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Synthesis of hydroxyphenylglycine-derived novel poly(silylenevinylenephenyleneethynylene)s

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ABSTRACT

The hydrosilylation polymerization of D-(-)-p-hydroxyphenylglycine-derived diethynyl monomers **1p** and **1m** with dihydrosilanes **Si1** and **Si2** was carried out using Rhl(PPh₃)₃ as a catalyst to give optically active novel poly(silylenevinylenephenyleneethynylene)s [(*E*)-poly(**1p-Si1**), (*E*)-poly(**1p-Si2**), (*E*)-poly(**1m-Si2**), and (*Z*)-poly(**1p-Si1**)] with number-average molecular weights ranging from 2800 to 17,000 in 41–92% yields. Polymers having (*E*)- and (*Z*)-olefin moieties were obtained, wherein the (*E*)-/(*Z*)-ratios depended on the reaction conditions. The UV–vis absorption edge of (*E*)-poly(**1p-Si1**) was positioned at a wavelength longer than that of (*Z*)-poly(**1p-Si1**), indicating that (*E*)-vinylene-linkage extends the conjugation more largely than the (*Z*)-counterpart. This was also confirmed by fluorescence spectroscopy. Alkaline hydrolysis of ester moieties of these polymers gave the corresponding polymers having carboxy groups. The (*E*)-polymers showed different solubility in hydrophobic solvents before and after hydrolysis, but the non-hydrolyzed and hydrolyzed (*Z*)-polymers exhibited the same solubility.

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1. Introduction

Silicon-containing polymers are expected as photoresist, conductive materials, photo- and electroluminescent materials [1]. Recently, conjugated polymers containing silicon–carbon bonds gather interest because of their high solubility originating from the rotatable σ – π conjugated bond [2]. Various poly(silylenevinylene)s are synthesized by the hydrosilylation polymerization of hydrosilanes with diethynyl compounds catalyzed by platinum [3], rhodium [4], ruthenium [5], iridium [6], and palladium [7]. Among them, RhI(PPh₃)₃-catalyzed hydrosilylation polymerization enables control over regio- and stereostructures of poly(silylenevinylene)s according to the reaction conditions [8]. Masuda and coworkers including us have synthesized a series of poly(silylenevinylene)s [9], some of which show photoluminescence, electroluminescence, redox property, and undergo photo-isomerization.

Meanwhile, optically active conjugated polymers are under hot pursuit due to their potential applications such as circularly polarized photo- and electroluminescent materials and chiral recognition (separation, catalysis, sensory functions) [10]. Although there are a vast amount of examples of such polymers, no report regarding poly(silylenevinylene)s bearing chiral substituents have been reported as far as we know. We have recently synthesized optically active poly(phenyleneethynylene)s by the Sonogashira-Hagihara coupling polymerization of D-hydroxyphenylglycinederived diyne monomers with diethynylbenzene. The polymers adopt helical structures with predominantly one-handed screw sense consisting of hydrophobic exterior and hydrophilic interior in organic solvents [11]. If we utilize such diyne monomers as components of poly(silylenevinylene)s, we can obtain novel optically active silicon-containing polymers that possibly form higherorder structures. In this article, we report the hydrosilylation polymerization of diethynyl monomers 1p and 1m synthesized from D-(-)-p-hydroxyphenylglycine with dihydrosilanes Si1 and Si2 catalyzed by RhI(PPh₃)₃ (Schemes 1 and 2), and examination of the optical and photoluminescent properties of the obtaining polymers [(E)-poly(1p-Si1), (E)-poly(1p-Si2), (E)-poly(1m-Si1), (E)poly(1*m*-Si2), and (*Z*)-poly(1*p*-Si1)].

2. Experimental

2.1. Instruments

Mass spectra were measured on a JEOL JMS-T100CS AccuTOF mass spectrometer or a JEOL JMS-HX110A mass spectrometer. $^{1}\mathrm{H}$ (400 MHz) and $^{13}\mathrm{C}$ (100 MHz) NMR spectra were recorded on





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Scheme 1. Hydrosilylation polymerization of diethynyl monomers **1***p* and **1***m* with dihydrosilanes **Si1** and **Si2** giving (*E*)-polymers.

a JEOL EX-400 or a JEOL AL-400 spectrometer. IR spectra were measured on a JASCO FTIR-4100 spectrophotometer. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Specific rotations ($[\alpha]_D$) were measured on a JASCO DIP-1000 digital polarimeter. CD, UV–vis and fluorescence spectra were measured using a quartz cell (path length: 1 cm) on JASCO J-820, V-550 and FP-750 spectrophotometers, respectively. Number- and weight-



Scheme 2. Hydrosilylation polymerization of diethynyl monomer **1***p* with dihydrosilane **Si1** giving a (*Z*)-polymer.

average molecular weights (M_n and M_w) and polydispersity indices (M_w/M_n) of polymers were determined by gel permeation chromatography (GPC) on a JASCO GULLIVER system (PU-980, DG-980-50, CO-965, UV-1570, RI-930), columns KF-805 (Shodex) × 3, molecular weight limit up to 4 × 10⁶, eluent THF, column temperature 40 °C, flow rate 1 mL/min; calibrated with polystyrene standards. Cyclic voltammograms were measured on an HCH Instruments ALS600A-n electrochemical analyzer.

