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Synthesis and optical properties of organosilicon–oligothiophene branched polymers

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ABSTRACT

Star-shaped monomers bearing three bromobithiophenyl units linked by an organosilicon core were polymerized with 1:1 mixtures of (tributylstannyl)hexylterthiophene and bis[(tributylstannyl)thienyl] arenes under the Stille coupling conditions leading to the formation of the corresponding branched polymers bearing quinquethiophenyl side groups and an Si-linked bis(bithiophenylene)arylene backbone as yellow–dark brown and red solids that are soluble in organic solvents, such as chloroform and THF. Optical properties of the resulting polymers were investigated with respect to the UV–vis absorption and photoluminescence spectra, suggesting the efficient energy transfer between the π-conjugated systems at the photo-excited states. Semi-conducting properties of the polymer films were also investigated.

1. Introduction

Polymers having alternate organosilicon and π-conjugated units are of interest because of their functionalities [1]. High carrier transporting properties are often found for those polymers, leading to the potential use of the polymer films as hole-transporting materials for organic light emitting diodes (OLEDs) and organic thin film transistors (OTFTs) [2,3]. In addition, it is known that the silicon-substitution on the π-conjugated systems often enhances the photoluminescence (PL) efficiency [4] and several Si-π alternate polymers with excellent PL and electroluminescence (EL) properties have been reported to date [3d,5,6]. For some of the polymers with different π-systems linked by organosilicon units, smooth intramolecular photo-induced energy and electron transfer between the π-systems have been also demonstrated, making it possible to utilize these polymers as light-harvesting materials [6].

In this connection, we have been interested in Si-oligothiophene alternate polymers [3] and reported the synthesis of poly(mono-, di-, and trisilanyleneoligothienylene)s (Chart 1(a), $x = 1–3$ and $m = 3–5$) and the utilities of their spin-coated films as the hole-transport layers of multi-layered OLEDs [3a–c]. More recently, we prepared similar polymers with longer oligothiophene units ($x = 1$ and $m = 8–14$) that were potentially useful as the active materials for OTFTs, although the mobility of the films was not very high ($\sim 10^{-5}$ cm^2/Vs) [3d]. In an effort to obtain better understanding about the TFT activity of the Si-linked oligothiophene derivatives, we prepared a series of compounds with two or three oligothiophene units linked by an organosilicon linkage (Chart 1(b) and (c), $m = 3–5$) [3e,f]. The TFT activity of the vapor-deposited films of the Si-linked oligothiophenes was highly dependent on the oligothiophene chain lengths and their elongation markedly improved the TFT activity. Molecular shapes also affected the activity and the star-shaped compounds (Chart 1(c)) always showed higher TFT activity than the linear ones (Chart 1(b)). The highest hole mobility of 6.2×10^{-2} cm^2/Vs among those Si-linked oligothiophenes was obtained for the star-shaped quinquethiophene derivative ($m = 5$, ER = SiMe) [3f]. Influence of the nature of the center element was also studied for the star-shaped compounds and it was found that the silicon-centered compound (ER = SiMe) exhibited higher mobility than the carbon-centered analog (ER = CH) for $m = 3$, while elongation of the oligothiophene chain length changed the tendency and a little higher but almost comparable mobility was observed for the carbon-centered compound with $m = 4$ as compared with the silicon-centered analog [3g]. The hole-transporting properties of those Si-linked oligothiophene oligomers and polymers originate from the stabilization of the cation charge in the oxidized states. Indeed, the DFT calculations on radical cations of the model molecules indicated the delocalization of the cation charge over the Si-linked oligothiophene systems [3g].

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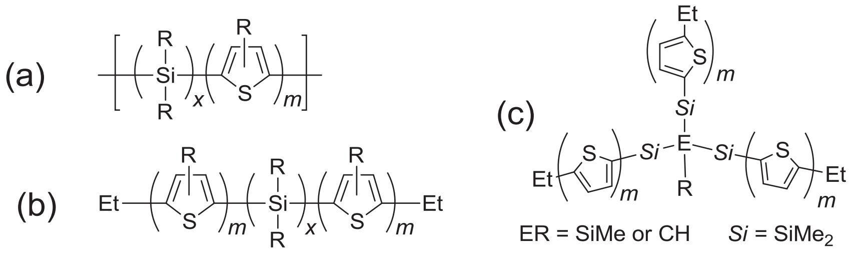


