#### Polymer 52 (2011) 5282-5289

Contents lists available at SciVerse ScienceDirect

# Polymer

journal homepage: www.elsevier.com/locate/polymer

# Synthesis and properties of cyclopentadithiophene-based poly(silarylenesiloxane) derivatives

# Hitoshi Hanamura, Nobukatsu Nemoto\*

Department of Chemical Biology and Applied Chemistry, College of Engineering, Nihon University, Tamura-machi, Koriyama, Fukushima 963-8642, Japan

#### A R T I C L E I N F O

Article history: Received 5 August 2011 Received in revised form 16 September 2011 Accepted 19 September 2011 Available online 22 September 2011

*Keywords:* Cyclopentadithiophene Polysiloxane Photoluminescence

# ABSTRACT

Poly(silarylenesiloxane) derivatives with 4,4-dimethylcyclopenta[2,1-b:3,4-b']dithiophene moiety, bearing dimethyl- (P1), methylphenyl- (P2) and diphenyl- (P3) substituents on silyl moieties, were prepared via polycondensation of the corresponding disilanol monomers, that is, 2,6-bis(dimethylhydroxysilyl)-4,4-dimethylcyclopenta[2,1-b:3,4-b']dithiophene (M1), 2,6-bis(methylphenylhydroxysilyl)-4,4-dimethylcyclopenta[2,1-b:3,4-b']dithiophene (M2), and 2,6-bis(diphenylhydroxysilyl)-4,4-dimethylcyclopenta[2,1-b:3,4-b']dithiophene (M3), respectively. P1-P3 exhibited the good solubility in common organic solvents, such as benzene, toluene, chloroform, dichloromethane, THF, and so on. The glass transition temperatures ( $T_{gs}$ ) of **P1**, **P2** and **P3** were determined by differential scanning calorimetry to be 56, 97 and 137 °C, respectively, depending on the substituent on the silyl moieties. No melting temperatures  $(T_{ms})$  of **P1**, **P2** and **P3** were observed, suggesting the obtained **P1–P3** are amorphous polymers. The temperatures at 5% weight loss ( $T_{d5}$ s) of P1, P2 and P3 were 460, 459 and 479 °C, respectively, indicating that the larger number of phenyl group on the silyl moieties resulted in the better thermostability. Bathochromic and hyperchromic effects were observed in the absorption and fluorescence spectra by introducing silyl substituents onto 4,4-dimethylcyclopenta[2,1-b:3,4-b']dithiophene moiety. In addition, the bathochromic shift of the maximum absorption ( $\lambda_{abs}$ ) and the increase in the fluorescence quantum yield ( $\Phi_{\rm F}$ ) were observed by the introduction of phenyl group onto the silvl moieties.

© 2011 Elsevier Ltd. All rights reserved.

# 1. Introduction

Conjugated polymers [1,2] obtained by polymerization of fused ring derivatives have emerged as attractive materials for flexible, low cost and low power electro-optic devices. Thiophene-based polymers and oligomers, including fused ring bithiophene derivatives [3] such as dithienothiophene [4] derivatives, exhibit efficient charge transport in organic field-effect transistors (OFETs) [5,6], while polyfluorenes are representatives of conjugated polymers which are suitable for applications in electronics and optoelectronics, such as organic light emitting diodes (OLEDs) [7–9]. On the other hand, cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) [10,11] is regarded as an analogous compound of fluorene where the benzene rings are replaced by thiophene rings and composed of a fused ring bithiophene derivative. There have been few reports on the fluorescent properties of CPDT derivatives or conjugated polymers based on CPDT [12], while CPDT derivatives have been rigid

E-mail address: nemoto@chem.ce.nihon-u.ac.jp (N. Nemoto).

precursors of polymeric semiconducting materials for the development of organic photovoltaic devices [13–17].

In the meantime, the incorporation of silvl substituents onto aromatic species has been reported to result in high fluorescence quantum yield [18-26]. The use of polysiloxane derivatives as polymeric OLED materials seems to be inadequate because of their low glass transition temperature  $(T_g)$  [27,28] allowing the formation of aggregates and/or interchain excimers to induce the decline of the color stability of light emission, even though the other properties of polysiloxanes such as good thermostability and stability against atomic oxygen [27-29] seem to be appropriate for the polymeric OLED materials. Raising  $T_g$  of polysiloxane derivatives would be desirable to solve this problem. One of the methods for raising  $T_g$  is incorporation of bulky and rigid moieties into the main chain [30-36]. For example, the  $T_g$  of poly(dimethylsiloxane) has been reported to be  $-123 \degree C$  [27]; however, those of a series of poly (tetramethylsilarylenesiloxane) derivatives to be in the range from -52 °C to 156 °C depending on the arylene moiety introduced [32–36]. From these points of view, we have reported the synthesis of several poly(tetramethylsilarylenesiloxane) derivatives with pyrene or dibenzosilole moieties which exhibited the high  $T_{\rm g}$  as





<sup>\*</sup> Corresponding author. Tel./fax: +81 24 956 8812.

<sup>0032-3861/\$ –</sup> see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.polymer.2011.09.031

well as the good thermostability and fluorescence property [22,24]. In addition, it has been revealed that the introduction of phenyl silyl substituents onto CPDT skeleton allowed CPDT to have good fluorescent property [37].

