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SUPPORTING INFORMATION

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The First Synthesis of Well-Defined Poly(2,5-silole)

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General. Melting point (mp) determination was performed by using a Yanaco MP-S3 instrument. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were measured with a JEOL EX-270 (270 MHz for ^{1}H, 67.8 MHz for ^{13}C, and 53.5 MHz for ^{29}Si) spectrometer in $CDCl_3$. Chemical shifts are reported in δ ppm with reference relative to residual protio-solvent, i.e., $CHCl_3$ peak for ^{1}H, to $CDCl_3$ for ^{13}C, and to TMS for ^{29}Si, respectively. UV-visible absorption spectra were recorded on a Shimadzu UV-3100PC spectrometer. Thin layer chromatography (TLC) was performed on plates coated with a 0.25 mm thickness of Silica Gel 60F-254 (Merck). Column chromatography was performed using Kieselgel 60 (70-230 mesh) (Merck). High-performance liquid chromatography (HPLC) was done using a 20 mm x 250 mm Wakosil 5Sil column (Wako). The molecular weights of polymers were estimated with a Shimadzu gel permeation chromatography with polystyrene standards using THF as an eluent at 40 °C.

Materials. Tetrahydrofuran and diethyl ether were freshly distilled before use from sodium/benzophenone or sodium-potassium alloy. Tetramethoxysilane was purchased from the Shin-Etsu Chemical Co. and distilled before use. Titanium tetraisopropoxide was purchased from the Wako Co. and used without further purification. $ZnCl_2$(tmen) was purchased from the Aldrich Co. and used after drying with P_2O_5 at 120 °C *in vacuo* (1 mmHg) for three days. 1,7-Bis(trimethylsilyl)-4,4-bis(methoxymethyl)-1,6-heptadiyne **3** was prepared in four steps from diethyl malonate by the following sequence: (1) propargyl bromide, NaOEt, EtOH, 97%; (2) $LiAlH_4$, Et_2O, 84%; (3) MeI, NaH, 94%; (4) i; *n*-BuLi, THF, ii; Me_3SiCl, 93%. All reactions were carried out under nitrogen unless otherwise stated.

1,4-Diiodo-1,3-butadiene 4. To an ether (10 mL) solution of $Ti(O\textit{i}\text{-}Pr)_4$ (0.37 mL, 1.26 mmol) and diyne **3** (0.32 g, 1.00 mmol) was added an ether solution of *i*-PrMgCl (1.70 mL, 1.66 M, 2.70 mmol) at –70 °C. The mixture was allowed to warm to –50 °C over 1h. After stirring for an additional 1 h, iodine (0.63 g, 2.50 mmol) was added as a solid to the mixture at the same temperature. The mixture was warmed to room temperature and stirred for 10 h. A saturated aqueous solution of $Na_2S_2O_3$ was added and the mixture was extracted with hexane. The combined extract was washed with brine, dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was subjected to column chromatography on silica gel using hexane/EtOAc (10:1) as an eluent (R_f = 0.4) to afford **4** (0.44 g, 0.75 mmol) in 75% yield as a white solid: mp 72-74 °C. ^{1}H NMR ($CDCl_3$) δ 0.27 (s, 18H), 1.96 (d, J = 14.0 Hz, 2H), 2.51 (d, J = 14.0 Hz, 2H), 3.14 (d, J = 8.9 Hz, 2H), 3.25 (d, J = 8.9 Hz, 2H), 3.31 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 1.06, 37.97, 43.40, 59.10, 75.44, 103.52, 160.52. Anal. Calcd for $C_{17}H_{32}I_2O_2Si_2$: C, 35.30; H, 5.58. Found: C, 35.51; H, 5.63.

1,1-Dimethoxy-2,5-bis(trimethylsilyl)silole 5. To a solution of **4** (0.43 g, 0.74 mmol) in Et_2O (3 mL) was added a hexane solution of *n*-BuLi (0.99 mL, 1.54 M, 1.49 mmol) at –78 °C. The mixture was stirred for 1 h and tetramethoxysilane (0.11 mL, 0.74 mmol) was added to the mixture at the same temperature. The resulting mixture was gradually warmed to room temperature and stirred for 12 h. The mixture was hydrolyzed with water and extracted with hexane. The combined extract was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was passed through a short silica gel column and then subjected to HPLC on silica gel (hexane/EtOAc = 10/1; R_f = 0.34) to afford **5** (0.13 g, 0.31 mmol) in 42% yield as a light yellow solid: mp 31-33 °C. ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 18H), 2.40 (s, 4H), 3.20 (s, 4H), 3.31 (s, 6H), 3.41 (s, 6H). ^{13}C NMR ($CDCl_3$) δ –0.43, 37.27, 46.56, 49.96, 59.32, 75.58, 124.39, 172.92. ^{29}Si NMR ($CDCl_3$) δ –9.42, 0.68. Anal. Calcd for $C_{19}H_{38}O_4Si_3$: C, 55.02; H, 9.23. Found: C, 55.24; H, 9.08.