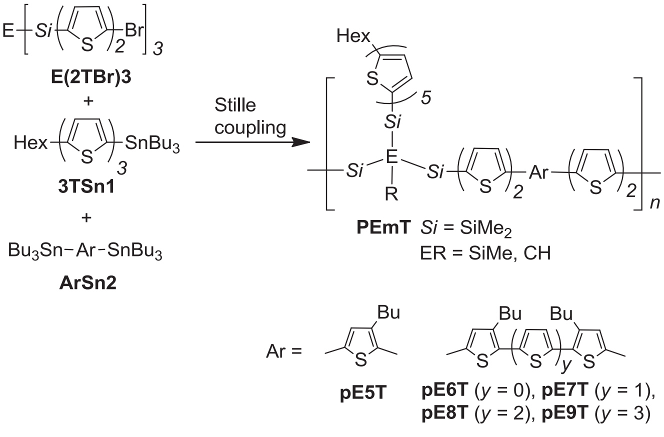
Chart 1. Structures of Si-oligothiophene polymers (a), and linear (b) and star-shaped Si-oligothiophene compounds (c).

In this paper, we report the synthesis, and optical and semiconducting properties of branched polymers bearing Si-linked oligothiophene units. The semi-conducting properties were not as high as that we had expected. However, efficient energy transfer between the oligothiophene units at the photo-excited states was observed for these polymers, suggesting their potential as light-harvesting materials. Although monosilane-linked branched oligothiophene polymers have been reported previously [7], this is the first example of those with flexible organosilicon linkages.

2. Experimental

2.1. General

All reactions were carried out in dry argon. Tetrahydrofuran (THF) and ether, and toluene used as the reaction solvents were distilled from sodium/benzophenone and calcium hydride, respectively and stored over activated molecular sieves until use. Starting monomers tris[(bromobithiophenyl)dimethylsilyl]methylsilane [3f] and -methane [3g] (**E(2TBr)3**, ER = SiMe or CH in Scheme 1), bisstannylarenes (**ArSn2** in Scheme 1), hexyl(tributylstannyl)terthiophene (**3TSn1**) [8], and bis(bromobutylthienyl)benzothiadiazole [9] were prepared as reported in the literature. Bis(tributylstannyl)butylthiophene (**1TSn2**), bis(tributylstannyl)dibutylbithiophene (**2TSn2**), bis(tributylstannyl)dibutylterthiophene (**3TSn2**), bis(tributylstannyl)dibutylquarterthiophene (**4TSn2**), and bis[(tributylstannyl)thienyl]benzothiadiazole) were prepared by dilithiation of the corresponding dibromooligothiophenes by the reactions with two equivalents of *n*-butyllithium, followed by treatment of the resulting dilithiooligothiophenes with tri(*n*-butyl)tin chloride, in a similar fashion to that of hexyl(tributylstannyl)terthiophene [8]. NMR spectra were recorded on Varian MR400 and System500 spectrometers. UV absorption and PL spectra were measured on Shimadzu UV-3150 and HITACHI F4500 spectrophotometers, respectively. PL quantum yields were determined in an integration sphere attached to a Hamamatsu Photonics C7473 multi-channel analyzer. Polymer molecular weights were measured by gel permeation chromatography (GPC) using Shodex KF804 and KF806 columns connected in series eluted with THF. The polymers were detected by a UV detector at 240 nm and the molecular weights were calculated relative to the polystyrene standards on a SIC-480 data station.



Scheme 1. Synthesis of branched Si-linked oligothiophene polymers.