2.2. Materials

Thionyl chloride (Wako), D-(-)-p-hydroxyphenylglycine (Wako), di-*tert*-butyl dicarbonate [(BOC)₂O, Tokuyama], 1-bromo-4-ethynylbenzene (Sigma–Aldrich), PdCl₂(PPh₃)₂ (Sigma–Aldrich), Cul (Sigma–Aldrich), PPh₃ (Wako), ethynyltrimethylsilane (Shin-Etsu), 1,4-bis(dimethylsilyl)benzene (Wako), and diphenylsilane (Wako) were purchased or gifted, and used without purification. Rhl(PPh₃)₃ was prepared according to the literature [12]. Toluene used for polymerization was distilled over Na prior to use.

2.3. Monomer synthesis

Novel diyne monomers 1p and 1m were synthesized from D(-)-p-hydroxyphenylglycine by the route illustrated in Scheme 3.

2.3.1. 3',5'-Diiodo-N- α -tert-butoxycarbonyl- $_D$ -p-hydroxyphenyl-glycine methyl ester (i)

Thionyl chloride (8.0 mL 110 mmol) was added to a dispersion of $p_{-}(-)-p_{-}$ hydroxyphenylglycine (10.2 g. 61 mmol) in MeOH (100 mL) dropwise at 0 °C over 30 min. The resulting solution was stirred at room temperature overnight. After removing the solvent, the residual mass was washed with Et₂O to obtain white solid. A portion of the solid (13.1 g, 60.3 mmol) and NaHCO₃ (10 g, 119 mmol) were dissolved in distilled water (100 mL). After checking the solution became basic, a solution of $(BOC)_2O$ (16.0 g, 73.5 mmol) in 1,4-dioxane (50 mL) was added to the solution at 0 °C. The resulting solution was stirred at room temperature overnight. After neutralizing the solution with 2M HCl, the resulting solution was extracted with AcOEt. The organic layer was washed with saturated aqueous NaHCO₃, and saturated aqueous NaCl. It was dried over anhydrous MgSO₄ and concentrated on a rotary evaporator to obtain $N-\alpha$ -tert-butoxycarbonyl-p-phydroxyphenylglycine methyl ester as white powder quantitatively. $N-\alpha$ -tert-butoxycarbonyl-D-p-hydroxyphenylglycine methyl ester (15.2 g, 54.0 mmol), NaCl (12.6 g, 216 mmol), and NaIO₄ (11.6 g, 54.0 mmol) were dissolved in AcOH/H₂O [9/1 (v/v), 180 mL]. The mixture was stirred for 15 min. Then, KI (26.9 g, 162 mmol) was added to the mixture at 0 °C, and the resulting mixture was stirred at 40 °C for 6 h. After H₂O (500 mL) was added, the solution was extracted with CHCl₃. The organic layer was washed first with 1 M aqueous Na₂S₂O₃ and saturated aqueous NaCl, dried over anhydrous MgSO₄, and concentrated on a rotary evaporator. The residue was purified by silica gel column chromatography eluted with hexane/AcOEt [4/1 (v/v)] to obtain (i) as white powder in 80% yield (23.0 g, 43.1 mmol) [13]. ¹H NMR (400 MHz, CDCl₃): δ 1.43 [s, 9H, -(CH₃)₃], 3.74 (s, 3H, -CO₂CH₃), 5.17 (s, 1H, -NHCH-), 5.61 (s, 1H, -NHCO-), 5.81 (br, 1H, -OH), 7.66 (s, 2H, Ar).

2.3.2. 3',5'-Diiodo-N- α -tert-butoxycarbonyl- $_D$ -4'-methoxyphenyl-glycine methyl ester (**ii**)

Compound (i) (23.0 g, 43.1 mmol) and K_2CO_3 (8.93 g, 64.7 mmol) were dissolved in acetone (150 mL). Mel (3.22 mL, 51.7 mmol) was added to the solution at 0 °C, and the resulting mixture was heated with refluxing for 3 h. The mixture was poured into iced water, and the mixture was extracted with CHCl₃. The organic layer was



Scheme 3. Synthesis of monomers 1p and 1m.

washed with saturated aqueous NaCl, dried over anhydrous MgSO₄, and concentrated on a rotary evaporator to obtain yellow solid in 95% yield (22.5 g, 41.1 mmol) [12]. ¹H NMR (400 MHz, CDCl₃): δ 1.43 [s, 9H, $-(CH_3)_3$], 3.75 (s, 3H, $-CO_2CH_3$), 3.84 (s, 3H, $-OCH_3$), 5.23 (s, 1H, -NHCH-), 5.77 (s, 1H, -NHCO-), 7.76 (s, 2H, Ar).

2.3.3. $Bis[(4-ethynylphenyl)ethynyl]-N-\alpha-tert-butoxycarbonyl-D-4'-methoxyphenylglycine methyl ester ($ **1p**)

