FULL PAPER

Rodlike Macromolecules through Spatial Overlapping of Thiophene Dendrons

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Abstract: Two novel dendritic macromonomers 7 and 8 functionalized with electroactive conjugated thiophene oligomers were synthesized by stepwise cross-coupling reactions and the introduction of a vinyl group at the focal point. Both macromonomers were polymerized into dendronized polymers 9 and 10 by using a radical polymerization method. The photophysical and redox behaviors of dendronized polymers 9 and 10 are significantly different from those of the corresponding macromonomers. This difference may result from the spatial overlapping of thiophene dendrons through π - π interactions when the dendrons are connected to a polymer backbone. The dendronized polymers can organize into large-area two-dimensional sheets with a thickness of 4.8 nm. Polymer **9**,

Keywords: amphiphiles • dendrons • oligothiophenes • organic electronics • polymerization which has all-dendritic thiophene side chains, exhibited enhanced conductivity by partial doping with iodine or nitrosonium tetrafluoroborate (NOBF₄). The novel amphiphilic dendronized polymer **15** was synthesized by the atom-transfer radical polymerization of macromonomer **7** from a poly(ethylene glycol) (PEG) macroinitiator and was found to have a self-organized structure in water.

Introduction

Since the discovery of electrical conductivity in π -conjugated polymers in the late 1970s,^[1] conjugated oligomers and polymers have been the subject of intense study owing to their potential applications in fields such as organic lightemitting diodes, photovoltaic cells, field-effect transistors, and chemical sensors.^[2] Oligo- and polythiophenes are the most prominent organic semiconductors applied in organic electronics.^[3] For example, linear and discrete oligothiophene derivatives have been investigated as semiconductors in field-effect transistors and the structural modification affects the charge-transport characteristics of the bulk solid.^[4] A combination of regioregular poly(3-hexylthiophene) and [6,6]-phenyl-C₆₁-butyric acid methyl ester shows excellent performance as an active layer of bulk heterojunction solar cells.^[5] The self-assembling processes of oligo- and polythiophenes are crucial to the overall charge mobility in these devices and charge can be transported along the π - π stacking direction within two- or three-dimensional molecular assem-

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blies.^[6] The fabrication of highly efficient optoelectronic devices requires strict control over the spatial organization of oligomers and polymers.^[7]

New topological architectures of oligothiophenes with cyclic, star, and spherical shapes have recently been synthesized to control spatial organization as well as improve solubility and processability.^[8] Dendrimers are well-defined, spherical, and nanoscopic macromolecules constructed from an interior core with a regular array of branching units.^[9] Conjugated dendrimers based on polyphenylene, polyphenylacetylene, and polythiophene moieties have been synthesized by step-wise cross-coupling reactions and the rigid linkages in conjugated dendrimers can control the mobility of the dendron units.^[10] The shape and size of the conjugated dendrimers persist in all physical environments. All-thiophene dendrons and dendrimers were first synthesized by Advincula and co-workers.^[11a] They also reported the assembly of thiophene dendrimers on solid substrates. Bäuerle and co-workers synthesized very large functionalized thiophene dendrimers composed of 90 thiophene rings for application in solar-energy conversion, photon harvesting, and optoelectronics.^[12] Hexa-peri-hexabenzocorones functionalized with a series of thiophene dendrons that exhibited high power-conversion efficiency in bulk heterojunction solar cells were reported by Wong et al.^[13] The design of a thiophene array in the dendrimers allows the creation of molecular-based components with well-defined properties.[14]

Dendronized polymers have been synthesized by attaching branched dendrons with a central polymer backbone as side chains.^[15] At high degrees of dendron attachment, dendronized linear polymers gain stiffness and adopt a rodlike morphology by the organization of dendron units

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around the polymer backbone. Although numerous reports have focused on the attachment of flexible dendrons with polymer backbones,^[15] the organization of conjugated dendron units in dendronized polymers has rarely been addressed. Schlüter and co-workers synthesized thiophenebased dendronized polymers by the polymerization of macromonomers with different-sized thiophene dendrons.^[16] Herein, a series of dendronized polymers with all-thiophene dendrons were synthesized and characterized. Moreover, the electronic conductivities of dendronized polymers with different conjugated dendritic side chains were investigated. It is concluded that the organization of thiophene dendrons within the dendronized polymer may enable a long-range charge transport in the solid films.

Experimental Section

General: ¹H NMR spectra were measured on a Bruker Avance 400 FT-NMR spectrometer. Mass-spectrometric data were obtained on a PerSeptive Biosystems Voyager DE-Pro spectrometer with dithranol as the matrix. FTIR spectra were obtained on a Shimazu FTIR-8400 spectrometer. UV/Vis and fluorescence spectra were measured on a Shimazu Multi-Spec-1500 spectrophotometer and a JASCO FP-750 machine, respectively. Differential scanning calorimetry (DSC) thermograms were recorded on a SII Exstar 6000 DSC 6200 machine. Atomic force microscopy images were acquired in noncontact mode by a JEOL JSPM-5400 system. Fluorescence quantum efficiencies were determined by Hamamatsu Photonics absolute PL Quantum Yield Measurement system C9920-02. Gel-permeation chromatography (GPC) analyses were carried out with a JASCO HPLC system (pump 1580, UV detector 1575, refractive index detector 930) and a Showa Denko GPC KF-804L column $(8.0 \times 300 \text{ mm}, \text{ polystyrene standards}, M_w = 900-400000 \text{ g mol}^{-1})$ with THF as the eluent at 35 °C (1.0 mL min⁻¹).

Cyclic voltammetric measurements were recorded on an ALS 700 potentiostat using a three-cell electrode system with a Pt working electrode, a Pt counterelectrode, and an Ag/AgCl reference electrode. Tetrabutylammonium perchlorate (TBAP) was used as the electrolyte.