In this article, we report the synthesis of novel poly(silarylenesiloxane) derivatives with CPDT moieties, as shown in Scheme 1. The effects of the introduction of CPDT moieties into poly(silarylenesiloxane) derivatives as well as the substituent on the silyl moieties on their thermal and optical properties will be also discussed.

## 2. Experimental procedure

#### 2.1. Materials

4,4-Dimethylcyclopenta[2,1-*b*:3,4-*b*']dithiophene (**1**) [13,14,37] was prepared by the method reported in the literature. Tetrahydrofuran (THF, Wako Pure Chemical Industries, Ltd.), diethyl ether (Wako Pure Chemical Industries, Ltd.), and benzene (KANTO KAGAKU) were used after distillation over sodium. N,N,N',N'-Tetramethylethylenediamine (TMEDA, Tokyo Kasei Kogyo Co., Inc.) and N,N-dimethylformamide (DMF, Wako Pure Chemical Industries, Ltd.) were used after distillation over calcium hydride. 1,1,3,3-Tetramethylguanidinium 2-ethylhexanoate was obtained from the equimolar mixture of 1,1,3,3-tetramethylguanidine and 2ethylhexanoic acid (Tokyo Kasei Kogyo Co., Inc.) [33-36]. N-Bromosuccinimide (NBS, KANTO KAGAKU), 2.6 mol/L n-butyllithium in hexane (KANTO KAGAKU), chlorodimethylsilane (Tokyo Kasei Kogyo Co., Inc.), chloromethylphenylsilane (Sigma-Aldrich, Inc.), chlorodiphenylsilane (Sigma-Aldrich, Inc.), 5% palladium on charcoal (Wako Pure Chemical Industries, Ltd.) were commercially available and used as received.

## 2.2. Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE 400F spectrometer in deuterated chloroform (CDCl<sub>3</sub>) or dimethylsulfoxide [(CD<sub>3</sub>)<sub>2</sub>SO] at ambient temperature. IR spectra were measured on a Perkin–Elmer Spectrum One FT–IR spectrometer. Glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) were determined by differential scanning calorimetry (DSC) on a RIGAKU ThermoPlus DSC 8230 at a heating rate of 10 °C/min under a nitrogen flow rate of 10 mL/min. Thermogravimetry analysis (TGA) was performed on a RIGAKU ThermoPlus TG8110 at a heating rate of 10 °C/min under a nitrogen atmosphere. Numberaverage ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights were estimated by size-exclusion chromatography (SEC) on a SHOWA DENKO Shodex GPC-101 system with polystyrene gel columns (a pair of Shodex GPC LF-804), eluted with THF using a calibration curve of polystyrene standards. Gas chromatography–mass spectroscopy (GC/MS) was carried out using an Agilent 6890/5973 instrument. Absorption spectra were measured on a Shimadzu UV–2450 spectrophotometer. Emission spectra were measured on a Shimadzu RF-5300PC spectrophotometer by use of the solution degassed by argon bubbling for 30 min. Fluorescence quantum yields ( $\Phi_{FS}$ ) were determined by use of pyrene ( $\Phi_{F}$ : 0.19) [22] as a standard. The optimized geometrical structures and the energies for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were estimated by the density functional theory (DFT) calculations at B3LYP/6-31G(d) level of theory using Spartan '08 for Windows (Wavefunction, Inc., Irvine, CA, USA) [38].

# 2.3. Synthesis of 2,6-dibromo-4,4-dimethylcyclopenta[2,1-b:3,4-b'] dithiophene (**2**)

Under a dry argon atmosphere with shielding light, 4,4dimethylcyclopenta[2,1-*b*:3,4-*b*']dithiophene (1) (0.200 g, 0.97 mmol) and NBS (0.345 g, 1.94 mmol) in 7 mL of DMF were stirred at ambient temperature for 1 h. The reaction mixture was poured into 10 mL of saturated sodium thiosulfate aqueous solution, and the crude product was extracted with hexane. The combined organic layers were washed with saturated sodium chloride aqueous solution several times, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure and purified by silica gel chromatography with hexane eluent. The collected fraction with  $R_{\rm f}$  value of 0.57 was concentrated under reduced pressure and the residue was recrystallized from hexane to afford **2** as colorless crystals with the yield of 0.343 g (97%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, δ): 6.99 (s, 2H, thienyl protons), 1.40 (s, 6H, -CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, δ): 158.3 (thienyl carbon), 135.1 (thienyl carbon), 124.0 (thienyl carbon), 111.4 (thienyl carbon), 46.4 [>C(CH<sub>3</sub>)<sub>2</sub>], 24.8 (-CH<sub>3</sub>). M.p.: 106 °C.