A solution of (ii) (24.1 g, 44.0 mmol), 1-bromo-4-ethynylbenzene (16.1 g, 89.1 mmol), $PdCl_2(PPh_3)_2$ (618 mg, 0.88 mmol), Cul (671 mg, 3.5 mmol) and PPh₃ (692 mg, 2.64 mmol) in THF/Et₃N [2/5 (v/v), 350 mL] was stirred at room temperature under nitrogen overnight. The resulting mixture was filtered, and the filtrate was concentrated on a rotary evaporator. The residual mass was dissolved in CHCl₃. The organic layer was washed with 1.0 M HCl, saturated aqueous NaHCO₃, then saturated aqueous NaCl. It was

dried over anhydrous MgSO4 and concentrated on a rotary evapo-
rator to obtain crude 3',5'-bis[(4-bromophenyl)ethynyl]-N-α-tert-
butoxycarbonyl-D-4'-methoxyphenylglycine methyl ester as brown
solid. It was dissolved in THF/Et ₃ N [5/11 (v/v), 320 mL], and
PdCl ₂ (PPh ₃) ₂ (618 mg, 0.88 mmol), CuI (671 mg, 3.5 mmol), PPh ₃
(692 mg, 2.64 mmol) and ethynyltrimethylsilane (16.0 mL,
113 mmol) were added to the solution. The resulting mixture was
stirred at 50 °C under nitrogen overnight. After the workup process
with a manner similar to that described above, obtained brown
solid was dissolved in THF/MeOH [1/1 (v/v), 220 mL], then K ₂ CO ₃
(12.2 g, 88.0 mmol) was added to the solution at 0 °C. This solution
was stirred at room temperature for 1 h. After filtration and
concentration on a rotary evaporator, residual mass was dissolved
in CHCl3. The solution was washed with 1.0 M HCl, saturated
aqueous NaHCO3, then saturated aqueous NaCl. It was dried over
anhydrous MgSO ₄ and concentrated on a rotary evaporator to

Table 1

Run	Method	Monomers	Cat (mM)	Temp (°C)	Time (h)	Polymer				
						Yield ^c (%)	$M_n^{\rm d}$	$M_w/M_n^{\rm d}$	E/Z ^e	$[\alpha]_{D}^{f}(^{\circ})$
1	1	1p + Si1	2.0	30	6	75	12,000	2.8	100/0	-6.0
2	1	1 <i>p</i> + Si1	2.0	60	0.5	80	14,000	2.6	97/3	-3.5
3	1	1 <i>p</i> + Si2	2.0	60	24	59	6600	2.1	100/0	_ g
4	1	1 <i>p</i> + Si2	2.0	80	15	91	11,000	3.5	100/0	+3.5
5	1	1 <i>m</i> + Si1	2.0	60	1	91	10,000	5.5	79/21	-3.7
6	1	1 <i>m</i> + Si2	2.0	80	38	90	6300	3.8	100/0	-4.8
7	2	1 <i>p</i> + Si1	2.0	0	24	61	_ g	_ ^g	100/0	_ ^g
8	2	1 <i>p</i> + Si1	2.0	30	6	41	6500	1.8	94/6	_ ^g
9	2	1 p + Si1	2.0	60	0.5	79	17,000	3.4	100/0	+2.3
10 ^b	2	1 <i>p</i> + Si1	0.2	$25 \rightarrow 50$	38	92	12,000	4.4	29/71	-9.9
11	2	1 p + Si1	0.1	0	25 days	65	2800	2.7	25/75	g

^a $[1p \text{ or } 1m]_0 = [Si1 \text{ or } Si2]_0 = 0.1 \text{ M in toluene.}$

^b $[1p]_0 = [Si1]_0 = 0.2$ M in toluene.

^c MeOH-insoluble part.

^d Estimated by GPC, eluent THF, PSt standards.

^e Determined by ¹H NMR.

^f Measured in THF, c = 0.1 g/dL.

^g Not determined.

obtain brown solid. The residue was purified by silica gel column chromatography eluted with hexane/AcOEt [4/1 (v/v)] and recrystallization twice to obtain **1p** as slightly yellow powder in 29% yield (6.99 g, 12.9 mmol). Mp 126–127 °C [α]_D – 1.2° (c = 0.100 g/dL in THF at room temperature). ¹H NMR (400 MHz, CDCl₃): δ 1.44 [s, 9H, –(CH₃)₃], 3.20 (s, 2H, –C=CH), 3.75 (s, 3H, –CO₂CH₃), 4.13 (s, 3H, –OCH₃), 5.27 (s, 1H, –NHCH–), 5.66 (s, 1H, –NHCO–), 7.41–7.49 (m, 10H, Ar). ¹³C NMR (100 MHz, CDCl₃): δ 28.3, 53.0, 56.6, 61.4, 79.1, 80.4, 83.2, 86.7, 93.8, 117.6, 122.2, 123.3, 131.3, 132.0, 132.3, 154.5,



Fig. 1. UV–vis spectra of 1*p*, 1*m*, and the polymers measured in THF (c = 6.44–7.59 \times 10⁻⁶ M).

161.6, 170.9. HRMS. Calcd for $C_{35}H_{29}NO_5 (m/z) [M + NH_4]^+$ 561.2384. Found: 561.2397.

2.3.4. 3',5'-Bis[(3-ethynylphenyl)ethynyl]-N-α-tert-butoxycarbonyl -D-4'-methoxyphenylglycine methyl ester (**1m**)

The title compound was synthesized in a manner similar to **1***p*. Yield 28% (white solid). Mp 136–137 °C [α]_D +2.0° (c = 0.100 g/dL in THF at room temperature). ¹H NMR (400 MHz, CDCl₃): δ 1.46 [s, 9H, –(CH₃)₃], 3.14 (s, 2H, –C≡CH), 3.78 (s, 3H, –CO₂CH₃), 4.13 (s, 3H, –OCH₃), 5.28 (s, 1H, –NHCH–), 5.68 (s, 1H, –NHCO–), 7.28–7.69 (m, 10H, Ar). ¹³C NMR (100 MHz, CDCl₃): δ 28.3, 53.0, 56.6, 61.4, 78.0, 80.4, 82.6, 85.4, 93.3, 117.6, 122.5, 123.3, 128.5, 131.8, 132.1, 132.4, 135.0, 154.7, 161.7, 171.0. HRMS. Calcd for C₃₅H₂₉NO₅ (*m*/*z*) [M + Na]⁺ 566.1943. Found: 566.1932.