Materials: All the chemicals were purchased from commercial suppliers and used without purification. All the solvents were distilled before each procedure. The purification of the product was carried out by the combination of adsorption column chromatography on silica gel (Wakogel C-200) and recycling preparative HPLC (Japan Analytical Industry, Model LC-908). Analytical TLC was performed on commercial plates coated with silica gel (Merck 60 F₂₅₄). 5,5"-Dimethyl-[2,2';3',2"]terthiophene (1) and tributyl(5,5"-dimethyl-[2,2';3',2"]terthiophen-5'-yl)stannane were synthesized according to the method reported by Advincula and co-workers.^[11] The PEG macroinitiator was synthesized from poly(ethylene glycol) methyl ether with a mass of M_w =2000 gmol⁻¹ and 2-boromo-2methylpropionyl chloride according to the method reported by Iyoda and co-workers.^[17]

Thiophene dendron 3: A solution of tributyl(5,5''-dimethyl-[2,2';3',2'']terthiophen-5'-yl)stannane (3.6 g, 7.23 mmol), 2,3-dibromothiophene (0.5 g, 2.07 mmol), and [Pd(PPh₃)₄] (0.2 g, 0.174 mmol) in dry DMF (17 mL) was stirred at 100 °C for 48 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into water, extracted with CH₂Cl₂, and washed with an aqueous solution of KF to remove tributyltin chloride. The organic layer was dried over magnesium sulfate and the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with petroleum ether/CH₂Cl₂ (7:3) as the eluent to give **3** as orange solid (2.9 g, 63%). ¹H NMR (CDCl₃, 400.13 MHz): δ =7.27 (1H, d, *J* =5.3 Hz, ArH), 7.20 (1H, s, ArH), 7.18 (1H, s, ArH), 7.17 (1H, d, *J* =5.3 Hz), 6.93 (2H, d, *J* =3.4 Hz, ArH), 6.85 (1H, d, *J* =3.5 Hz, ArH), 6.84 (1H, d, *J* =3.5 Hz, ArH), 6.49–6.52 (4H, m, ArH), 2.47 ppm (12H, s, CH₃); ¹³C NMR (CDCl₃, 100.61 MHz): $\delta =$ 147.6, 147.4, 146.2, 146.1, 135.0, 134.8, 134.5, 132.9, 132.6, 132.2, 131.9, 131.7, 131.4, 131.1, 130.5, 129.7, 127.9, 127.8, 126.7, 126.5, 125.4, 125.3, 124.9, 122.6, 15.3 ppm; MALDI-TOF-MS: *m*/*z* (%): 633 (100) [*M*+H]⁺. 2,3-(4'-Methylphenyl)thiophene (2): 2,3-Dibromothiophene (2.0 g, 8.27 mmol) and 4-methylphenylboronic acid (28 g, 20.7 mmol) were dissolved in the mixed solvent of toluene (10 mL), THF (12 mL), and Na₂CO₃ aqueous solution (2.0 m, 8 mL). After degassing with nitrogen gas, [Pd(PPh₃)₄] (0.19 g, 0.17 mmol) was added to the mixed solution. The reaction mixture was stirred at 70 °C for 48 h in a nitrogen atmosphere, after which the reaction mixture was diluted with diethyl ether (50 mL) and washed with water. The organic layer was dried over magnesium sulfate and concentrated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether as the eluent (2.0 g, 91 %). $R_f = 0.6$ (petroleum ether); ¹H NMR (CDCl₃, 400.13 MHz): $\delta = 7.27$ (1 H, d, J = 5.2 Hz, ArH), 7.25 (1 H, d, J = 7.6 Hz, ArH), 7.20 (2H, d, J=7.8 Hz, ArH), 7.18 (2H, d, J=8.1 Hz, ArH), 7.09 (2H, d, J= 7.8 Hz, ArH), 7.07 (2H, d, J=8.1 Hz, ArH), 2.33 ppm (6H, s, CH₃); ¹³C NMR (CDCl₃, 100.61 MHz): $\delta = 158.1$, 138.4, 133.5, 131.2, 129.2, 129.1, 128.9, 128.8, 126.9, 21.2 ppm.

Phenyl-terminated dendron 4: Compound **4** was synthesized from 2,3-dibromothiophene and a stannyl derivative of **2** by the same procedure used to prepare **3** (78%). ¹H NMR (CDCl₃, 400.13 MHz): δ =7.23–7.27 (2H, m, Ar*H*), 7.22 (1H, s, Ar*H*), 7.21 (1H, s, Ar*H*), 7.18 (4H, d, *J*=7.8 Hz, Ar*H*), 7.15 (4H, d, *J*=7.8 Hz, Ar*H*), 7.09 (4H, d, *J*=8.0 Hz, Ar*H*), 7.06 (4H, d, *J*=8.0 Hz, Ar*H*), 2.34 ppm (6H, s, CH₃); ¹³C NMR (CDCl₃, 100.61 MHz): δ =159.1, 140.3, 139.1, 138.3, 137.7, 133.3, 130.2, 129.5, 129.4, 129.3, 1280, 127.3, 1212, 21.6 ppm; MALDI-TOF-MS: *m*/z (%): 608 (100) [*M*+H]⁺.