# 2.4. Synthesis of 2,6-bis(diphenylsilyl)-4,4-dimethylcyclopenta[2,1-b:3,4-b']dithiophene (5)

Under a dry argon atmosphere, 2.6 mol/L *n*-butyllithium in hexane (2.5 mL, 6.59 mmol) with TMEDA (0.767 g, 6.59 mmol) was added dropwise to **2** (0.600 g, 1.65 mmol) in dry diethyl ether (50 mL) at -78 °C. The mixture was stirred for 30 min, and warmed to ambient temperature. After the mixture was stirred for 1 h, chlorodiphenylsilane (1.44 g, 6.59 mmol) was added to this solution at ambient temperature. The reaction mixture was stirred for 24 h and poured into 50 mL of water with stirring. The crude product was extracted with ethyl acetate. The combined organic layer was



Scheme 1. Polycondensation of CPDT derivatives having hydroxysilyl substituents.

washed with water several times, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure and purified by silica gel chromatography using the mixed solvent of hexane and chloroform (4/1 v/v) as eluent. The collected fraction with  $R_{\rm f}$  value of 0.60 was concentrated under reduced pressure and the residue was recrystallized from a mixed solvent of chloroform/methanol to afford **5** as colorless crystals with the yield of 0.45 g (48%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$ ): 7.61 (m, 8H, aromatic ring), 7.46 (m, 14H, aromatic ring), 5.50 [s, 2H,  $-Si(Ph)_2-H$ ] 1.40 (s, 6H,  $-CH_3$ ). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz,  $\delta$ ): 164.4 (thienyl carbon), 141.9 (thienyl carbon), 135.3 (phenyl carbon), 132.7 (thienyl carbon), 132.6 (phenyl carbon), 131.8 (thienyl carbon), 130.6 (phenyl carbon), 128.6 (phenyl carbon), 44.3 [>C(CH\_3)\_2], 24.9 ( $-CH_3$ ). IR (KBr, cm<sup>-1</sup>): 2132 (Si–H). Mass (EI, *m*/*z*): 570 (M<sup>+</sup>). M.p.: 105 °C.

#### 2.5. Spectral data for 3 and 4

2,6-Bis(dimethylsilyl)-4,4-dimethylcyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**3**) and 2,6-bis(methylphenylsilyl)-4,4-dimethylcyclopenta [2,1-*b*:3,4-*b'*]dithiophene (**4**) were prepared by the similar method as the preparation of **5** using chlorodimethylsilane and chloromethylphenylsilane as the raw material, respectively. The spectral data for **3** and **4** are as shown below.

**3** was obtained as colorless liquid with the yield of 86%. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, δ): 7.38 (s, 2H, thienyl protons), 4.50 [m, 2H,  $-Si(CH_3)_2-H$ ], 1.41 [s, 6H,  $>C(CH_3)_2$ ], 0.38 [s, 12H,  $-Si(CH_3)_2-H$ ]. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz, δ): 163.6 (thienyl carbon), 140.1 (thienyl carbon), 136.4 (thienyl carbon), 129.5 (thienyl carbon), 43.7 [ $>C(CH_3)_2$ ], 24.8 [ $>C(CH_3)_2$ ], -3.1 [ $-Si(CH_3)_2-H$ ]. IR (KBr, cm<sup>-1</sup>): 2134 (Si–H). Mass (EI, *m/z*): 322 (M<sup>+</sup>).

4 was obtained as colorless crystals with the yield of 58%. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$ ): 7.60 (m, 4H, phenyl protons), 7.43 (m, 8H, aromatic protons), 4.98 [m, 2H,  $-Si(CH_3)(Ph)-H$ ], 1.40 [s, 6H,  $-Si(CH_3)_2$ ], 0.42 [s, 6H,  $-Si(CH_3)(Ph)-H$ ]. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz,  $\delta$ ): 164.1 (thienyl carbon), 141.1 (thienyl carbon), 134.8

(phenyl carbon), 134.6(thienyl carbon), 134.4 (phenyl carbon), 130.6 (thienyl carbon), 130.2 (phenyl carbon), 128.4 (phenyl carbon), 44.1 [>C(CH<sub>3</sub>)<sub>2</sub>], 24.0 [>C(CH<sub>3</sub>)<sub>2</sub>], -4.3 [-Si(CH<sub>3</sub>)(Ph)-H]. IR (KBr, cm<sup>-1</sup>): 2135 (Si-H). Mass (EI, *m*/*z*): 446 (M<sup>+</sup>). M.p.: 62 °C.

# 2.6. Synthesis of 2,6-bis(diphenylhydroxysilyl)-4,4dimethylcyclopenta[2,1-b:3,4-b']dithiophene (**M3**)

Under a dry argon atmosphere, **5** (0.55 g, 0.94 mmol) in dry THF (6.5 mL) was added dropwise to 5%-Pd on C (5.0 mg) with H<sub>2</sub>O (51 mg, 2.83 mmol) in THF (2.2 mL) at room temperature. The reaction mixture was stirred for 14 h and filtered. The filtrate was concentrated under reduced pressure and the residue was recrystallized from a mixed solvent of benzene/hexane to afford **M3** as colorless crystals with the yield of 0.47 g (82%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$ ): 7.61 (m, 8H, aromatic protons), 7.42 (m, 14H, aromatic protons), 7.31 [s, 2H, -Si(Ph)<sub>2</sub>-OH], 1.39 (s, 6H, -CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz,  $\delta$ ): 163.9 (thienyl carbon), 134.5 (phenyl carbon), 130.5 (thienyl carbon), 130.2 (phenyl carbon), 128.1 (phenyl carbon), 44.1 [>C(CH<sub>3</sub>)<sub>2</sub>], 25.1 (-CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 3293 (-OH). Mass (EI, *m/z*): 602 (M<sup>+</sup>). M.p.: 178 °C.