2.4. Hydrosilylation polymerization

2.4.1. Synthesis of (E)-polymers [(E)-poly(1p-Si1), (E)-poly(1p-Si2), (E)-poly(1m-Si1), and (E)-poly(1m-Si2)]: typical procedure

All the polymerizations were carried out under nitrogen in a glass tube equipped with a three-way stopcock. A typical experimental procedure for the polymerization of **1***p* with 1,4-bis(dimethylsilyl)benzene (**Si1**) is given below. A solution of **1***p* (163.3 mg, 0.300 mmol), Rhl(PPh₃)₃ (6.10 mg, 6.00 µmol) and 1,4-bis(dimethylsilyl)benzene (**Si1**, 66.3 µL, 0.300 mmol) in toluene (3 mL) was stirred at 60 °C for 0.5 h. After that, the resulting mixture was poured into MeOH (250 mL) to precipitate a polymer. It was separated by filtration using a membrane filter (ADVANTEC T300A047A) and dried under reduced pressure.

2.4.2. Synthesis of (Z)-poly(1p-Si1): typical procedure

All the polymerizations were carried out under nitrogen. A solution of RhI(PPh₃)₃ (1.1 mg, 1.0 µmol) and 1,4-bis(dimethylsilyl) benzene (**Si1**, 1.0 mmol) in toluene (1.0 mL) was stirred for 1 h. A portion of this solution (0.1 mL) was fed into a screw-capped glass tube, and the solution was further stirred at 0 °C for 1 h. Then **1***p* (54.5 mg, 0.1 mmol) and toluene (0.5 mL) were added to the solution at 0 °C. The resulting mixture was allowed to warm to room temperature over a period of 2 h, and then stirring was continued at room temperature for 14 h, at 40 °C for 4 h, and at 50 °C for 20 h. The polymer was isolated in a manner similar to (*E*)-polymers.



Fig. 2. Photograph of THF solutions of 1p (left), (*Z*)-poly(1p-Si1) (center) and (*E*)-poly(1p-Si1) (right) (c = 1 mg/mL).

2.5. Alkaline hydrolysis of ester groups of the polymers: typical procedure

Aqueous NaOH (1 M, 0.17 mL) was added to a solution of (*E*)-poly(**1***p***-Si1**) (40 mg, 54 µmol) in THF (1.25 mL) dropwise at 0 °C, and then the resulting mixture was stirred at 50 °C for 12 h. The reaction mixture was poured into 0.5 M aqueous citric acid (100 mL) to precipitate a polymer. It was separated by filtration using a membrane filter (ADVANTEC H100A047A) and dried under reduced pressure.

2.6. Spectroscopic data of the polymers

(*E*)-Poly(**1***p*-Si1) (run 1 in Table 1) ¹H NMR (400 MHz, CDCl₃): δ 0.30–0.45 [br, 12H, -Si(CH₃)₂–], 1.44 [s, 9H, -(CH₃)₃], 3.75 (s, 3H, -CO₂CH₃), 4.14 (s, 3H, -OCH₃), 5.26 (s, 1H, -NHCH–), 5.63 (s, 1H, -NHCO–), 6.61 [d, *J* = 18.8 Hz, 2H, -CH = CH–], 6.92 [d, *J* = 18.8 Hz, 2H, -CH = CH–], 6.92 [d, *J* = 18.8 Hz, 2H, -CH = CH–], 7.45–7.63 (m, 14H, Ar). IR (cm⁻¹, KBr): 3423, 2954, 1750, 1718, 1602, 1507, 1250, 1162, 1134, 818.

(*E*)-Poly(**1***p*-Si2) (run 4 in Table 1) ¹H NMR (400 MHz, CDCl₃): δ 1.44 [s, 9H, -(CH₃)₃], 3.75 (s, 3H, -CO₂CH₃), 4.15 (s, 3H, -OCH₃), 5.26 (s, 1H, -NHCH-), 5.64 (s, 1H, -NHCO-), 6.88 (d, *J* = 19.0 Hz, 2H, -CH = CH-), 7.01 (d, *J* = 19.0 Hz, 2H, -CH = CH-), 7.17-7.63 (m, 20H, Ar). IR (cm⁻¹, KBr): 3423, 2975, 1746, 1718, 1599, 1509, 1244, 1161, 1111, 997, 797, 700.

(*E*)-Poly(**1***m*-Si1) (run 5 in Table 1) ¹H NMR (400 MHz, CDCl₃): δ 0.29–0.45 [br, 12H, -Si(CH₃)₂–], 1.43 [s, 9H, -(CH₃)₃], 3.74 (s, 3H, -CO₂CH₃), 4.14 (s, 3H, -OCH₃), 5.26 (s, 1H, -NHCH–), 5.62 (s, 1H, -NHCO–), 6.04 [d, *J* = 14.8 Hz, 2H, -CH = CH–, (*Z*)-vinyl protons], 6.61 [d, *J* = 19.2 Hz, 2H, -CH = CH–- (*E*)-vinyl protons], 6.91 [d, *J* = 19.2 Hz, 2H, -CH = CH–- (*E*)-vinyl protons], 7.19–7.62 (m, 14H, Ar). IR (cm⁻¹, KBr): 3423, 2953, 1749, 1719, 1591, 1477, 1249, 1161, 1132, 987, 843, 782.

