C. Although the origin of the higher thermal stability of polymers **4a**−**c** is still unclear, a high degree of conjugation in the polymer chains of **4a**−**c** may be responsible for the improved stability of these polymers.

Polymers **4a**−**c** are anodically active, and their cyclic voltammograms (CV) reveal reversible waves with the oxidation peaks around 0.52−0.62 V and their reductive couples around 0.42−0.52 V vs SCE, as shown in Table 2. In contrast, polymer **5** was found to be electrochemically inactive in the range from 0.0 to +1.2 V under the same conditions, again indicating the absence of extended electron delocalization in **5**. Polymer **4a** is oxidized at 0.18 V lower potential, as compared with **6** with the same substituents on the silicon atoms, in agreement with the results of MO calculations which predict a higher HOMO level for the model compound **8** relative to **9**.

Polymers **4a**−**c**, **5**, and **6** are insulators in their undoped state. Of these, **4a**−**c** and **6** became conducting when doped with $\mathrm{FeCl_3}$ vapor. While the conductivity of polymer **5** treated with $\mathrm{FeCl_3}$ was less than 10^{-10} S/cm, the conductivities of the films of polymers **4a**−**c** and **6** increased during the doping period and reached the maximum values listed in Table 2, after about 20 h. We have not yet obtained any information concerning the doped polymer structures. However, it is not likely that some decomposition is involved in the doping of the polymers, since their structures are highly stable toward electrochemical oxidation as evidenced by reversible CVs in the range of 0.0−1.2 V vs SCE.[13] As shown in Table 2, the maximum conductivities achieved for polymers **4a**−**c** were much higher than that of **5**, but slightly lower than that of **6**. Regarding the higher conductivity of **6**, it is likely that factors other than just the band gap of the polymer molecule are important (e.g., morphology of the polymer film, which can effect to the hole-drift mobility and carrier density in the solid film.)

In conclusion, we have prepared polymers **4a**−**c** having 2,5-diethynylenesilole systems linked by a organosilicon bridge and demonstrated that these polymers exhibit extended conjugation along the polymer backbone. As a consequence, these polymers are presented as new conjugated polymers with small band gaps and high thermal stability.

Experimental Section. All reactions were carried out under an atmosphere of purified nitrogen. Triethylamine was dried over KOH and distilled just before use.

Preparation of compound **2**: A mixture of 0.544 g (1.00 mmol) of **1**, 0.097 g (0.178 mmol) of trimethylsilylacetylene, 3.7 mg (0.02 mmol) of CuI, and 0.024 g (0.02 mmol) of $\mathrm{Pd(PPh_3)_4}$ in 10 mL of $\mathrm{NEt_3}$ was heated to reflux for 13 h. The resulting salts were filtered off. After evaporation of the solvent, the residue was recrystallized from hexane to give 0.51 g (94% yield) of **2**: UV $\lambda_{\max}$ (THF) 390 nm; IR $\nu_{\mathrm{C\equiv C}}$ 2115 cm^{-1}; ^{1}H NMR

δ ($CDCl_3$) 0.06 (s, 18H, Me), 7.35−7.87 (m, 20H, Ph); ^{13}C NMR δ ($CDCl_3$) 1.0 (MeSi), 107.6, 113.8 ($C\equiv C$), 121.7 (silole), 125.0, 127.7, 127.9, 128.4, 130.2, 132.2, 132.4, 134.3 (Ph), 162.0 (silole).

Polymers **4a**−**c** were obtained from similar procedures as described for **2**, except for a longer reaction period of 44 h. For **4c**, the reaction was carried out not at the refluxing temperature but at 50 °C. Spectral data for **4a**: mp 88−91 °C; $M_w = 8\,000$ ($M_w/M_n = 1.6$); UV λ_{max} (THF) 412 nm; IR $\nu_{C\equiv C}$ 2111 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.02 (s, 6H, Me), 7.04−7.67 (m, 30H, Ph); ^{13}C NMR δ ($CDCl_3$) −3.9 (MeSi), 102.0, 109.7 ($C\equiv C$), 121.4 (silole), 127.4, 127.7, 128.3, 128.8, 129.2, 130.3, 130.6, 134.5, 134.8, 135.5, 136.7, 137.1 (Ph), 164.5 (silole). Anal. Calcd for $(C_{46}H_{36}Si_3)_n$: C, 77.41; H, 5.01. Found: C, 77.63; H, 5.39. Spectral data for **4b**: yellow powder; mp 78−84 °C; $M_w = 12\,000$ ($M_w/M_n = 1.2$); UV λ_{max} (THF) 415 nm; IR $\nu_{C\equiv C}$ 2110 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.08 (s, 6H, Me), 0.85−1.52 (m, 26H, Hex), 7.06−7.84 (m, 20H, Ph); ^{13}C NMR δ ($CDCl_3$) −4.4, −4.6 (MeSi), 14.2, 22.6, 24.5, 29.7, 31.5, 33.6 (Hex), 104.5, 108.1 ($C\equiv C$), 121.3 (silole), 127.1, 127.5, 128.1, 129.0, 130.4, 135.3, 135.5, 137.1 (Ph), 163.58 (silole). Spectral data for **4c**: yellow powder; mp 84−88 °C; $M_w = 13\,900$ ($M_w/M_n = 2.4$); UV λ_{max} (THF) 408 nm; IR $\nu_{C\equiv C}$ 2113 cm^{-1}; ^1H NMR δ ($CDCl_3$) 0.37−1.31 (m, 18H, Bu), 6.74−7.89 (m, 20H, Ph); ^{13}C NMR δ ($CDCl_3$) 13.8, 14.8, 25.8, 26.1 (BuSi), 102.1, 106.4 ($C\equiv C$), 121.3 (silole), 127.1, 127.7, 128.2, 129.3, 130.6, 134.2, 135.3, 136.9 (Ph), 164.4 (silole); ^{29}Si NMR δ ($CDCl_3$) −34.8, −9.9.

Polymer **6** was prepared as reported in the literature.[14] The ab initio MO calculations were carried out with a Gaussian 94 program at the RHF/6-31G level on a J932 server (CRAY) at Information Processing Center, Hiroshima University. Tamao et al. have previously reported the results of MO calculations of compound **7** at a higher level, RHF/6-31G*.[4c] However, the HOMO and LUMO energy levels reported are consistent with the present data.

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