

Selective Substitution of Hex₂SiFCl for the Preparation of Polymers with Two Different Alternate π -Electron Systems Linked by Hex₂Si Units

Joji Ohshita, Kazuaki Kawashima, Arihiro Iwata, Heqing Tang, Miho Higashi, and Atsutaka Kunai

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Reprint requests to Dr. J. Ohshita or Prof. Dr. A. Kunai. E-mail: jo@hiroshima-u.ac.jp or akunai@hiroshima-u.ac.jp

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Organosilicon polymers having a regular alternate arrangement of –Hex₂Si– π –Hex₂Si– π' – (π , π' = π -electron system) were prepared by successive treatment of Hex₂SiFCl with dilithiated π -conjugated compounds, Li– π –Li and Li– π' –Li (π = diethynylanthracene, diethynylpyrene, diethynylcarbazole; π' = bithiophenediyl, terthiophenediyl). UV-vis absorption spectra and cyclic voltammograms of the resulting polymers indicated that the two π -electron systems, π and π' , are electronically isolated, while the emission spectra indicated that energy transfer between the π -electron systems occurred in the excited states.

Key words: Organosilicon Polymers, Chlorofluorosilanes, Selective Addition

Introduction

There has been an interest in polymers whose backbone consists of π -conjugated units linked by organosilanylene bridges [1, 2]. Red-shifted UV absorption bands and lower CV oxidation potentials relative to the respective monomeric π -conjugated compounds are often observed for these polymers. This is probably due to the interaction between the silicon- σ - and carbon- π -orbitals [1–3] and/or electron-donating properties of the silicon moiety, which elevates the HOMO energy level of the π -electron system [4]. Enhanced through-space interactions between π -electron systems by a silicon bridge were also noted [5]. Due to these unique electronic states, these polymers have been extensively studied as functional materials for hole-transport in EL devices, photoconductors, and conducting organic films upon p-type doping. However, there is still a demand for novel synthetic procedures leading to these types of the polymers and further studies to develop new methodologies seem to be necessary.

Recently, we reported the selective synthesis of chlorofluorosilanes from dihydrosilanes [6]. Treatment of dihydrosilanes with a mixture of 2 equiv of CuCl₂ and 1 equiv of KF in the presence of a catalytic amount

of CuI gives fluorohydrosilanes that can be then transformed to chlorofluorosilanes by similar CuI-catalyzed reactions with 2 equiv of CuCl₂, as shown in Scheme 1. Fluoro-chlorosilanes are potentially useful as bifunctional organosilicon reagents with graded reactivities. Different bond energies of Si–Cl and Si–F (*e. g.* Me₃Si–Cl 113 kcal mol^{–1} and Me₃Si–F 159 kcal mol^{–1}) [7] allow selective substitution of the Si–Cl bond upon interaction with 1 equivalent of a nucleophile, while the Si–F bond remains untouched. In this paper we report the synthesis of polymers with a regularly alternating arrangement of two different π -electron systems linked by organosilanylene units, by the successive treatment of Hex₂SiFCl with two kinds of dilithiated π -conjugated compounds. Optical and electrochemical properties of the resulting polymers also are described.



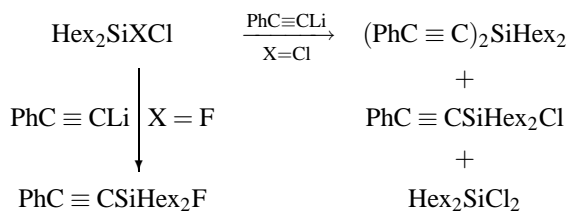
Scheme 1.

Results and Discussion

Polymer syntheses

First, we carried out a model reaction to examine the selectivity of the nucleophilic substitution of a chlo-

rofluorosilane (Scheme 2). The reaction of Hex₂SiFCl with 1 equiv of PhC≡CLi in ether at -50 °C afforded the mono-substituted PhC≡CSiHex₂F in 86% isolated yield. Neither di-substituted (PhC≡C)₂SiHex₂ nor F-substituted PhC≡CSiHex₂Cl was detected by GC-MS analysis of the reaction mixture, indicating the high selectivity of this reaction. This is in marked contrast to the reaction of Hex₂SiCl₂ with PhC≡CLi under the same conditions, which gave a mixture of PhC≡CSiHex₂Cl, (PhC≡C)₂SiHex₂, and the starting material Hex₂SiCl₂ in a ratio of 17 : 42 : 41.