(*E*)-Poly(**1***m*-Si2) (run 6 in Table 1) ¹H NMR (400 MHz, CDCl₃): δ 1.42 [s, 9H, -(CH₃)₃], 3.73 (s, 3H, -CO₂CH₃), 4.13 (s, 3H, -OCH₃), 5.25 (s, 1H, -NHCH-), 5.62 (s, 1H, -NHCO-), 6.93 (d, *J* = 18.8 Hz,

2H, –CH = CH–), 7.04 (d, *J* = 18.8 Hz, 2H, –CH = CH–), 7.36–7.64 (m, 20H, Ar). IR (cm⁻¹, KBr): 3423, 2977, 1747, 1718, 1591, 1245, 1163, 999, 780, 700.

(*Z*)-Poly(**1***p*-Si1) (run 10 in Table 1) ¹H NMR (400 MHz, CDCl₃): δ 0.30–0.45 [br, 12H, -Si(CH₃)₂–], 1.44 [s, 9H, -(CH₃)₃], 3.73 (s, 3H, -CO₂CH₃), 4.12 (s, 3H, -OCH₃), 5.25 (s, 1H, -NHCH–), 5.63 (s, 1H, -NHCO–), 6.05 [d, *J* = 14.8 Hz, 2H, -CH = CH–, (*Z*)-vinyl protons], 6.62 [d, *J* = 19.0 Hz, 2H, -CH = CH–, (*E*)-vinyl protons], 6.92 [d, *J* = 19.0 Hz, 2H, -CH = CH–, (*E*)-vinyl protons], 7.23–7.59 [m, 16H, Ar and (*Z*)-vinyl protons]. IR (cm⁻¹, KBr): 3432, 2957, 1746, 1719, 1602, 1507, 1250, 1162, 1132, 816.

(*E*)-Poly(**1***p*-**Si1**)-hydrolyzed ¹H NMR (400 MHz, DMSO-*d*₆): δ 0.22–0.41 [br, 12H, -Si(CH₃)₂–], 1.37 [s, 9H, -(CH₃)₃], 4.05 (s, 3H, -OCH₃), 5.14 (s, 1H, -NHCH–), 6.68–6.82 (m, 2H, -CH = CH–), 6.87–7.09 (m, 2H, -CH = CH–), 7.22–7.55 (m, 14H, Ar). IR (cm⁻¹, KBr): 3423, 2955, 1719, 1602, 1507, 1249, 1161, 1133, 817.

(*E*)-Poly(**1***p*-**Si2**)-hydrolyzed ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.40 [s, 9H, -(CH₃)₃], 4.10 (s, 3H, -OCH₃), 5.16 (s, 1H, -NHCH-), 6.94–6.96 (m, 2H, -CH = CH-), 7.09–7.13 (m, 2H, -CH = CH-), 7.42–7.70 (m, 20H, Ar). IR (cm⁻¹, KBr): 3422, 2976, 1718, 1600, 1507, 1243, 1159, 1111, 996, 795, 699.

(*E*)-Poly(**1m-Si1**)-hydrolyzed ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.35 [s, 9H, -(CH₃)₃], 4.05 (s, 3H, -OCH₃), 5.16 (s, 1H, -NHCH-), 6.72-6.82 (m, 2H, -CH = CH-), 6.82-7.08 (m, 2H, -CH = CH-), 7.08-7.87 (m, 20H, Ar). IR (cm⁻¹, KBr): 3423, 2955, 1719, 1592, 1475, 1249, 1161, 1133, 987, 845, 780.

(*E*)-Poly(**1***m*-Si2)-hydrolyzed ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.35 [s, 9H, -(CH₃)₃], 4.07 (s, 3H, -OCH₃), 5.16 (s, 1H, -NHCH-), 6.93-6.99 (m, 2H, -CH = CH-), 7.03-7.15 (m, 2H, -CH = CH-), 7.42-7.82 (m, 20H, Ar). IR (cm⁻¹, KBr): 3422, 2977, 1718, 1591, 1477, 1246, 1161, 998, 778, 700.

(*Z*)-Poly(**1***p*-Si1)-hydrolyzed ¹H NMR (400 MHz, DMSO-*d*₆): δ 0.23–0.42 [br, 12H, -Si(CH₃)₂–], 1.38 [s, 9H, -(CH₃)₃], 4.04 (s, 3H, -OCH₃), 5.28 (s, 1H, -NHCH–), 6.06–6.13 [m, 2H, -CH = CH–, (*Z*)-vinyl protons], 6.62–6.86 [m, 2H, -CH = CH–, (*E*)-vinyl protons],



Fig. 3. UV-vis spectra of (E)- and (Z)-model compounds predicted by the DFT (B3LYP/6-31G*) calculation.



Fig. 4. Fluorescence spectra of 1p, 1m, and the polymers excited at the λ_{max} wavelength measured in THF ($c = 5.89-7.59 \times 10^{-7}$ M).