5: The stannyl compound was synthesized by the conversion of the α -position in 3 with tributyltin chloride. BuLi (1.6 m in hexane; 0.54 mL, 0.85 mmol) was added to solution of 3 (0.45 g, 0.71 mmol) in THF (5 mL) at -78°C. After lithiation, tributyltin chloride (0.29 mL, 1.1 mmol) was added to the reaction mixture and stirred for 30 min at -78 °C in a nitrogen atmosphere. After 30 min, the reaction mixture was allowed to warm to room temperature for 6 h. The reaction mixture was diluted with nhexane (50 mL) and the formed precipitate was removed by filtration. The filtered solution was evaporated, and the product was used without further purification (0.66 g). A solution of the stannyl derivative of 3 (0.66 g, 0.71 mmol), 5-bromo-2,2-bithiophene-5'-carboxylic acid methyl ester (0.26 g, 0.85 mmol), and [Pd(PPh₃)₄] (0.05 g, 0.174 mmol) in dry DMF (7 mL) was stirred at 100 °C for 48 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into water, extracted with CH2Cl2, and washed with an aqueous solution of KF to remove the tributyltin chloride. The organic layer was dried over magnesium sulfate and the solvent was evaporated. The residue was purified by column chromatography on silica gel with CH2Cl2 as the eluent and recycling preparative HPLC to give 5 as a dark-red solid (0.27 g, 45%). FTIR (ATR): $\tilde{\nu} = 1708 \text{ cm}^{-1}$ (-COOCH₃); ¹H NMR (CDCl₃, 400.13 MHz): $\delta =$ 7.70 (1 H, d, J=4.0 Hz, ArH), 7.18–7.22 (4 H, m, ArH), 7.15 (2 H, d, J= 3.6 Hz, ArH), 6.94 (2H, d, J=5.3 Hz, ArH), 6.85-6.90 (4H, m, ArH), 6.60-6.65 (2H, m, ArH), 3.88 (3H, s, -COOCH₃), 2.47 ppm (12H, s, CH₃); MALDI-TOF-MS: m/z (%): 855 (100) [M+H]⁺.

6: Compound **6** was synthesized from **4** and methyl 4-(5'-bromothiophene) benzoate by the same procedure used to prepare **5** (34%). FTIR (ATR): $\tilde{\nu}$ =1707 cm⁻¹ (-COOCH₃); ¹H NMR (CDCl₃, 400.13 MHz): δ = 8.04 (2H, d, *J*=8.4 Hz, Ar*H*), 7.65 (2H, d, *J*=8.2 Hz, Ar*H*), 7.18–7.28 (5H, m, Ar*H*), 7.18–7.20 (8H, m, Ar*H*), 7.06–7.10 (8H, m, Ar*H*), 3.91 (3H, s, -COOCH₃), 2.32 ppm (12H, s, CH₃); ¹³C NMR (CDCl₃, 100.61 MHz): δ =159.2, 140.2, 139.7, 139.0, 138.7, 138.4, 138.1, 137.2, 136.7, 136.6, 133.4, 130.3, 130.1, 129.2, 129.0, 126.9, 121.4, 52.1, 24.5 ppm; MALDI-TOF-MS: *m/z* (%): 825 (100) [*M*+H]⁺.

Hydrolysis of the ester group in 5: KOH aqueous solution (10 mL, 1.0 M) was added to a solution of 5 (0.2 g, 0.234 mmol) in THF (20 mL). The resulting mixture was stirred at 80 °C for 6 h. The reaction mixture was poured into water, extracted with CH₂Cl₂, and washed with HCl aqueous solution (0.1 M) for neutralization. The organic layer was dried over magnesium sulfate and the solvent was evaporated to give the target mole-

6822

cule as a dark-red solid (1.8 g, 94%). FTIR (ATR): $\tilde{\nu}$ =1697 cm⁻¹ (-COOH); ¹H NMR (CDCl₃, 400.13 MHz): δ =7.70 (1H, d, *J*=4.0 Hz, Ar*H*), 7.17–7.22 (4H, m, Ar*H*), 7.15 (2H, d, *J*=3.6 Hz, Ar*H*), 6.93 (2H, d, *J*=5.3 Hz, Ar*H*), 6.84–6.89 (4H, m, Ar*H*), 6.60–6.64 (2H, m, Ar*H*), 3.66 (1H, br, -COO*H*), 2.47 ppm (12H, s, C*H*₃); ¹³C NMR (CDCl₃, 100.61 MHz): δ =160.5, 147.2, 144.6, 140.7, 139.3, 139.0, 137.5, 136.2, 135.6, 133.9, 133.7, 127.7, 15.8 ppm; MALDI-TOF-MS: *m/z* (%): 841 (100) [*M*+H]⁺.

Compound **6** was hydrolyzed by using the same procedure (95%). FTIR (ATR): $\bar{\nu}$ =1698 cm⁻¹ (-COOH); ¹H NMR (CDCl₃, 400.13 MHz): δ =8.12 (2H, d, *J*=8.4 Hz, Ar*H*), 7.70 (2H, d, *J*=8.4 Hz, Ar*H*), 7.39(1H, d, *J*=4.0 Hz, Ar*H*), 7.28 (1H, d, *J*=3.6 Hz, Ar*H*), 7.22–7.24 (3H, m, Ar*H*), 7.17–7.21 (8H, m, Ar*H*), 7.07–7.10 (8H, m, Ar*H*), 3.65 (1H, br, -COO*H*), 2.32 ppm (12H, s, C*H*₃); ¹³C NMR (CDCl₃, 100.61 MHz): δ = 169.6, 160.1, 140.8, 140.7, 139.4, 138.9, 138.1, 137.7, 136.4, 133.6, 130.3, 129.2, 127.8, 126.5, 121.5, 23.2 ppm. MALDI-TOF-MS: *m*/*z* (%): 810 (100) [*M*+H]⁺.