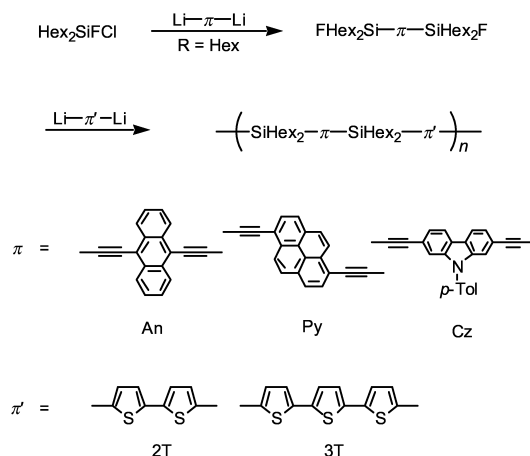
Scheme 2.

Next, we carried out a two-step polymerization reaction using Hex₂SiFCl as a monomer (Scheme 3). When Hex₂SiFCl was treated with 0.5 equiv of di(lithioethynyl)arenes under the same conditions as those of the model reaction, the corresponding bis[(fluorodihexylsilyl)ethynyl]arenes were found to be formed quantitatively by GC-MS analysis. No other volatile products were detected in the reaction mixtures. Further addition of dilithio- or terthiophene to the mixtures led to disappearance of the GC peaks of bis[(fluorodihexylsilyl)ethynyl]arenes. After hydrolysis, the organic products were subjected to reprecipitation from methanol-ether or to preparative GPC to remove the low molecular weight oligomers. Yields and molecular weights of the resulting copolymers are given in Table 1. These copolymers were obtained as a dark-orange viscous oil and are soluble in common organic solvents, such as hexane, toluene, ether, THF, chloroform, and ethyl acetate, but barely soluble in acetonitrile and water. They are also slightly soluble in alcohols except for **An-2T**. Polymer **An-2T** is insoluble in methanol, but soluble in the higher alcohols. The polymer structures were verified by spectrometric analysis. IR spectra revealed single bands due to the bond stretches $\nu(\text{C}\equiv\text{C})$ at about 2100 cm^{-1} . Although some unidentified signals of low intensity were observed in the ¹³C NMR spectra, probably due to the end groups, all intense signals could be assigned to the expected alternating structures. The integral ratios of

Table 1. Data for polymer synthesis.

Polymer ^a	Yield [%] ^b	M _w (M _w /M _n) ^c
An-2T	72	7300 (1.6)
An-3T	24	5600 (1.5)
Py-2T	36	8800 (1.5)
Cz-2T	40	5400 (1.2)
Cz-3T	22	3500 (1.3)

^a Abbreviation of the polymer stands for π -electron systems involved in the backbone (see Scheme 3); ^b after purification by preparative GPC, except for **An-2T**, which was purified by reprecipitation from chloroform-ethanol; ^c determined by GPC, relative to polystyrene standards.



Scheme 3.

the ¹H NMR spectra were also consistent with the proposed structures.

Optical and electrochemical properties of the polymers

Table 2 summarizes UV-vis spectral data of the present copolymers, together with those of the corresponding homo polymers, **An** [4], **Py** [8], **Cz** [9], **2T**, and **3T** [10], reported previously, for comparison (Chart 1). As can be seen in Table 2, the absorptions of the new copolymers are composed from the different kinds of π -conjugated systems in the polymer backbone represented by the bands of the homo polymers.

Cyclic voltammograms of the polymer films prepared by spin-coating from chloroform solutions on ITO glass plates were recorded in acetonitrile containing LiClO₄ as the supporting electrolyte in a sweep rate of 50 mV/sec. The oxidation occurred irreversibly and no cathodic counterparts were observed in CVs, similar to other polymers with alternating organosilanylene- π -electron system, reported previously [4]. After sweeping in the potential range of 0.0–2.0 V vs. Ag/Ag⁺, the polymer films were completely

Table 2. UV and CV data of the polymers.