### 2.7. Spectral data for M1 and M2

2,6-Bis(dimethylhydroxysilyl)-4,4-dimethylcyclopenta[2,1-b: 3,4-b']dithiophene (**M1**) and 2,6-bis(methylphenylhydroxysilyl)-4,4-dimethylcyclopenta[2,1-b:3,4-b']dithiophene (**M2**) were prepared by the similar method as the preparation of **M3** using **3** and **4** as the raw material, respectively. The spectral data for **M1** and **M2** are as shown below.

**M1** was obtained as colorless solids with the yield of 71%. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$ ): 7.30 (s, 2H, thienyl protons), 6.12 [s, 2H, -Si(CH<sub>3</sub>)<sub>2</sub>-OH], 1.41 [s, 6H, >C(CH<sub>3</sub>)<sub>2</sub>], 0.31 [s, 12H, -Si(CH<sub>3</sub>)<sub>2</sub>-OH]. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz,  $\delta$ ): 163.6 (thienyl carbon), 141.4 (thienyl carbon), 139.4 (thienyl carbon), 128.4



Scheme 2. Synthetic pathways for CPDT derivatives having hydroxysilyl substituents.

Table 1Results of polycondensation and thermal properties of P1-P3.

Polymer	Yield (%)	$M_n^c$	$M_{\rm w}/M_{\rm n}^{\rm c}$	$T_{d5} (^{\circ}C)^d$
P1	40 <sup>a</sup>	13000	1.34	460
P2	69 <sup>a</sup>	17000	1.78	459
P3	30 <sup>b</sup>	25000	1.49	479

<sup>a</sup> Insoluble part in methanol.

<sup>b</sup> Insoluble part in acetone.

<sup>c</sup> Estimated from SEC eluted with THF based on polystyrene standards.

 $^{\rm d}$  Temperature at 5% weight loss determined by TG in N<sub>2</sub>.

(thienyl carbon), 43.9 [>C(CH<sub>3</sub>)<sub>2</sub>], 25.2 [>C(CH<sub>3</sub>)<sub>2</sub>], 1.6 [-Si(CH<sub>3</sub>)<sub>2</sub>-OH]. IR (KBr, cm<sup>-1</sup>): 3170 (-OH). Mass (El, *m*/*z*): 478 (M<sup>+</sup>). M.p.: >106 °C (polymerization).

**M2** was obtained as colorless solids with the yield of 76%. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz,  $\delta$ ): 7.62 (m, 4H, phenyl protons), 7.39 (m, 6H, phenyl protons), 7.31 (s, 2H, thienyl protons), 6.75 [s, 2H, -Si(CH<sub>3</sub>)(Ph)-OH], 1.39 [s, 6H, >C(CH<sub>3</sub>)<sub>2</sub>], 0.57 [s, 6H, -Si(CH<sub>3</sub>)(Ph)-OH], <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz,  $\delta$ ): 163.7 (thienyl carbon), 140.5 (thienyl carbon), 139.8 (phenyl carbon), 138.3 (thienyl carbon), 133.7 (phenyl carbon), 129.8 (thienyl carbon), 129.3 (phenyl carbon), 128.0 (phenyl carbon), 44.0 [>C(CH<sub>3</sub>)<sub>2</sub>], 0.3 [-Si(CH<sub>3</sub>)(Ph)-OH]. IR (KBr, cm<sup>-1</sup>): 3293 (-OH). Mass (EI, *m/z*): 354 (M<sup>+</sup>), M.p.; >115 °C (polymerization).

# 2.8. Synthesis of poly(tetraphenyl-4,4-dimethyl-2,6-silcyclopenta [2,1-b:3,4-b']dithiophenylenesiloxane) (**P3**)

Under a dry atmosphere, 1,1,3,3-tetramethylguanidinium 2ethylhexanoate (0.02 g) was added to **M3** (0.27 g, 0.45 mmol) dissolved in benzene (15.5 mL), and the reaction mixture was refluxed for 12 h. The reaction mixture was poured into acetone (100 mL) to isolate **P3** as white precipitates with the yield of 0.08 g (30%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ ): 7.56 (m, 8H, phenyl protons), 7.30 (m, 12H, phenyl protons), 6.91 (s, 2H, thienyl protons), 1.20 (s, 6H, -CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz,  $\delta$ ): 164.2 (thienyl carbon), 143.3 (thienyl carbon), 136.8 (phenyl carbon), 135.8 (thienyl carbon), 135.6 (phenyl carbon), 131.4 (thienyl carbon), 130.7 (phenyl carbon), 128.3 (phenyl carbon), 44.6 [>C(CH<sub>3</sub>)<sub>2</sub>], 25.7 (-CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 1067 (Si–O).

#### 2.9. Spectral data for P1 and P2

Poly(tetramethyl-4,4-dimethyl-2,6-silcyclopentadithiophenylenesiloxane) (**P1**) and poly(dimethyldiphenyl-4,4-dimethyl-2,6silcyclopentadithiophenylenesiloxane) (P2) were prepared by the similar method as the preparation of P3 using M1 and M2 as a monomer, respectively. The spectral data for P1 and P2 are as shown below.