6.86–7.07 [m, 2H, –CH = CH–, (*E*)-vinyl protons], 7.25–7.52 (m, 14H, Ar). IR (cm⁻¹, KBr): 3423, 2954, 1746, 1719, 1602, 1507, 1249, 1161, 1132, 817.

3. Results and discussion

3.1. Hydrosilylation polymerization

The hydrosilylation polymerization of **1***p* and **1***m* with **Si1** and **Si2** was carried out using RhI(PPh₃)₃ as a catalyst at 0–80 °C in toluene.



Fig. 5. Photograph of THF solutions (c = 1 mg/mL) of **1p** (left), (*Z*)-poly(**1p-Si1**) (center), and (*E*)-poly(**1p-Si1**) (right) under irradiation of light (365 nm).

Polymers with M_n 's ranging from 2800 to 17,000 were obtained in 41–92% yields as listed in Table 1. The polymerization was properly monitored by sampling a small portion of the reaction mixture. The reaction was continued until a powdery polymer got precipitated when the sample solution was poured into a large amount of MeOH. When a diyne, a dihydrosilane, and RhI(PPh₃)₃ were mixed simultaneously (runs 1–6, method 1), diyne 1p gave polymers with higher M_n 's in higher yields in shorter reaction times than 1m did. In a similar fashion, dihydrosilane Si1 was more satisfactory than Si2. It seems that the higher polymerizabilities of 1p and Si1 than those of 1m and Si2 come from the less steric hindrance around the diyne and hydrosilane parts, respectively. The polymer yield and M_n became high by raising temperature. The regio- and stereostructures of the polymers were examined by ¹H NMR spectroscopy. It was confirmed that the hydrosilylation took place regioselectively as illustrated in Scheme 1. No ¹H NMR signal assignable to α -adducts was observed [14] in the all cases as reported in RhI(PPh₃)₃-catalyzed hydrosilylation [8d]. Polymers having olefin moieties with (E)form were obtained almost exclusively except for run 5.

We tried to obtain polymers with (*Z*)-form by premixing 1p with the Rh catalyst (runs 7–11, method 2) according to the literature [8d]. However, (*Z*)-polymers did not form but (*E*)-rich polymers regardless of the reaction temperature when the catalyst

Table 2 Alkaline hydrolysis of the polymers.^a

polymer	yield ^b (%)	M_n^c	M_w/M_n^c	$[\alpha]_{D}^{d}$
(E)-poly(1p–Si1)-hydrolyzed ^e	88	9100	3.7	-13.6
(E)-poly(1p–Si2)-hydrolyzed ^f	91	6600	3.6	-1.1
(E)-poly(1m–Si1)-hydrolyzed ^g	91	8500	4.0	-0.9
(E)-poly(1m–Si2)-hydrolyzed ^h	96	5300	3.5	+4.9
(Z)-poly(1 <i>p</i> - Si1)-hydrolyzed ⁱ	74	8300	2.6	-6.1

^a Conditions : in THF, 50 °C, 2–12 h.

^b Insoluble part in 0.5 M aqueous citric acid.

^c Estimated by GPC, eluent THF, PSt standards, where the carboxy groups in the polymers were transformed into methyl ester groups using TMSCHN₂.

^d Measured in THF, c = 0.1 g/dL.

^e Sample: run 2 in Table 1.

^f Sample: run 4 in Table 1.

^g Sample: run 5 in Table 1.

^h Sample: run 6 in Table 1.

concentration was 2.0 mM (runs 7–9). On the other hand, (*Z*)-rich polymers formed when the catalyst concentrations were decreased to 0.2 and 0.1 mM (runs 10 and 11). The possible reason for the formation of (*Z*)-rich polymers is suppression of isomerization from (*Z*)-form to (*E*)-form [15]. Since the Rh complex catalyzes the olefin isomerization as well as hydrosilylation, it is considered that decreasing the Rh concentration enabled the isolation of (*Z*)-rich polymers. (*Z*)-Selectivity was somewhat improved by decreasing the reaction temperature from 25 to 50 to 0 °C. There was no evidence for formation of α -adducts in these cases as well.

Fig. 1 shows the UV–vis spectra of the obtained polymers together with those of diynes **1***p* and **1***m*. The λ_{max} 's of the **1***p*-based (*E*)-polymers were 12–14 nm red-shifted from that of **1***p*, indicating the extension of conjugation of the polymers compared to that of **1***p*. On the other hand, the λ_{max} 's of the **1***m*-based polymers were not red-shifted but rather blue-shifted from that of **1***m*. The *m*-phenylenevinylenesilylene linkage seems to have poor conjugation.

The λ_{max} of (*E*)-poly(**1***p*-**Si1**) was 6 nm more red-shifted than that of (*Z*)-poly(**1***p*-**Si1**). Furthermore, the absorption edge of (*E*)poly(**1***p*-**Si1**) was positioned at a wavelength approximately 30 nm longer than that of (*Z*)-poly(**1***p*-**Si1**). In fact, the THF solution of (*E*)poly(**1***p*-**Si1**) was more yellowish than that of (*Z*)-poly(**1***p*-**Si1**) as shown in Fig. 2. It is considered that (*E*)-vinylene-linkage enhances the conjugation more largely than the (*Z*)-counterpart.

Fig. 3 depicts the UV—vis spectra of model compounds (chemical structures are also shown) of (E)- and (Z)-polymers, simulated by the DFT (B3LYP/6-31G*) calculation [16]. The predicted spectra well agrees with the longer conjugation of the (E)-vinylene-containing polymer than that of (Z)-polymer.