Polymer	UV $\lambda_{\max}/\text{nm}^a$ ($\epsilon \times 10^3$) ^b	CV oxidation peak potential ^c / V vs. Ag/Ag ⁺
An-2T	445 (47), 418 (41), 396 (16), 323 (18), 272 (145)	(1.1), 1.2
An-3T	446 (52), 419 (44), 395 (27), 379 (23), 272 (140)	(1.0), 1.1
Py-2T	402 (140), 394 (87), 376 (83), 357 (45), 322 (34), 295 (87), 283 (48), 252 (85), 242 (78), 230 (77)	(1.0), 1.2, 1.4
Cz-2T	320 (50), 296 (86), 259 (76)	1.2, 1.5
Cz-3T	361 (22), 297 (75), 259 (73)	1.0, 1.1, 1.5
An	448 (30), 419 (21), 394 (9), 271 (50)	(0.8), 1.2
Py	403 (64), 394 (43), 374 (41), 356 (20), 294 (48), 283 (27), 252 (44), 242 (37), 230 (31)	(0.8), 1.2
Cz	295 (66), 258 (61)	1.2
2T	336 (17)	1.1
3T	384 (17)	0.9, 1.0

^a Italic number indicates the absorption maximum ascribed to bi- or terthiophene unit, respectively; ^b ϵ is based on the polymer unit mole; ^c number in parenthesis indicates the potential of a shoulder.

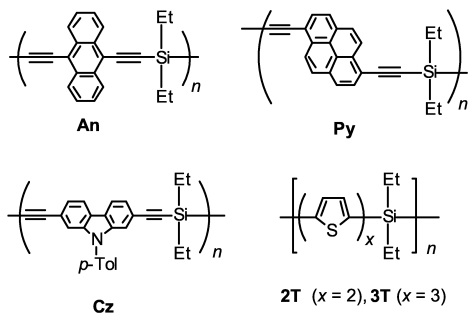


Chart 1.

dissolved. As listed in Table 2, the oxidation peaks of the copolymer films at the first scan appeared around 1.0 V, almost the same potentials as those observed for the homo polymers **An**, **Py**, **Cz**, **2T**, and **3T**. These results indicated that no obvious interaction took place between the π -electron systems in the present copolymers.

However, the emission spectra of the polymers in THF clearly proved interaction between π -electron systems in the excited states. Fig. 1(a) represents emission spectra of polymers **An-2T**, **An-3T**, and **An**. Interestingly, the polymers exhibited quite similar profiles, regardless of the presence or absence and chain length of the oligothiophene units in the polymers. No emission bands were observed for **An-2T** and **An-3T** in the region below 440 nm. This is in contrast to the emission spectra of silanylene-oligothienylene

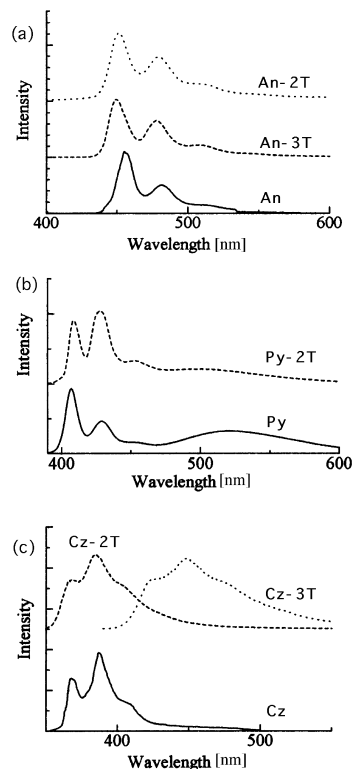


Fig. 1. Emission spectra of (a) diethynylantracene-, (b) diethynylpyrene, and (c) diethynylcarbazole-containing polymers.

polymers **2T** and **3T** in THF, which showed intense bands at 372 and 423 nm, respectively. Excitation spectra of **An-2T** and **An-3T** monitored for the emission at 520 nm closely resembled the UV-vis absorption spectra. Furthermore, excitation of the polymers at the absorption maxima of oligothiophene units again led to emission only from the diethynylantracene units, with approximately the same intensity as obtained by excitation of the diethynylantracene units. These results indicated clearly that the effective energy transfer from the excited oligothiophenylene units to the diethynylantracene units occurred. Similar energy transfer was observed also for polymer **Py-2T**, as depicted in Fig. 1(b). Again, emission bands only from diethynylpyrene units appeared even when the bithiophene units were excited. Broad emission bands centered at about 520 nm in this spectrum may be due to the intramolecular stacking of π -systems. Similar π -stacking giving rise to red-shifted broad emission bands was reported for di- and trisilanylene-diethynylantracene alternating polymers, previously [4]. In contrast to the diethynylantracene- and pyrene-containing polymers,

diethynylcarbazole-polymers **Cz-2T** and **Cz-3T** exhibited different emission profiles depending on the oligothiophene chain length. Thus, as can be seen in Fig. 1(c), **Cz-2T** emitted light arising mainly from the diethynylcarbazole units, although the emission from bithiophene unit may overlap the band to some extent, whereas the spectrum of **Cz-3T** revealed a broad band centered at 450 nm without any detectable emission from diethynylcarbazole units. In this case, energy transfer from diethynylcarbazole units to terthiophene units may be involved. A shoulder at about 420 nm is probably due to the terthiophene emission, but broad bands in the lower energy region may result from intramolecular interaction of the π -units.