**P1** was obtained as colorless powder with the yield of 40%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ ): 7.08 (s, 2H, thienyl protons), 1.45 [s, 6H, >C(CH<sub>3</sub>)<sub>2</sub>], 0.39 [s, 12H, -Si(CH<sub>3</sub>)<sub>2</sub>-]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz,  $\delta$ ): 163.3 (thienyl carbon), 141.2 (thienyl carbon), 140.2 (thienyl carbon), 127.6 (thienyl carbon), 44.0 [>C(CH<sub>3</sub>)<sub>2</sub>], 25.3 [>C(CH<sub>3</sub>)<sub>2</sub>], 1.7 [-Si(CH<sub>3</sub>)<sub>2</sub>-]. IR (KBr, cm<sup>-1</sup>): 1054 (Si–O).

**P2** was obtained as colorless powder with the yield of 69%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,  $\delta$ ): 7.60 (m, 4H, phenyl protons), 7.34 (m, 6H, phenyl protons), 7.01 (s, 2H, thienyl protons), 1.33 [s, 6H, >C(CH<sub>3</sub>)<sub>2</sub>], 0.56 [s, 6H, -Si(CH<sub>3</sub>)(Ph)-]. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz,  $\delta$ ): 163.5 (thienyl carbon), 141.9 (thienyl carbon), 138.2 (phenyl carbon), 137.1(thienyl carbon), 133.9 (phenyl carbon), 129.9 (thienyl carbon), 129.1 (phenyl carbon), 127.8 (phenyl carbon), 44.0 [>C(CH<sub>3</sub>)<sub>2</sub>], 25.2 [>C(CH<sub>3</sub>)<sub>2</sub>], 0.5 [-Si(CH<sub>3</sub>)(Ph)-]. IR (KBr, cm<sup>-1</sup>): 1053 (Si-O).

### 3. Results and discussion

#### 3.1. Synthesis of monomer and polymer

Scheme 2 shows the synthetic pathways for disilanol monomers, that is, **M1**, **M2** and **M3**. **M1–M3** were obtained by hydrolysis reaction of **3–5**, respectively, catalyzed by 5% palladium on charcoal. **3–5** were obtained from 2,6-dibromo-4,4-dimethylcyclopenta [2,1-b:3,4-b'] dithiophene (**2**) via the lithiation reaction and successive reaction using chlorosilane reagents.

The obtained **M1**, **M2** and **M3** underwent polycondensation using 1,1,3,3-tetramethylguanidinium 2-ethylhexanoate as a catalyst to afford the corresponding poly(silarylenesiloxane) derivatives **P1**, **P2** and **P3**, respectively, as shown in Scheme 1. As reported previously [33–36], any solvents forming azeotropic mixtures with water and dissolving both monomer and the resulting polymer, such as benzene and toluene, can be used for the present polycondensation. The <sup>1</sup>H and <sup>13</sup>C NMR and IR spectroscopy confirmed the structures of **P1–P3**. The results of the polycondensation of **M1**, **M2** and **M3** are summarized in Table 1.

**P1–P3** were soluble in common organic solvents such as THF, chloroform, dichloromethane, toluene, and so on. The formation of **P1–P3** was confirmed by SEC measurement and NMR spectroscopy. The SEC profiles of **P1–P3** indicated that the obtained polymers were unimodal and that the low-molecular weight species such as a cyclic dimer or trimer were almost completely removed



Fig. 1. (a) <sup>1</sup>H NMR (solvent: DMSO-*d*<sub>6</sub>, 400 MHz) and (b) <sup>13</sup>C NMR spectra (solvent: DMSO-*d*<sub>6</sub>, 100 MHz) of **M3** at ambient temperature.



Fig. 2. (a) <sup>1</sup>H NMR (solvent: CDCl<sub>3</sub>, 400 MHz) and (b) <sup>13</sup>C NMR spectra (solvent: CDCl<sub>3</sub>, 100 MHz) of P3 at ambient temperature.

by reprecipitation in methanol or acetone. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **M3** and **P3** are shown in Figs. 1 and 2, respectively, where each signal was consistently assigned. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **P3** were almost similar to those of **M3** except the disappearance of a signal of 7.31 ppm based on hydroxy groups as observed in the <sup>1</sup>H NMR spectrum of **M3**. The integrated ratio of each <sup>1</sup>H NMR signal and the assignment of <sup>13</sup>C NMR signals were consistent with the structure of **P3** as described in Fig. 2. These results would support that no side-reactions occurred during the polycondensation of **M3**. It was confirmed that the similar results were obtained in the polycondensation of **M1** and **M2**.