Fig. 4 shows the fluorescence spectra of the obtained polymers together with those of divnes 1p and 1m. The emission peaks of 1pbased polymers were broad compared with that of **1***p*, indicating the delocalization and conjugation extension [17]. On the other hand, **1m**-based polymers emitted fluorescence with almost the same pattern as that of **1m**, indicating the slight extension of conjugation. These results support the conclusion that **1***p*-based polymers have conjugation lengths longer than those of 1m-based polymers. In addition, the emission peak of (E)-poly(1p-Si1) was broad compared with that of (*Z*)-poly(**1***p*-**Si1**). It is suggested that the conjugation length of the (E)-polymer is longer than that of the (Z)-polymer. These trends agree with the results of UV-vis spectroscopy. The fluorescence quantum yields of the polymers ranged from 0.04 to 0.48. Among them, (*E*)-poly(1*p*-Si1) and (*Z*)-poly(1*p*-Si1) clearly emitted florescence as shown in the picture in Fig. 5. The CD spectra of the polymers were also measured in THF/H₂O and THF/hexane mixtures with various compositions (1/9-9/1, v/v), but no signal was observed. There was no evidence for the polymers to adopt chiral higher-order structures such as helix.

3.2. Alkaline hydrolysis of the polymers

Poly(phenyleneethynylene)s substituted with polar groups are amphiphilic. Their backbones are hydrophobic, whereas the polar side groups control hydrophilic interactions. This amphiphilic character leads to folding of main chains to adopt helical conformations in polar media. Oligo(m-phenyleneethynylene)s carrying hydrophilic short ethylene glycol chains fold into helical conformations, which are thermodynamically driven by solvophobic effects [18]. Amphiphilic poly(*m*-phenyleneethynylene)s undergo conformational transition that is consistent with folding of the main chains into helices [19]. Thus we focused on the methyl ester part of the present polymers. As mentioned above, it seems that the polymers do not adopt chiral conformations. By hydrolyzing the ester moieties into carboxy, it is expected that the polymers transform into regulated structures based on the increase of amphiphilicity and possible formation of hydrogen bonding between the carboxy groups. Table 2 summarizes the results of hydrolysis of the polymers by NaOH. Polymers bearing carboxy groups were obtained in 74-96% yields. The molecular weights of the polymers were measured by transforming the carboxy groups of the formed polymers into methyl esters again using TMSCHN₂, because the polymers having carboxy groups were not eluted out from GPC columns presumably due to the high affinity with polystyrene gels. The M_n 's of the polymers became 60–85% of those before hydrolysis. The $[\alpha]_D$ values of **1***p*-based *E*-polymers became 5–10° larger in the minus direction than those before hydrolysis, while the $[\alpha]_D$ values of **1m**-based *E*-polymers became $3-10^\circ$ larger in the plus direction than those before hydrolysis. The absolute $[\alpha]_{D}$ values of the all hydrolyzed polymers were not so large (less than 14°) similar to those of non-hydrolyzed polymers (less than 10°).

Table 3 summarizes the solubility of the polymers before and after hydrolysis. The (*E*)-polymers tended to become insoluble or poorly soluble in toluene, CH_2Cl_2 , and $CHCl_3$ after hydrolysis as predicted from the hydrophilic feature of carboxy group. On the other hand, the (*Z*)-polymer exhibited the same solubility in the solvents listed in Table 3 before and after hydrolysis. It is presumed that the hydrolyzed (*Z*)-polymer positions the carboxy groups at the inner space of the polymer chain to shield the hydrophilic part from solvents. As a result, it is soluble in hydrophobic solvents like toluene, CH_2Cl_2 , and $CHCl_3$.

Figs. 6 and 7 show the UV–vis and fluorescence spectra of the polymers before and after hydrolysis. The shapes and intensities slightly changed upon hydrolysis. It is considered that the substituents affected the way of conjugation of the polymer main chain to some extent. The CD spectra of the hydrolyzed polymers were also measured in THF/H₂O and THF/hexane mixtures with various compositions (1/9-9/1, v/v), but no signal was observed unfortunately. It seems that the silylene linkage is not enough rigid for the polymers to adopt chiral higher-order structures such as helix.

Table 3			
Solubility	of the	polymers.	1

Polymer	Hexane	Toluene	CHCl₃	CH ₂ Cl ₂	THF	MeOH	DMF	DMSO	0.1 M NaOH aq.
(E)-poly(1 <i>p</i> - Si1)	_	+	+	+	+	_	+	+	±
(E)-poly(1p–Si1)-hydrolyzed	-	-	±	-	+	-	+	+	±
(E)-poly(1 <i>p</i> -Si 2)	-	+	+	+	+	-	+	+	-
(E)-poly(1p-Si2)-hydrolyzed	_	-	_	_	+	_	+	+	-
(E)-poly(1m–Si1)	_	+	+	+	+	-	+	+	-
(E)-poly(1m–Si1)-hydrolyzed	_	-	-	-	+	-	+	+	-
(E)-poly(1m–Si2)	_	+	+	+	+	-	+	+	-
(E)-poly(1m–Si2)-hydrolyzed	_	-	-	-	+	-	+	+	-
(Z)-poly(1 p -Si1)	_	+	+	+	+	-	+	+	-
(Z)-poly(1p–Si1)-hydrolyzed	-	+	+	+	+	_	+	+	-

^a Symbols: +soluble, ±partly soluble, -insoluble.