In conclusion, we prepared polymers with two alternating kinds of π -electron systems linked by dihexylsilylene bridges. In these polymers, energy transfer occurred between the π -electron systems in the excited states. Since no obvious electronic interactions between the π -electron systems were observed with respect to the UV-vis spectra and CVs, it seems unlikely to assume a through-bond interaction for the energy transfer. Presumably, through-space interactions would be responsible for the observed energy transfer [5].

Experimental Section

General procedures

All reactions were carried out under an inert atmosphere. Diethyl ether and THF used as the solvents were dried over sodium-potassium alloy and distilled just before use. Monomers, diethynylanthracene [11], diethynylpyrene [8], and diethynylcarbazole [9] were prepared as reported in the literature.

Model reaction

To a solution of 1.38 g (5.46 mmol) of chlorofluorodihexylsilylene in 80 ml of ether was added slowly a solution of phenylethynyllithium prepared from 0.557 g (5.45 mmol) of ethynylbenzene and an equimolar amount of *n*-butyllithium in 50 ml of ether at -50 °C. The mixture was stirred at -50 °C for 1 h then allowed to warm to room temperature. After filtration from the resulting salts and evaporation of the solvent, the residue was subjected to trap-to-trap-type distillation with gentle heating of the distillation flask under reduced pressure to give 1.49 g (86% yield) of fluorodihexyl(phenylethynyl)silane: MS m/z 318 [M^+], 299 [$M^+ - F$], 233 [$M^+ - Hex$], 217 [$M^+ - C\equiv CPh$]. $-^1H$ NMR (395 MHz, $CDCl_3$) δ = 0.65–0.75 (m, 4H, $SiCH_2C_5H_{11}$), 0.91 (t, 6H, $SiC_5H_{10}CH_3$, J_{H-H} = 6.6 Hz), 1.30–1.55 (m, 16H, $SiCH_2C_4H_8CH_3$), 7.30–7.40 (m, 3H, Ph), 7.50–7.55 (m,

2H, Ph). $-^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 14.10 (d, $SiCH_2C_5H_{11}$, J_{C-F} = 15.8 Hz), 14.05, 22.05, 22.54, 31.48, 32.71 ($SiCH_2C_5H_{11}$), 88.77 (d, $SiC\equiv CPh$, J_{C-F} = 24.4 Hz), 106.74 ($SiC\equiv CPh$), 122.09 (ipso Ph), 128.27, 129.17, 132.18 (phenyl ring HC). $-C_{20}H_{31}FSi$: calcd. C 75.41, H 9.81; found C 75.33, H 9.75.

Polymer synthesis

To a solution of 0.405 g (1.60 mmol) of chlorofluorodihexylsilylene in 60 ml of ether was added slowly a solution of 9,10-di(lithioethynyl)anthracene prepared from 0.181 g (0.800 mmol) of 9,10-diethynylanthracene and two equivalents of methyllithium in 50 ml of ether at -50 °C. The mixture was stirred at -50 °C for 12 h. The flask was then cooled to -80 °C and a solution of 5,5'-dilithio-2,2'-bithiophene prepared from 0.259 g (0.800 mmol) of 5,5'-dibromo-2,2'-bithiophene and two equivalents of *n*-butyllithium in 50 ml of ether was added to the mixture. The resulting mixture was allowed to warm to room temperature and stirred at this temperature for 12 h. 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 dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was reprecipitated from methanol-ether to give 0.452 g (72% yield) of **An-2T**: Mw = 7300, Mw/Mn = 1.6. $-^1H$ NMR (395 MHz, $CDCl_3$) δ = 0.7–1.9 (m, 52H, SiC_6H_{13}), 7.2–7.5 (m, 4H, thiophene H), 7.55–7.6 (m, 4H, anthracene H), 8.6–8.75 (m, 4H, anthracene H). $-^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 14.12, 15.15, 22.57, 23.98, 31.52, 32.96 (Hex), 104.06, 104.13 ($C\equiv C$), 118.48, 127.06, 127.26, 132.50 (anthracene), 125.48, 134.38, 136.74, 143.33 (thiophene). $-IR$ ν_{2129} ($C\equiv C$) cm^{-1} . $-(C_{50}H_{64}Si_2S_2)_n$: calcd. C 76.46, H 8.21; found C 74.01, H 8.47. Lower carbon content determined by combustion analysis than the theoretical value is often observed for organometallic polymers [4, 12]. This is probably due to the formation of carbon-containing inorganic materials, such as silicon carbide, during the analysis.