1,1-Diethyl-2,5-bis(trimethylsilyl)silole 6. A THF solution of EtMgBr (1.58 mL, 1.90 M, 3.00 mmol) was added to a mixture of **5** (415 mg, 1.0 mmol) and CuCN (90 mg, 1 mmol) in 1 mL of THF at room temperature. The resulting mixture was refluxed with stirring for 60 h. The mixture was cooled to 0 °C and hydrolyzed by the slow addition of a saturated NH_4Cl aqueous solution. After extracted with Et_2O, the combined extract was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was subjected to silica gel column chromatography using hexane/EtOAc (15:1) as an eluent (R_f = 0.35) to afford **6** (315 mg, 0.77 mmol) in 77% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 18H), 0.66-0.85 (m, 10H), 2.36 (s, 4H), 3.23 (s, 4H), 3.32(s, 6H). ^{13}C NMR ($CDCl_3$) δ 0.09, 5.73, 7.37, 36.79, 48.30, 59.35, 75.65, 132.27, 173.01. ^{29}Si NMR ($CDCl_3$) δ –9.97, 41.63. Anal. Calcd for $C_{21}H_{48}O_2Si_3$: C, 61.40; H, 10.30. Found: C, 61.14; H, 10.34.

1,1-Diethyl-2,5-diiodosilole 2. To a mixture of **6** (206 mg, 0.50 mmol) and $AgBF_4$ (200 mg, 1.03 mmol) in 3 mL of MeOH/THF = 2/1 mixed solvent was added iodine (262 mg, 1.03 mmol) as a solid under nitrogen stream at –78 °C. The mixture was stirred at the same temperature for 1 h and then at 0 °C for 30 min. After filtration of the mixture through a celite layer, water was added to the filtrate. After extracted with ether, the combined extract was washed with a saturated aqueous solution of $Na_2S_2O_3$ and brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated by rotary evaporation. The residue was subjected to silica gel column chromatography using hexane/EtOAc (15:1) as an eluent (R_f = 0.42) to afford **2** (216 mg, 0.42 mmol) in 84% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.69-0.85 (m, 4H), 0.91-1.03 (m, 6H), 2.37 (s, 4H), 3.25 (s, 4H), 3.33 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 1.85, 6.47, 40.24, 47.33, 59.28, 75.49, 83.77, 167.15. ^{29}Si NMR ($CDCl_3$) δ 21.64. UV ($CHCl_3$) λ_{max} = 330 nm, log ε = 3.91. Anal. Calcd for $C_{15}H_{24}O_2Si_1$: C, 34.76; H, 4.67. Found: C, 34.97; H, 4.73.

Poly(2,5-silole) 1. To an ether (6 mL) solution of **2** (634 mg, 1.22 mmol) was added a hexane solution of *n*-BuLi (0.79 mL, 1.62 M, 1.28 mmol) at –78 °C. The mixture was stirred at the same temperature for 1 h. $ZnCl_2$(tmen) (324.3 mg, 1.28 mmol) was added as a solid to the mixture. The resulting mixture was allowed to warm to room temperature over 2 h to give a light yellow

suspension. After removal of the volatile materials *in vacuo* (1 mmHg) at room temperature for 1 h, $PdCl_2(PPh_3)_2$ (8.6 mg, 0.012 mmol) was added to the mixture as a solid under nitrogen stream. After addition of dry THF (6 mL) at room temperature, the reaction mixture was refluxed for 44 h and then condensed under reduced pressure. The residue was dissolved in a small amount of THF and poured into MeOH. The precipitate was collected by filtration and washed successively with water and MeOH to give 164.3 mg of the poly(2,5-silole) **1** (51% crude yield) as a deep red powder. Its molecular weight was estimated by GPC analysis to be M_w = 3,580, M_n = 2,630 (n ≈ 10), and M_w/M_n = 1.36. The red powder was dissolved again in a small amount of THF and reprecipitated from EtOH to give 93.4 mg of the poly(2,5-silole) **1** in 29% yield: ^{1}H NMR ($CDCl_3$) δ 0.66-1.05 (m, 10H, ethyl), 2.16 (s, 4H, ring CH_2), 3.27 (s, 4H, $MeOCH_2$), 3.31 (s, 6H, OCH_3), and a small singlet peak assignable to the terminal proton is observed at 5.45 ppm. ^{13}C NMR ($CDCl_3$) δ 5.59, 7.51, 37.06, 48.72, 59.18, 75.54, 131.45, 155.63, and, in addition, small peaks at 5.59, 8.00, 114.48, 134.14, 154.16, 164.92. The peaks only for H-terminated silole ring seem to be observed among several possible terminal silole rings. ^{29}Si NMR ($CDCl_3$) δ 23.24 and small peaks at 21.57 and 24.12 ppm. UV-vis ($CHCl_3$) λ_{max} 485 nm, log ε 3.73 (per silole unit), at 293K.

MALDI-TOF Mass Spectrometry. The matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass measurement of the polymer **1** was carried out with a Vision 2000 spectrometer (Finnigan MAT, Bremen), equipped with a 337 nm nitrogen laser. The mass spectrum was recorded in the reflectron mode with an acceleration potential of 20 kV and calibrated external with insulin before the measurement. The matrix (*trans*-3-Indole acrylic acid, IAA) was dissolved in THF (0.05 mol/L). A 10 μL aliquot of the matrix solution was mixed with 10 μL of a THF solution of the polymer (2 g/L). A 1 μL sample of the resulting solution was applied to the target and air-dried at room temperature.