Macromonomer 7: A mixture of the hydrolysis product of 5 (0.1 g, 0.124 mmol) and 2-hydroxyethyl methacrylate (HEMA; 19 µL, 0.157 mmol) were dissolved in dry dichloromethane in a nitrogen atmosphere. 4-Dimethylaminopyridium toluene-para-sulfonate (DPTS; 10 mg, 36.3 µmol) and 1,3-dicyclohexylcarbodiimide (DCC; 75 mg, 0.36 mmol) were added to this solution. The reaction mixture was stirred for two days at room temperature. The reaction mixture was filtered and the filtrate was concentrated to dryness by using a vacuum evaporator. The residue was purified by column chromatography on silica gel and recycling preparative HPLC with CHCl₃ as the eluant to give the desired product (33%). FTIR (ATR): $\tilde{\nu} = 1708 \text{ cm}^{-1}$ (-COOCH₃); ¹H NMR (CDCl₃, 400.13 MHz): $\delta = 7.72$ (1H, s, ArH), 7.24 (1H, s, ArH), 7.22 (2H, d, J =8.1 Hz, ArH), 7.15 (2H, d, J=8.0 Hz, ArH), 6.94 (2H, d, J=3.6 Hz, ArH), 6.87 (2H, d, J=3.6 Hz, ArH), 6.62-6.65 (4H, m, ArH), 6.16 (1H, s, -C=CH₂), 5.60 (1H, s, -C=CH₂), 4.55 (2H, t, J=5.2 Hz, -CH₂-), 4.47 (2H, t, J=5.6 Hz, -CH₂-), 2.48 (12H, s, CH₃), 1.96 ppm (3H, s, -CH₃); ¹³C NMR (CDCl₃, 100.61 MHz): $\delta = 168.1$, 160.1, 145.5, 141.5, 139.3, 138.8, 137.6, 136.8, 136.0, 134.7, 129.4, 128.3, 127.6, 126.6, 126.2, 125.3, 122.7, 62.9, 62.4, 17.2, 15.4 ppm; MALDI-TOF-MS: m/z (%): 953 (100) $[M+H]^+$; elemental analysis (%) calcd for $C_{47}H_{36}O_4S_9$: C 59.21, H 3.81, O 6.71; found: C 59.1, H 3.9, O 6.7.

Macromonomer **8** was synthesized by the same procedure used to prepare **7** (56%). FTIR (ATR): $\tilde{\nu}$ =1707 cm⁻¹ (-COOCH₃); ¹H NMR (CDCl₃, 400.13 MHz): δ =8.04 (2H, d, *J*=8.4 Hz, Ar*H*), 7.64 (2H, d, *J*=8.0 Hz, Ar*H*), 7.26 (1H, s, Ar*H*), 7.24 (1H, s, Ar*H*), 7.22 (1H, s, Ar*H*), 7.08–7.20 (16H, m, Ar*H*), 6.15 (1H, s, -C=CH₂), 5.59 (1H, s, -C=CH₂), 4.56 (2H, t, *J*=5.1 Hz, -CH₂-), 4.50 (2H, t, *J*=5.5 Hz, -CH₂-), 2.32 (12H, s, CH₃), 1.96 ppm (3H, s, -CH₃); ¹³C NMR (CDCl₃, 100.61 MHz): δ = 167.2, 165.9, 160.1, 142.0, 139.7, 138.7, 138.4, 137.9, 137.4, 136.7, 136.0, 133.4, 130.6, 129.2, 129.1, 128.9, 127.3, 126.6, 125.2, 125.1, 120.9, 62.9, 62.4, 21.2, 18.3 ppm; MALDI-TOF-MS: *m*/*z* (%): 923 (100) [*M*+H]⁺; elemental analysis calcd for C₅₇H₄₆O₄S₄: C 74.15, H 5.02, O 6.93; found: C 74.1, H 5.0, O 7.0.

Dendronized polymer 9: Toluene (1.05 mL) was added to **7** (50 mg, 52.5 µmol) and 2,2'-azoisobutyronitrile (AIBN; 20 µg, 0.25 mol%) in a Schlenk tube, and the reaction mixture was degassed by three freeze/ pump/thaw cycles. The homogeneous solution was placed into an oil bath heated to 60°C. After stirring overnight, the solution was evaporated and dissolved in the minimum amount of CH₂Cl₂. The addition of acetone caused a precipitate to form, which was collected by filtration. Finally, the polymer was purified by gel permeation chromatography (GPC; Biorad Biobeads SX-1, THF; 66% conversion). M_w =2.1×10⁵ gmol⁻¹; PDI=2.7 (determined by GPC analysis); ¹H NMR (CDCl₃, 400.13 MHz): δ =7.70 (1H, br, ArH), 7.24-6.85 (10H, br, ArH), 6.62-6.65 (4H, br, ArH), 4.50-4.75 (6H, br, -CH₂-), 2.48 (12H, s, -CH₃), 1.96 ppm (3H, s, -CH₃); ¹³C NMR (CDCl₃, 100.61 MHz): δ =173.1, 160.3, 145.0, 140.3, 140.2, 139.2, 139.2, 138.7, 138.4, 136.5, 135.8, 134.6, 134.0, 129.1, 128.6, 127.6, 127.2, 125.2, 121.2, 63.9, 63.1, 42.0, 26.1, 16.5, 15.3, 11.3 ppm.

Dendronized polymer **10** was synthesized by the same procedure used to prepares **9** (87% conversion). $M_w = 1.0 \times 10^5 \text{ g mol}^{-1}$; PDI=1.4 (determined by GPC analysis); ¹H NMR (CDCl₃, 400.13 MHz): δ =7.79 (2H,

br, Ar*H*), 7.37 (2 H, br, Ar*H*), 7.02 (5 H, br, Ar*H*), 7.00 (8 H, br, Ar*H*), 6.88 (8 H, br, Ar*H*), 4.30–4.41 (6 H, br, $-CH_{2}$ -), 2.16 (12 H, br, CH_{3}), 1.80 ppm (3 H, br, CH_{3}). ¹³C NMR (CDCl₃, 100.61 MHz): δ =167.2, 165.9, 160.1, 142.0, 139.7, 138.7, 138.4, 137.9, 137.4, 136.7, 136.0, 133.4, 130.6, 129.2, 129.1, 128.9, 127.3, 126.6, 125.2, 125.1, 120.9, 62.9, 62.4, 21.2, 18.3 ppm.