Polymers **An-3T**, **Py-2T**, **Cz-2T**, and **Cz-3T** were prepared in a similar fashion to above and purified by preparative GPC eluting with benzene. Data for **An-3T**: Mw = 5600, Mw/Mn = 1.5. $-^1H$ NMR (395 MHz, $CDCl_3$) δ = 0.5–1.9 (m, 52H, SiC_6H_{13}), 7.0–7.4 (m, 6H, thiophene H), 7.6–7.7 (m, 4H, anthracene H), 8.5–8.75 (m, 4H, anthracene H). $-^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 14.15, 15.13, 22.60, 24.19, 31.66, 32.97 (Hex), 103.42, 104.09 ($C\equiv C$), 118.50, 127.11, 127.26, 132.53 (anthracene), 124.49, 124.62, 125.06, 136.30, 136.68, 143.16 (thiophene). $-IR$ ν_{2129} ($C\equiv C$) cm^{-1} . $-(C_{54}H_{66}Si_2S_3)_n$: calcd. C 74.76, H 7.67; found C 74.64, H 7.61. Data for **Py-2T**: Mw = 8800, Mw/Mn = 1.5. $-^1H$ NMR (395 MHz, $CDCl_3$) δ = 0.75–1.85 (m, 52H, SiC_6H_{13}), 7.1–7.45 (m, 4H, thiophene), 8.0–8.25 (m, 6H, pyrene ring H), 8.6–8.75 (m, 2H, pyrene ring

H). – ¹³C{¹H} NMR (100 MHz, CDCl₃) δ = 14.13, 15.11, 22.61, 23.90, 31.52, 32.97 (Hex), 96.55, 106.53 (C≡C), 117.98, 123.90, 125.10, 126.51, 128.30, 130.46, 131.39, 132.50 (pyrene), 125.39, 134.60, 136.63, 143.32 (thiophene). – IR ν 2144 (C≡C) cm⁻¹. – (C₅₂H₆₄Si₂S₂)_n: calcd. C 77.16, H 7.97; found C 77.00, H 8.19. Data for **Cz-2T**: Mw = 5400, Mw/Mn = 1.2. – ¹H NMR (395 MHz, CDCl₃) δ = 0.7–1.7 (m, 52H, SiC₆H₁₃), 2.48 (s, 3H, CH₃-C₆H₄), 7.1–7.6 (m, 12H, aromatic H), 8.2–8.3 (m, 2H, aromatic H). – ¹³C{¹H} NMR (100 MHz, CDCl₃) δ = 14.14, 15.12, 22.63, 23.76, 31.50, 32.96 (Hex), 21.24 (CH₃-C₆H₄), 88.25, 108.76 (C≡C), 125.26, 134.85, 136.55, 143.20 (thiophene), 109.96, 114.55, 122.64, 124.74, 126.85, 130.47, 130.64, 134.02, 138.15, 141.31 (tolylcarbazole sp² C); IR ν 2152 (C≡C) cm⁻¹. – (C₅₅H₆₉NSi₂S₂)_n: calcd C 76.41, H 8.05, N 1.62; found C 75.46, H 8.07, N 1.63. Data for **Cz-3T**: Mw = 3500, Mw/Mn = 1.3. – ¹H NMR (395 MHz, CDCl₃)

δ = 0.75–1.6 (m, 52H, SiC₆H₁₃), 2.48 (s, 3H, CH₃-C₆H₄), 6.85–7.6 (m, 14H, aromatic H), 8.1–8.3 (m, 2H, aromatic H). – ¹³C{¹H} NMR (100 MHz, CDCl₃) δ = 14.14, 15.10, 22.63, 23.76, 31.49, 32.96 (Hex), 21.24 (CH₃-C₆H₄), 88.20, 107.61 (C≡C), 124.50, 124.77, 124.95, 136.30, 136.53, 142.97 (thiophene), 109.97, 114.50, 122.60, 124.59, 126.86, 130.32, 130.65, 134.03, 138.17, 141.29 (tolylcarbazole sp² C). – IR ν 2150 (C≡C) cm⁻¹. – (C₅₉H₇₁NSi₂S₃)_n: calcd. C 74.86, H 7.56, N 1.48; found C 74.88, H 7.57, N 1.53.

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