Fig. 6. UV-vis spectra of the polymers before and after hydrolysis measured in THF (6.77–7.59 \times 10⁻⁶ M).

Table 4 summarizes the UV—vis absorption and fluorescence spectroscopic data of the polymers before and after hydrolysis together with those of **1p** and **1m**. The fluorescence quantum yields (Φ 's) of the polymers were lower than those of the diynes, but enough high as photoluminescence materials regarding the **1p**based polymers. The low Φ 's of **1m**-based polymers seem to be related with the lower conjugation. Intersystem crossing may be also the reason because the **1m**-based polymers are more kinked than the **1p**-based ones. No significant difference of Φ 's was observed between the polymers before and after hydrolysis of the ester moieties. Some of the polymers exhibited two fluorescent emission peaks. The peaks at shorter wavelengths are assignable to the emission from the diyne units, because the positions almost agree with those of the diynes (377 and 369 nm). The emission peaks at longer wavelengths should come from the conjugated polymer backbones.

Fig. 8 shows the cyclic voltammograms of (E)-poly(1p-Si1) and (Z)-poly(1p-Si1). Regardless of the different geometric structures of the polymers, almost the same shaped voltammograms were



Fig. 7. Fluorescence spectra (excited at the λ_{max} wavelength) of the polymers measured in THF ($c=6.77-7.59\times10^{-7}$ M).

Table 4
UV-vis absorption and fluorescence spectroscopic data of 1 <i>p</i> . 1 <i>m</i> , and the polymers.

Compound	UV-vis	$\varepsilon^{a}(cm^{-1} M^{-1})$	emission	Φ^{c}
	$\lambda_{\max}^{a}(nm)$		$\lambda_{max}^{b}(nm)$	
1p	306	73,300	377	0.87
1 <i>m</i>	287	52,900	369	0.26
(E)-poly(1 <i>p</i> - Si1)	318	60,000	408 (381)	0.48
(E)-poly(1p–Si1)-hydrolyzed	310	62,900	408 (382)	0.51
(E)-poly(1 <i>p</i> - Si2)	320	65,900	407 (383)	0.43
(E)-poly(1p–Si2)-hydrolyzed	320	58,400	405 (384)	0.49
(E)-poly(1 <i>m</i> - Si1)	271	68,500	369	0.04
(E)-poly(1m–Si1)-hydrolyzed	271	66,300	370	0.10
(E)-poly(1m - Si2)	277	63,900	370 (382)	0.09
(E)-poly(1m–Si2)-hydrolyzed	277	59,000	383 (373)	0.09
(Z)-poly(1 p -Si1)	312	55,900	381	0.46
(Z)-poly(1 <i>p</i> – Si1)-hydrolyzed	311	47,800	382	0.53

^a Measured in THF ($c = 6.44 - 7.59 \times 10^{-6}$ M).

^b Measured in THF ($c = 5.89 - 7.59 \times 10^{-7}$ M). Excited at the wavelength of λ_{max} of the UV-vis absorption. Parentheses: emission wavelength of the second maximum. Photoluminescence quantum yield determined using anthracene as a standard.

observed. Since oxidation peaks were not clearly detected, the HOMO energy levels could not be calculated electrochemically. The LUMO levels of (E)-poly(1p-Si1) and (Z)-poly(1p-Si1) were estimated to be -4.98 and -4.97 eV, respectively [20].



Fig. 8. Cyclic voltammograms of (E)-poly(1p-Si1) and (Z)-poly(1p-Si1) (1 mM) and n- Bu_4NClO_4 (0.1 M) solutions in CH_2Cl_2 measured at a scan rate of 0.1 V/s versus Ag/Ag⁺, 1st-5th cycles.

4. Conclusion

In this paper, we have demonstrated the hydrosilylation polymerization of hydroxyphenylglycine-derived diynes 1p and 1m with dihydrosilanes Si1 and Si2 using RhI(PPh₃)₃ as a catalyst [21]. (E)-Stereoregular polymers were obtained in good yields by feeding a divne, a dihvdrosilane and the catalyst simultaneously. On the other hand, (Z)-rich polymers were obtained by mixing a disilane and a smaller amount of catalyst prior to the addition of a diyne. UV-vis and fluorescence spectroscopies revealed that the conjugation lengths of the (E)-polymers were extended more than those of the (Z)-counterparts, and those of the polymers containing *p*-phenylene linkages were longer than those of the polymers containing no pphenylene linkages, which were supported by the DFT calculation of the model compounds. The (E)-polymers tended to become insoluble or poorly soluble in hydrophobic solvents after hydrolysis of the ester groups as predicted from the hydrophilic feature of resulting carboxy groups. Meanwhile, the (Z)-polymer did not obey this trend presumably because the arrangement of the carboxy groups at the inner space of the polymer chain, leading to shielding the hydrophilic part from solvents. There was no different before and after hydrolysis of ester moieties of polymers in spectroscopic properties. Unfortunately, we could not observe the evidence for formation of higherorder structures of the present polymers. It is concluded that the $\sigma-\pi$ conjugated silvlenevinylene units are not enough rigid for the present polymers to adopt higher-order structures. Further studies on the synthesis of D-(-)-p-hydroxyphenylglycine-derived chirally ordered conjugated polymers are under progress.

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