Copolymerization of MMA and 7 (11–14): Two solutions of methyl methacrylate (0.2 M; MMA) and **7** in toluene (0.2 M) were prepared, and the two solutions were mixed in a Schlenk tube in different ratios (5:95, 20:80, 50:50, 80:20 v/v). AIBN (0.25 mol %) was added to each solution and the mixed solutions were degassed by three freeze/pump/thaw cycles. The homogeneous solutions were placed into an oil bath heated to 60°C. After stirring overnight, the solution was evaporated and dissolved in the minimum amount of CH₂Cl₂. The addition of acetone caused a precipitate to form, which was collected by filtration. Finally, the polymer was purified by GPC (Biorad Biobeads SX-1; THF).

11: Yield=5 mg; M_w =4.3×10³ g mol⁻¹; PDI=2.3 (determined by GPC analysis); ¹H NMR (CDCl₃, 400.13 MHz): δ =7.7 (br, Ar*H*), 7.3–6.9 (br, Ar*H*), 6.6 (br, Ar*H*), 5.0 (br, -COOC*H*₃), 4.5–4.7 (br, -C*H*₂-), 2.27 (s, -C*H*₃), 1.40–1.45 ppm (m, -C*H*₃).

12: Yield = 10 mg; M_w = 4.5 × 10³ gmol⁻¹; PDI = 2.1 (determined by GPC analysis); ¹H NMR (CDCl₃, 400.13 MHz): δ = 7.7 (br, Ar*H*), 7.3–6.9 (br, Ar*H*), 6.6 (br, Ar*H*), 5.0 (br, -COOC*H*₃), 4.5–4.8 (br, -C*H*₂-), 2.27 (s, -C*H*₃), 1.40–1.46 ppm (m, -C*H*₃).

13: Yield=10 mg; M_w =2.3×10⁴ gmol⁻¹; PDI=2.5 (determined by GPC analysis); ¹H NMR (CDCl₃, 400.13 MHz): δ =7.7 (br, Ar*H*), 7.3–6.9 (br, Ar*H*), 6.6 (br, Ar*H*), 4.9 (br, -COOC*H*₃), 4.4–4.7 (br, -C*H*₂-), 2.27 (s, -C*H*₃), 1.40–1.45 ppm (m, -C*H*₃).

14: Yield=49 mg; M_w =5.8×10⁴ gmol⁻¹; PDI=2.7 (determined by GPC analysis); ¹H NMR (CDCl₃, 400.13 MHz): δ =7.7 (br, Ar*H*), 7.3–6.8 (br, Ar*H*), 6.6 (br, Ar*H*), 5.0 (br, -COOC*H*₃), 4.4–4.6 (br, -C*H*₂-), 2.23 (s, -C*H*₃), 1.40–1.45 ppm (m, -C*H*₃).

Atom-transfer radical polymerization of 7 from the PEG macroinitiator: CuCl (3.0 mg, 0.31 mmol), PEG macroinitiator (8.1 mg, 4.26 µmol), and 7 (0.3 g, 0.31 mmol) were mixed in a Schlenk tube. A solution of 4,4'-dinonyl-2,2'-bipyridine (12.9 mg, 0.35 mmol) in anisole (60 µL) was added though a syringe and the mixed solutions were degassed by three freeze/ pump/thaw cycles. The homogeneous solutions were placed into an oil bath heated to 60°C and stirred at 60°C for 24 h. The solution was passed through a neutral Al₂O₃ column with THF as the eluent to remove the catalyst. Polymer 15 was purified by GPC (Biorad Biobeads SX-1; THF). Yield = 234 mg; $M_{\rm w} = 1.1 \times 10^4 \,{\rm g mol^{-1}}$; PDI = 1.1 (determined by GPC analysis); ¹H NMR (CDCl₃, 400.13 MHz): $\delta = 7.5$ (br, ArH), 7.3-6.9 (br, ArH), 6.8 (br, ArH), 6.6 (br, ArH), 5.0 (br, -COOCH₃), 4.5-4.7 (br, -CH₂-), 3.4-4.0 (m, -CH₂-), 2.4 (s, -CH₃), 1.2 ppm (m, -CH₃); ¹³C NMR (CDCl₃, 100.61 MHz): $\delta = 173.3$, 167.8, 159.7, 144.5, 140.5, 139.0, 138.0, 135.9, 135.1, 133.9, 129.4, 128.6, 126.8, 121.6, 71.9, 65.5, 63.6, 61.9, 58.7, 44.4, 38.5, 30.6, 28.4, 16.6, 15.3, 11.3 ppm.

Results and Discussion

Syntheses of macromonomers: Dendritic macromonomers 7 and 8 were synthesized from 2,3-dibromothiophene by using metal-catalyzed cross-coupling reactions (Scheme 1). Terthiophene 1 was synthesized by the nickel-catalyzed crosscoupling reaction of the Grignard regent of 2-bromo-5methylthiophene and 2,3-dibromothiophene according to the method reported by Advincula and co-wokers.^[11] The two α -positions in 1 were protected with methyl groups and one free α -position was used as the reaction point for building higher generational dendrons. The other component, that is, 2, was synthesized by using the Suzuki–Miyaura coupling reaction between 2,3-dibromothiophene and 4-methyl-

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Scheme 1. Synthesis of dendritic macromonomers **7** and **8**. a) BuLi, Bu₃SnCl; b) 2,3-dibromothiophene, [Pd-(PPh₃)₄], DMF; c) 5-bromo-2,2-bithiophene-5'-carboxylic acid methyl ester, [Pd(PPh₃)₄], DMF; d) methyl 4-(5'-bromothiophene)benzoate, [Pd(PPh₃)₄], DMF; e) 1 \bowtie KOH aq. THF; f) HEMA, DCC, DPTS, CH₂Cl₂.

phenylboronic acid in the presence of a palladium catalyst. These compounds were converted into the corresponding stannyl compounds by treatment with *n*-buthyllithium and tributyltin chloride. The Stille coupling reaction of the stannyl compounds with 2,3-dibromothiophene gave second-generation dendron units 3 and 4 in a yield of 70%. The synthesized dendrons 3 and 4 were treated with 5-bromo-2,2-bithiophene-5'-carboxylic acid methyl ester or methyl 4-(5'bromothiophene)benzoate to give 5 and 6. After hydrolysis of the ester group, 5 and 6 were subsequently converted into macromonomers 7 and 8 by a reaction with HEMA in the presence of DCC and DPTS. The synthesized macromonomers 7 and 8 were fully characterized by ${}^{1}\text{H}$, ${}^{13}\text{C}$ NMR, and FTIR spectroscopy, as well as MALDI-TOF mass spectrometry. Both macromonomers are highly soluble in common solvents, such as CH₂Cl₂, THF, toluene, DMF, and dimethyl sulfoxide (DMSO), at room temperature.