#### 3.2. Thermal characterization of polymer

Glass transition temperatures ( $T_g$ s) of **P1–P3** were determined by DSC. Fig. 3 shows the DSC traces of **P1–P3** on a second heating scan under a nitrogen atmosphere at a heating rate of 10 °C/min. The  $T_g$ s of **P1**, **P2** and **P3** were determined to be 56, 97 and 137 °C, respectively. The difference in the  $T_g$ s among **P1–P3** depended on the substituents on the silyl moieties. The introduction of bulky phenyl group onto the silyl moieties caused the raising of  $T_g$ , because bulky phenyl groups would restrict the motion of the main chain. No melting temperatures ( $T_m$ s) were observed in the DSC thermogram of **P1**, **P2** and **P3**. This result would indicate that **P1–P3** are noncrystalline polymers as observed in the other poly(silarylenesiloxane) derivatives [24,36].

The temperatures at 5% weight loss ( $T_{d5}$ s) of the present **P1–P3** were determined by TGA to be 460, 459 and 479 °C, respectively, as summarized in Table 1. It was revealed that the introduction of phenyl groups onto silyl moieties improved the thermostability, plausibly because of the restriction of the main chain motion by the bulky phenyl groups.

### 3.3. Optical properties

We investigated the optical properties of the obtained CPDT derivatives, including monomers and polymers. The absorption and fluorescence spectra of CPDT derivatives are shown in Fig. 4. Table 2 summarizes the optical properties of CPDT derivatives.

In the absorption spectra of CPDT derivatives, bathochromic and hyperchromic effects were observed by the introduction of silyl groups onto CPDT skeleton, presumably because of  $\sigma-\pi$  and  $\sigma^*-\pi^*$  conjugations between the silyl groups and aromatic moieties [18–26].

It has been known that the bathochromic effects are induced by lowering the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) states because of both destabilization of the HOMO state through  $\sigma$ - $\pi$  conjugation and stabilization of the LUMO state through  $\sigma^*$ - $\pi^*$  conjugation. The hyperchromic effects would be caused by the enhancement of the transition moment based on the increase in the dipole moments of the HOMO and LUMO states owing to the  $\sigma$ - $\pi$  conjugation in the HOMO and the  $\sigma^*$ - $\pi^*$  conjugation in the LUMO [18–26].

In addition, the bathochromic shift of the maximum absorption  $(\lambda_{abs})$  and the increase of the molar extinction coefficient ( $\varepsilon$ ) were observed by the introduction of phenyl group onto the silyl moieties. Namely, the introduction of phenyl group onto silyl moieties was also revealed to induce the bathochromic and hyperchromic effects.

In the meantime, we calculated the HOMO and LUMO energy levels of **M1**, **M2** and **M3** with the DFT method at the B3LYP/6-31G(d) level of theory for the confirmation of the effects of the introduction of silyl moieties on the absorption spectra.



**Fig. 3.** DSC thermograms of (a) **P1**, (b) **P2**, and (c) **P3** on a second heating scans under a  $N_2$  flow rate of 10 mL/min and a cooling or heating rate of 10 °C/min.



**Fig. 4.** Absorption [(a)-(c)] and fluorescence  $[(d)-(f), \lambda_{ex}: 317 \text{ nm}]$  spectra of CPDT derivatives in CHCl<sub>3</sub> at ambient temperature (conc.:  $2.0 \times 10^{-6} \text{ mol/L})$ ; (a) and (d): **1**, **3**, **M1**, **P1**; (b) and (e): **1**, **4**, **M2**, **P2**; (c) and (f) **1**, **5**, **M3**, **P3**.

Fig. 5 depicts the energy diagrams for the HOMO and LUMO energy levels as well as the energy gap between LUMO and HOMO. The difference in the LUMO energy level between **1** (-1.01 eV) and **M1** (-1.28 eV) and that in the HOMO energy level between **1** (-5.18 eV) and **M1** (-5.22 eV) means that stabilization of LUMO state through  $\sigma^* - \pi^*$  conjugation and destabilization of HOMO state through  $\sigma - \pi$  conjugation are induced by the introduction of dimethylsilyl moieties. Thus, the introduction of dimethylsilyl moieties caused the decrease in the energy gap between LUMO and HOMO, resulting in the bathochromic shift of the maximum absorption. The replacement of methyl group by phenyl one on silyl moieties was found to decrease both HOMO and LUMO energy levels as shown in Fig. 5. The degree of decrease in LUMO energy level was rather higher than that in HOMO energy level with the

increase in the number of phenyl group on silyl moieties, inducing the rather bathochromic shift of the maximum absorption with increase in the number of phenyl group on silyl moieties.

The wavelength at maximum emission ( $\lambda_{em}$ ) and fluorescence quantum yield ( $\Phi_F$ ) of CPDT derivatives are also summarized in Table 2. In the fluorescence spectra of CPDT derivatives, bathochromic effects were observed by the introduction of silyl groups onto CPDT skeleton. In addition, the bathochromic shifts of the maximum emission were observed by the introduction of phenyl group onto the silyl moieties.

The  $\Phi_{\rm F}$ s were improved by the introduction of silyl groups onto CPDT skeleton. The  $\Phi_{\rm F}$ s of unsubstituted cyclopenta[2,1-*b*:3,4-*b'*] dithiophene (**1**) and dimethylsilylated adducts (**3**, **M1**, **P1**) were 0.01, 0.09, 0.09, and 0.09, respectively, indicating that the

Table 2		
Optical properties	of CPDT deri	ivatives.