2.2. Polymer synthesis

In an autoclave was placed a mixture of 0.285 g (0.300 mmol) of **Si(2TBr)3**, 0.186 g (0.300 mmol) of **3TSn1**, 0.216 g (0.300 mmol) of **1TSn2**, 7 mg (0.008 mmol) of $Pd_2(dba)_3$, 18 mg (0.060 mmol) of (*o*-Tol)$_3$P, 24 mg (0.30 mmol) of CuO, 20 mL of toluene and the mixture was heated at 150 °C for 48 h. The resulting precipitates were filtered and the solvent was evaporated. After hydrolysis with water, 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 evaporation of the solvent, the residue was reprecipitated from chloroform/hexane to give 230 mg (65% yield) of **pSi5T** as orange solids: m.p. 95–100 °C; ^{1}H NMR (δ in $CDCl_3$) 0.41 (br s, 21H, $SiCH_3$), 0.95 (br s, 6H, CH_3), 1.29–1.41 (br m, 8H, CH_2), 1.58–1.70 (br m, 4H, CH_2), 2.72–2.80 (br m, 4H, CH_2), 6.67–7.27 (br m, 19H, aromatic protons); ^{13}C NMR (δ in $CDCl_3$) −11.79, −0.36, 13.64–14.14, 17.53, 22.61–22.73, 28.80, 29.30, 30.22, 31.59, 32.51, 123.59–124.87, 134.97, 135.73, 142.54.

Other polymers were prepared in a fashion similar to that above. Data for **pC5T**: orange solid; ^{1}H NMR (δ in $CDCl_3$) 0.43 (br s, 19H, $SiCH_3$ and CH), 0.90 (br s, 6H, CH_3), 1.31–1.39 (br m, 8H, CH_2), 1.56–1.68 (br m, 4H, CH_2), 2.78 (br s, 4H, CH_2), 6.65–7.26 (br m, 19H, aromatic protons); ^{13}C NMR (δ in $CDCl_3$) 2.71, 14.05–14.14, 22.61–22.73, 28.80, 29.27, 30.23, 31.60, 32.54, 123.40–124.85, 134.43–135.77. Data for **pSi6T**: orange solid; m.p. 98–103 °C; ^{1}H NMR (δ in $CDCl_3$) 0.39 (br s, 21H, $SiCH_3$), 0.88 (br s, 9H, CH_3), 1.31–1.43 (br m, 10H, CH_2), 1.57–1.67 (br m, 6H, CH_2), 2.51 (br s, 4H, CH_2), 2.77 (br s, 2H, CH_2), 6.64–7.23 (br m, 20H, aromatic protons); ^{13}C NMR (δ in $CDCl_3$) −11.83, −0.45, 13.98–14.13, 22.54–22.61, 28.77, 30.22, 31.58, 32.80, 123.39–123.59, 124.22–124.87, 125.14, 127.31, 135.00, 135.99, 136.76, 142.41, 143.37. Data for **pC6T**: yellow solid; m.p. 120–125 °C; ^{1}H NMR (δ in $CDCl_3$) 0.39 (br s, 19H, $SiCH_3$ and CH), 0.87 (br s, 9H, CH_3), 1.30 (br s, 10H, CH_2), 1.56–1.65 (br m, 6H, CH_2), 2.51 (br s, 4H, CH_2), 2.76 (br s, 2H, CH_2), 6.65–7.11 (br m, 20H, aromatic protons); ^{13}C NMR (δ in $CDCl_3$) 2.68, 13.99–14.14, 22.55–22.61, 28.77, 30.22, 31.58, 32.81, 123.41–123.58, 124.19–124.87, 125.13, 135.02, 135.77–136.77, 140.96, 143.37. Data for **pSi7T**: red solid; ^{1}H NMR (δ in $CDCl_3$) 0.41 (br s, 21H, $SiCH_3$), 0.88–0.96 (br m, 9H, CH_3), 1.30–1.43 (br m, 10H, CH_2), 1.57–1.68 (br m, 6H, CH_2), 2.77 (br s, 6H, CH_2), 6.70–7.26 (br m, 22H, aromatic protons); ^{13}C NMR (δ in $CDCl_3$) −11.83, −0.36, 14.03–14.12, 22.61–22.77, 28.77, 29.37, 30.22, 31.58, 32.62, 123.40–124.87, 126.50–126.67, 134.93, 135.74. Data for **pC7T**: red solid; m.p. 100–106 °C; ^{1}H NMR (δ in $CDCl_3$) 0.43 (br s, 19H, $SiCH_3$ and CH), 0.88–0.96 (br m, 9H, CH_3), 1.30–1.50 (br m, 10H, CH_2), 1.55–1.68 (br m, 6H, CH_2), 2.76 (br s, 6H, CH_2), 6.65–7.25 (br m, 22H, aromatic