Although the synthesized macromonomers contain linear sexithiophene and thiophene-phenylene co-oligomer, the absorption and fluorescence spectra of **7** and **8** are different from those of linear oligomers (Figure 1). The absorption spectra of **7** and **8** exhibited broad bands at $\lambda_{max} = 398$ and 402 nm, respectively. Although **7** has only one broad absorption peak, the spectrum of **8** exhibits two peaks at $\lambda_{max} = 355$ and 402 nm. The observed absorption maxima of **7** and **8** were blueshifted relative to the reported maxima of linear sexithiophene ($\lambda_{max} = 432 \text{ nm}$)^[18] and phenyl-terminated quaterthiophene^[18] ($\lambda_{max} = 426 \text{ nm}$),^[18] thus suggesting a sterically driven increase in the twisted angle within the oligomers

in Figure S1 in the Supporting Information. Although the torsion angle between the focal thiophene plain and the connecting thiophene plain in 7 is around 15°, the angle between the focal benzene plain and the first connecting thiophene plain is 26°. The all-thiophene macromoner 7 has a more planar conrelative formation to the phenyl-terminated macromonomer 8. The enhancement of conjugation in 7 may lead to one broad absorption peak. The steady-state fluorescence spectra of 7 and 8 in degassed CH_2Cl_2 are shown in Figure 1 b. Macromonomers 7 and 8 emitted fluorescence peaks at $\lambda_{max} =$ 550 and 520 nm by the excita-

owing to the attachment of bulky branches. The optimized geometries and the calculated torsion angles between aromatic rings for **7** and **8** are shown



Figure 1. a) Absorption and b) fluorescence spectra of macromonomers **7** (solid line) and **8** (dashed line) in CH_2Cl_2 .

tion at the absorption maxima. The fluorescence band has become somewhat broadened and structureless in contrast to those of linear oligomers.^[18,19] The fluorescence quantum yields of **7** and **8** ($\Phi_F = 8$ and 9%, respectively) are significantly lower than those of linear oligomers, thus suggesting a short length of the π -conjugated system in the dendritic macromonomers. The fluorescence of the dendritic oligothiophene macromonomers comes from the longest chromophoric α -conjugated unit in a branched structure and the substitution of the thiophene rings at the β -positions induces the twisted conformation of the α -conjugated unit.

Polymerization of macromonomers: Dendritic macromonomers **7** and **8** were polymerized in dry toluene by using 0.25 mol% AIBN as a radical initiator at 60 °C for 24 hours



Scheme 2. Synthesis of the dendronized polymers.

after three freeze/pump/thaw cycles (Scheme 2).^[20] Gel-permeation chromatography (GPC) of **9** and **10** with THF as the eluent revealed a monomodal distribution with weightaverage molecular weight of $M_w = 2.1 \times 10^5$ and $1.0 \times$ 10^5 gmol^{-1} (with a polydispersity index (PDI) of 2.7 and 1.4), respectively, relative to polystyrene standards (Table 1). The resulted dendronized polymers exhibit good solubility in toluene, THF, and chlorinated organic solvents (above 30 mgmL⁻¹) without any flexible and long terminal substituents. The thermal properties of polymers **9** and **10** were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in a nitrogen atmosphere. Whereas the DSC profile of **7** shows a sharp transition peak at 116 °C, which corresponds to a melting point,



FULL PAPER

Figure 2. a) Absorption and b) fluorescence spectra of dendronized polymers 9 (solid line) and 10 (dashed line) in CH_2Cl_2 . c) Fluorescence spectral shift with increasing molar ratio of 7 with copolymers 11, 12, and 14 in CH_2Cl_2 .

this peak disappeared in **9** and a glass-transition temperature was determined to be $T_g = 51.0$ °C (see Figure S2 in the Supporting Information). The decomposition temperatures for 5% weight loss are 356 and 360 °C for **9** and **10**, respectively. These results indicate that both polymers exhibited excellent thermal stability.

Figure 2 shows the absorption and fluorescence spectra of dendronized polymers 9 and 10 in CH₂Cl₂. Low concentrations were used to avoid aggregation among polymers. The absorption band of 9 is slightly broadened and the position of the absorption maximum in 9 is blueshifted with respect to 7. The absorption spectrum of the spin-coated film of 9 on quartz plates also shows a broadening relative to that of 7 (see Figure S3 in the Supporting Information). Schlüter and co-workers reported no difference between the absorption spectra of the thiophene-based macromonomers and the dendronized polymer.^[16] The observed broadening in the absorption spectrum of 9 may result in the overlapping of planer dithiophene segments in 7 through the polymerization. The fluorescence maxima is redshifted by $\Delta \lambda =$ 21 nm relative to their respective macromonomers. Furthermore, the fluorescence quantum yield of 9 ($\Phi_{\rm F}=2\%$) is decrease by the polymerization. On the other hand, the absorption spectrum of 10 is similar to that of 8. Furthermore, the shift of the fluorescence maximum and the decrease in the fluorescence quantum yield (i.e., $\Phi_{\rm F}=6\%$) for 10 are small relative to those for monomer 8 (Table 1). The fluores-