Compound	$\lambda_{abs}/nm \ (\epsilon/L \ mol^{-1} \ cm^{-1})$	$\lambda_{em}/nm$	$\Phi_{\rm F}{}^{\rm a}$
1	317 (15000) 329 (11800)	382	0.01
3	336 (24500) 348 (19200)	382	0.09
M1	335 (24300) 346 (19200)	381	0.09
P1	336 (23700) 348 (19200)	381	0.09
4	338 (30500) 349 (25000)	385	0.24
M2	337 (23700) 349 (22000)	383	0.21
P2	338 (27000) 350 (22000)	385	0.26
5	342 (32500) 354 (27500)	389	0.85
M3	341 (30000) 354 (25000)	387	0.81
P3	342 (31000) 354 (26500)	389	0.78

<sup>a</sup> Fluorescence quantum yields ( $\Phi_{\rm F}$ s) were determined by using pyrene ( $\Phi_{\rm F}$ : 0.19) [22] as a standard in CHCl<sub>3</sub>.

introduction of dimethylsilyl moieties onto CPDT skeleton rather increased  $\Phi_{\rm F}$ . In addition, the  $\Phi_{\rm F}$ s of methylphenylsilylated adducts (4, M2, P2) were 0.24, 0.21, and 0.26, respectively, and 2.7 times as large as that of dimethylsilylated adducts, indicating that the introduction of a phenyl group onto a silyl moiety drastically increases  $\Phi_{\rm F}$ . It should be still remarkable that the increase in the number of phenyl group on silyl moieties enhances the fluorescent efficiency, as observed that the  $\Phi_{\rm F}$ s of diphenylsilylated adducts (5, M3, P3) were 0.85, 0.81, and 0.78, respectively. The optical properties of 9,9-diphenylfluorene-based poly(tetramethylsilarylenesiloxane) have been reported [24]. 9,9-Diphenylfluorenebased poly(tetramethylsilarylenesiloxane) has the structural correlation with P1, though it bears the different substituents on the spiro-carbon moiety such as 9-position of fluorene and 4position of cyclopentadithiophene. The  $\Phi_{
m F}$ of 9.9diphenylfluorene-based poly(tetramethylsilarylenesiloxane) in chloroform solution has been reported to be 0.19 [24] and larger than that of **P1** (0.09) in chloroform solution: however, it would be much interesting that the substitution of the methyl groups on the silvl moieties with phenyl groups enlarges the  $\Phi_{\rm F}$ . Namely, it would be remarkable that the phenyl substituents on the silyl moieties provide the fluorescent ability to CPDT derivatives having essentially little fluorescent ability, indicating that the CPDT-based poly(silarylenesiloxane) with diphenyl substituent on the silyl moieties such as P3 would be one of promising candidates for the fluorescent materials.

Further detailed analysis of photochemical processes including the determination of the rate constants as radiative rate constant, intersystem crossing rate constant, and non-radiative rate constant would be necessary for the clarification of the reason for the



Fig. 5. Energy diagrams of CPDT derivatives. Calculated using DFT method at the B3LYP/6-31G(d) level.

increase in  $\Phi_F$ ; however, the plausible reasons for the increase in  $\Phi_F$  are as follows [18,20,26]. In the case of the present CPDT derivatives, the larger number of phenyl groups on the silyl moieties resulted in the larger molar extinction coefficient ( $\varepsilon$ ) as mentioned above. It would be likely that the increase in  $\Phi_F$  was induced by the increase in  $\varepsilon$  because the radiative rate constant has linear relation with  $\varepsilon$ . Another reason for the increase in  $\Phi_F$  would be that the intersystem crossing rate constant becomes negligible owing to the energy stabilization of the first singlet excited state ( $S_1$ ) by silyl substituted certain aromatic compounds [18,20,26]. It would be also likely that the increase in  $\Phi_F$  was induced by the energy stabilization of the first singlet excited state ( $S_1$ ) by the introduction of phenyl groups on the silyl moieties.

#### 4. Conclusions

We achieved the synthesis of three poly(silarylenesiloxane) derivatives with CPDT moieties (**P1–P3**). **P1–P3** exhibited the good solubility in common organic solvents such as benzene, toluene, chloroform, dichloromethane and THF. The  $T_{d5}$ s of **P1**, **P2** and **P3** were determined to be 460, 459 and 479 °C, respectively, indicating the introduction of phenyl group onto silyl moieties improved thermostability. As for the optical properties of the obtained CPDT derivatives, the bathochromic and hyperchromic effects were observed by introducing silyl moieties onto CPDT. The bathochromic shifts of wavelength at the maximum absorption and fluorescence were induced by both destabilization of HOMO state through  $\sigma^{+}-\pi^{*}$  conjugation. It should be remarkable that the increase in the number of phenyl group on silyl moieties enhances the fluorescent efficiency.

#### Acknowledgments

The authors would like to appreciate Ms. Satoko Tokiwa and Ms. Nami Sugashima, Nihon University College of Engineering Worldwide Research Center for Advanced Engineering and Technology (NEWCAT), for performing NMR measurements.

### Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2011.09.031.