Table 1. P	hotophysical ^[a]	and elec	ctrochemical	data for	the macromor	nomers and	dendronized	polymers. ^[b]
								p ==

Macromonome	rs λ_{\max} [ni (log ε [m] м ⁻¹ ст ⁻	λ. 1]) [r	^{em} nm]	$arPsi_{ m F}$ [%]	HOMO [eV]	LUMC [eV]	E_{g} [eV]	<i>E</i> _{1/2} [V vs S]	EC]
7 8	398 (4. 402 (4.	6) 5)	5: 5:	50 22	8 9	5.3 (5.3) 5.3 (5.4)	[c] 2.8 (2.8 [c] 2.7 (2.9	$(b)^{[c]} 2.5$ $(c)^{[c]} 2.6$	+0.70, +0.82,	+0.91, +1.33 +1.05, +1.10
Dendronized polymers	$M_{ m w} = [m gmol^{-1}]^{[m d]}$	PDI	T _g [°C]	λ _{max} [nm]	λ _{em} [nn	$\Phi_{ m F}$ n] [%]	HOMO [eV]	LUMO [eV]	E_{g} [eV]	E _{1/2} [V vs SEC]
9 10	$\begin{array}{c} 2.1 \times 10^{5} \\ 1.0 \times 10^{5} \end{array}$	2.7 1.4	51 41	389 423	571 531	2 6	5.4 (5.8) ^[c] 5.4 (5.8) ^[c]	$\begin{array}{c} 3.0 \ (3.4)^{[c]} \\ 2.9 \ (3.2)^{[c]} \end{array}$	2.4 2.5	+1.2 +1.1

[a] λ_{max} =maximum of absorption measured in CH₂Cl₂; ε =extinction coefficient at λ_{max} ; λ_{em} =maximum of fluorescence measured in degassed CH₂Cl₂; Φ_{F} =quantum yield. [b] Measured in CH₂Cl₂ containing 0.1 M Bu₄NPF₆ at 295 K, scan rate = 100 mV s⁻¹. [c] HOMO and LUMO energies estimated from electrochemical measurements. [d] Weight-average molecular weight relative to poly(styrene) standards.

cence changes are presumably the result of π - π interactions between the thiophene dendrons by the linkage of focal points through the polymerization. The difference between **9** and **10** can be attributed to the degree of interaction between the dendrons in the dendronized polymers. To investigate the influence of distance between the thiophene dendrons within the polymer chain on the fluorescence spectra, copolymers were synthe-

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sized by the radical polymerization of 7 and MMA in various molar ratios. Four copolymers 11-14 containing 7 at 5, 20, 50, and 80 mol % were prepared by copolymerization between 7 and MMA. The fluorescence spectra of 11--14 are shown in Figure 2c. The composition ratios of the copolymers were confirmed by ¹H NMR spectroscopic analysis and are almost the same as the initial molar ratios. Copolymer 11 containing 5 mol% of 7 shows a fluorescence maximum at $\lambda_{\text{max}} = 551$ nm, which is close to that of **7**. The fluorescence maximum is gradually redshifted with an increasing molar ratio of 7 in the copolymers and reaches $\lambda_{max} = 570 \text{ nm}$ for 14. Moreover, the fluorescence quantum yield decreases from 8 to 2% by increasing the molar ratio ($\Phi_{\rm F}=8, 7, 4,$ and 2% for 11-14, respectively). This result confirms the spatial overlapping of the thiophene dendrons through π - π interactions when they are connected to the polymer backbone.

The optical band gaps (E_g) for the dendritic macromonomers and dendronized polymers were determined from the cross point of the normalized absorbance and fluorescence spectra of thin films on quartz substrates. The HOMO and LUMO energies were estimated from the optical band gaps and the work functions measured by photoelectron spectroscopy in air. The band gaps and HOMO and LUMO energies of **7–10** are listed in Table 1. The band gaps of **7** and **8** are slightly decreased by the polymerization.

Electrochemistry: The electrochemical properties of the oligothiophenes provide important information on their electronic structures and the charge-transportation mechanism employed. In this context, many oligothiophenes and dendritic thiophenes have been investigated.^[11,12,18-20] The electrochemical properties of the macromonomers and dendronized polymers were investigated by using cyclic voltammetry (CV) experiments, which were performed in degassed CH₂Cl₂ containing Bu₄NClO₄ as a supporting electrolyte at 100 mV s⁻¹ at room temperature (Table 1). All the potentials were calibrated against a ferrocene/ferrocenium couple, which was used as an internal standard. The CV curve of 7 showed three quasireversible oxidation processes with halfwave potentials at +0.70, +0.91, and +1.33 V versus SCE (see Figure S4 in the Supporting Information). Furthermore, the phenyl-terminated macromonomer 8 also exhibited three oxidation potentials at +0.82, +1.05, and +1.10 V versus SCE. The presence of three oxidation peaks indicates a mixture of different conjugated lengths within the dendritic oligomers.^[21] In contrast, the voltammograms of dendronized polymers 9 and 10 show one irreversible and ill-defined oxidation peak at +1.20 and +1.08 V, respectively. The oxidation processes of the polymers occurred at higher potentials than those of the corresponding macromonomers. This outcome indicates that the overlapping of dendrons within the polymers induces an increased chemical stability of the oxidized species.