# References

- [1] Andrew CG, Klaus M. Adv Polym Sci 2006;199:1.
- [2] Grimsdale AC, Chan KL, Martin RE, Jokisz PG, Holmes AB. Chem Rev 2009;109: 897.
- [3] Ohshita J, Matsui S, Yamamoto R, Mizumo T, Ooyama Y, Harima Y, et al. Organometallics 2010;29:3239.
- [4] Ozturk T, Ertas E, Mert O. Tetrahedron 2005;61:11055.
- [5] Shirota Y, Kageyama H. Chem Rev 2007;107:953.
- [6] Zhang X, Zhu D. Polym Chem 2010;1:409.
- [7] Leclerc MJ. Polym Sci Part A Polym Chem 2001;39:2867.
- [8] Neher D. Macromol Rapid Commun 2001;22:1365.
- [9] Scherf U, List EJW. Adv Mater 2002;14:477.
- [10] Kraak A, Wiersema AK, Jordens P, Wynberg H. Tetrahedron 1968;24:3381.
- [11] Coppo P, Turner ML. J Mater Chem 2005;15:1123.
- [12] Pal B, Yen WC, Yang JS, Chao CY, Hung YC, Lin ST, et al. Macromolecules 2008; 41:6664.
- [13] Beyer R, Kalaji M, Kingscote-Burton G, Merphy PJ, Pereria VMSC, Taylor DM, et al. Synth Met 1998;92:25.
- [14] Chochos CL, Economopoulos SP, Deimede V, Gregoriou VG, Lloyd MT, Malliaras GG, et al. J Phys Chem C 2007;111:10732.
- [15] Li KC, Huang JH, Hsu YC, Huang PJ, Chu CW, Lin JT, et al. Macromolecules 2009;42:3681.

- [16] Chen CH, Hsieh CH, Dubosc M, Cheng YJ, Hsu CS. Macromolecules 2010;43: 697.
- [17] Ko S, Mondal R, Risko C, Lee JK, Hong S, McGehee MD, et al. Macromolecules 2010;43:6685.
- [18] Shizuka H, Sato Y, Ueki Y, Ishikawa M, Kumada M. J Chem Soc Faraday Trans I 1984;80:341.
- [19] Declercq D, Delbeke P, De Schryver FC, Van Meervelt L, Miller RD. J Am Chem Soc 1993;115:5702.
- [20] Kyushin S, Ikarugi M, Goto M, Hiratsuka H, Matsumoto H. Organometallics 1996;15:1067.
- [21] Maeda H. Inoue Y. Ishida H. Mizuno K. Chem Lett 2001:40:1224.
- [22] Imai K, Sasaki T, Abe J, Kimoto A, Tamai Y, Nemoto N. Polym J 2009;41: 584.
- [23] Imai K, Hatano S, Kimoto A, Abe J, Tamai Y, Nemoto N. Tetrahedron 2010;66: 8012.
- [24] Imai K, Kihara Y, Kimoto A, Abe J, Tamai Y, Nemoto N. Polym J 2011;43:58.
- Ponomarenko SA, Kirchmeyer S. Adv Polym Sci 2011;235:33. [25]
- Karatsu T. J Photochem Photobiol C Photochem Rev 2008;9:111. [26] [27]
- Mark JE. Silicon-containing polymers. In: Ziegler JM, Gordon FW, editors. Silicon-based polymer science. Advances in chemistry series, vol. 224. Washington, DC: American Chemical Society; 1990. p. 47–90.

- [28] Brook MA. Silicon in organic, organometallic, and polymer chemistry. New York: John Wiley and Sons, Inc.; 2000 [chapter 9].
- Kitamura N, Yamamoto T. Appl Organomet Chem 2003;17:840. [29]
- 1301 Day GM, Hibberd AI, Habsuda J, Sharp GJ. Thermally stable siloxane polymers for gas chromatography. In: Clarson SJ, Fitzgerald JJ, Owen MJ, Smith SD, van Dyke ME, editors. Synthesis and properties of silicones and silicone-modified materials. ACS symposium series, vol. 838. Washington, DC: American Chemical Society; 2003. p. 127–36.
- [31] Dvornic PR. Lenz RW. High temperature siloxane elastomers. Basel. Heidelberg, New York: Hüthig and Wepf Verlag; 1990 [chapter 2].
- [32] Zhang R. Pinhas AR. Mark IE. Macromolecules 1997:30:2513.
- İ33İ Otomo Y, Nagase Y, Nemoto N. Polymer 2005;46:9714.
- [34] Sato I, Takeda S, Arai Y, Miwa H, Nagase Y, Nemoto N. Polym Bull 2007;59: 607
- [35] Hattori Y, Miyajima T, Sakai M, Nagase Y, Nemoto N. Polymer 2008;49:2825. Nemoto N, Yamaguchi T, Ozawa Y, Nigorikawa M, Yanai Y, Nagase Y. Polym [36] Bull 2008.61.165
- Hanamura H, Haneishi R, Nemoto N. Tetrahedron Lett 2011;52:4039. [37]
- Calculated using Spartan '08 for Windows (Wavefunction, Inc., Irvine, CA, [38] USA), Shao Y, Molnar LF, Jung Y, Kussmann J, Ochsenfeld C, Brown ST, et al. Phys Chem Chem Phys 2006;8:3172.