Assembly of dendronized polymers: The dendronized polymers were visualized by atomic force scanning microscopy (AFM) to investigate their individual molecular dimensions and morphologies. The interaction between the dendrons in the dendronized polymers can lead to highly ordered materials in the solid state. The two-dimensional arrays of rodlike dendronized polymers on the substrates were visualized by AFM.^[22] Thin layers of dendronized polymers were prepared by spin-coating from a dilute solution of **9** in THF (1.0 mgmL⁻¹) on mica. The AFM image of a thin film of **9** shows terraces with height differences of 4.8 nm between adjacent terraces (Figure 3). The molecular dimension of the



Figure 3. a) AFM image of the spin-coated film of 9 on a mica substrate and b) cross-sectional profile along the line. The inset shows the schematic model of the dendronized polymer 9.

dendritc monomonomer 7 was estimated to have a length of 2.6 nm according to computer-generated modeling. The observed terrace height was almost double of the length of 7. The polymer backbone was encapsulated in a cylindrical shell of tightly packed thiophene dendrons with a thickness of approximately 4.9 nm. The estimated diameter of the dendronized polymer almost agrees with the terrace height observed in the AFM image. The other dendronized polymer 10 showed a similar AFM image with a terrace height of 4.7 nm. It is concluded from these results that dendronized polymers 9 and 10 can assemble into two-dimensional packing arrangements on the solid.

Electronic conductivity: The electric conductivities of the thin films were measured by a conventional two-point probe by using interdigitated microcircuit electrodes (IMEs) with spacing of approximately $5 \,\mu m$ with 65 finger pairs per device. A thin film of **9** was prepared by spin-coating, and the finger electrode array in the IMEs was fully covered with a thin film of **9**. The coverage area was confirmed by

6826

FULL PAPER



Figure 4. Current/voltage (I/V) curves of thin films of 9 on IMEs before and after doping with I₂ and NOBF₄ at room temperature: (\bigcirc) 9 without doping, (\bigcirc) 9 doped with I₂, (\blacktriangle) 9 doped with 10 mol% NOBF₄, and (\bigtriangleup) 9 doped with 30 mol% NOBF₄.

using optical microscopy and the film thickness was determined by the surface profiler (thickness of tested films: 100 ± 30 nm). Figure 4 shows the current/voltage curves of the thin film of dendronized polymer 9 at room temperature. The film of 9 exhibits low conductivity in the range 10^{-10} – 10^{-9} S cm⁻¹. After exposure of the films to I₂ vapor, the conductivity of the film increased to 10^{-7} – $10^{-6} \, \mathrm{S \, cm^{-1}}$ owing to the partial oxidation of the thiophene dendrons in the dendronized polymers.^[23] Polymer 9 was oxidized by nitrosonium tetrafluoroborate (NOBF₄) in toluene.^[24] The absorption band in the $\lambda = 400-500$ nm region decreased and a broad absorption band in the $\lambda = 600-800$ nm region appeared by adding NOBF₄ to a solution of 9 in toluene. This spectral change indicates that the dendritic thiophene is oxidized by NOBF₄. The electronic conductivities of 9 increased with an increasing concentration of NOBF4 and reached 10⁻⁷–10⁻⁶ S cm⁻¹ above a NOBF₄ concentration of 30 mol%. On the other hand, the film of 10 showed low conductivity (i.e., 10^{-10} – 10^{-9} S cm⁻¹) after exposure to I₂. The absorption spectrum of 10 in toluene remained unaltered by the addition of NOBF₄, thus suggesting a decreased stability relative to the all-thiophene dendron in 9.

Self-organization of amphiphilic dendronized polymers: Amphiphilic block copolymers composed of hydrophilic and hydrophobic segments can organize into well-defined largescaled objects.^[25] Iyoda and co-workers reported an organization of amphiphilic diblock copolymers synthesized by using atom-transfer radical polymerization (ATRP) of liquid crystalline monomers from a hydrophilic PEG chain.^[26] This diblock polymer was organized into a two-dimensional phase-separated structure in which PEG cylinders are oriented vertically with respect to the plane of the films coated onto the substrates. Incorporating the dendrons into the amphiphilic block copolymers could lead to unique organized structures.

An amphiphilic block copolymer **15** was synthesized by the copper-mediated ATRP of **7** from the PEG macroinitia-



Scheme 3. Synthesis of the amphiphilic dendronized polymer. dNbpy=4,4'-d(5-nonyl-2,2'-bipyridine).

tor (Scheme 3). ATRP, developed by Matyjaszewski and coworkers, is a versatile method for preparing well-defined polymers with a narrow molecular-weight distribution.^[27] GPC analysis of 15 revealed a monomodal distribution of $M_{\rm w} = 1.1 \times 10^4 \, {\rm g \, mol^{-1}}$. Block copolymer **15** exhibited a narrow PDI of 1.1, thus implying successful polymerization of the dendritic macromonomers from the PEG macroinitiator by ATRP. Broadening of the absorption band and the redshift of the fluorescence peak in 15 relative to monomer 7 were also observed, thus indicating the overlapping of dendrons in the block copolymers. Block copolymer 15 can disperse readily in water and the dispersed aqueous solution is stable over a period of several months. The morphologies of the aggregate in water were examined by TEM. The sample used for TEM analysis was prepared by drop-casting the dispersed solution onto a carbon-coated grid. Amphiphilic diblock copolymer 15 produced a good contrast in the TEM image without staining, and spherical hollow objects were observed with a diameter of approximately 20 nm (Figure 5). The dark image is ascribed to an accumulation of π -conjugated thiophene dendrons. The amphiphilic block copolymer is composed of a hydrophobic dendronized polymer and hydrophilic coil organized in aqueous media to produce capsules by the segregation of the hydrophobic and hydrophilic segments.

Conclusion

Dendronized polymers containing thiophene dendrons as a pendant group were synthesized. Absorption, fluorescence, and electrochemical changes in solution revealed that the linkage of dendrons with a polymer backbone leads to spatial overlapping of the thiophene dendrons. Furthermore, the polymerization of the macromonomers from the PEG macroinitiator produced an amphiphilic diblock copolymer, and the synthesized copolymer organized into spheres. These redox-active objects will provide a new way of design-



Figure 5. TEM image of the self-organized structures of 15.

ing nanoscopic functional modules with directional electron and energy transportation.

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6828

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