

Synthesis and Self-Assembly of Thiophene-Based All-Conjugated Amphiphilic Diblock Copolymers with a Narrow Molecular Weight Distribution

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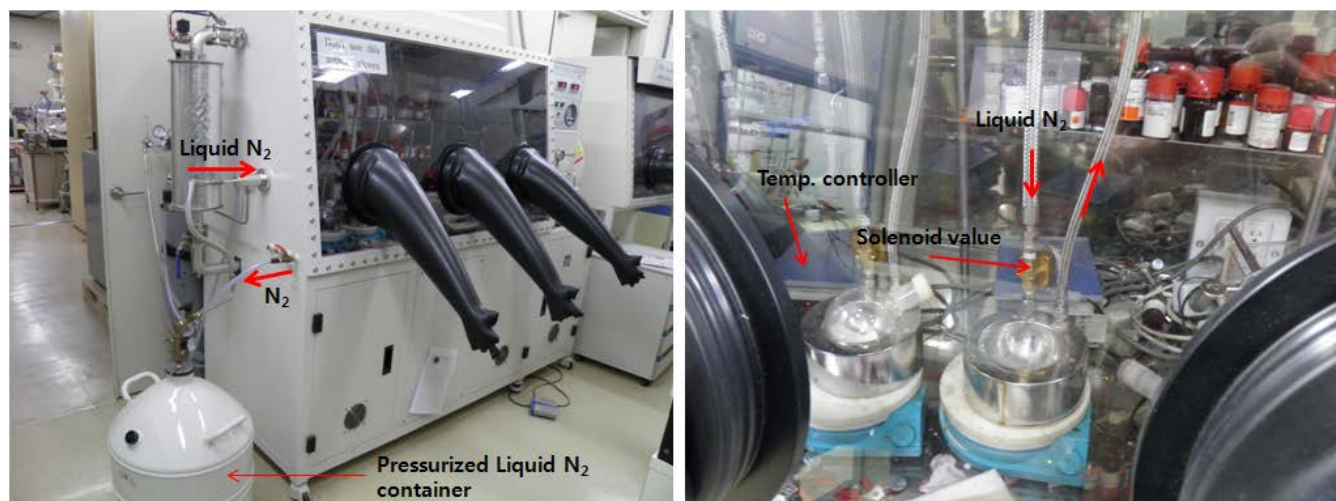
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1. Pictures of the ‘Glove Box’ equipped with temperature-controllable reactors and oxygen/water sensors



2. Experimental details

Materials. 2-bromo-3-hexyl-5-iodothiophene and 3-(3,6,9,12-tetraoxatridecanyl)thiophene were synthesized following previous literatures.^{1,2} All other chemicals were phased from Sigma-Aldrich Co, Junsei Co and used without purification except tetrahydrofuran (THF) which was purified using a J. C. Meyer solvent dispensing system.

Characterization. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX-300 (300 MHz) FT NMR system operating at 300 MHz and 75 MHz, respectively. High resolution mass spectra were obtained from Deagu Branch Analytical Laboratory of the Korea Basic Science Institute (high resolution mass spectrometer; JEOL JMS 700 model). Elemental analyses were performed by Organic Chemistry research center (Elemental analyzer; CE Instruments Flash EA 1112 series). XRD spectra were obtained from X-ray diffraction (XRD) measurements (Rigaku X-ray diffractometer, D/MAX-2500) operating with Cu as a target material and the distance of slits was 0.4 mm/ 10 mm, which set 40 kV/ 100 mA and 2 theta mode from 3 to 30 ° with 4 ° min of scan rate. Differential scanning calorimetric (DSC) measurements of the polymers were performed using a Perkin-Elmer Pyris 1 DSC instrument under a nitrogen atmosphere at a heating and cooling rate of 10 °C/min and only that of BP26 was 3 °C/min due to slow thermal behavior of this polymer. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a size exclusion chromatography (SEC) with SHIMADZU LC solution with chloroform eluent using a calibration curve of polystyrene standards. The UV-Vis absorption spectra were measured with a Mecasys Optizen Pop UV/Vis spectrophotometer and photoluminescence (PL) spectra of the copolymers were measured on a Jasco FP-6500 spectrometer. Transmission electron microscopy (TEM) (S-7600, Hitachi) was operated at 60kV.

Precipitation method. 0.5 mL of $1 \times 10^{-3} \sim 1 \times 10^{-5}$ M of **BP26** solutions in THF were dropwised into 50 mL of stirred anhydrous methanol. Resulting solutions were drop casted on Cu grid and dried at ambient temperature for TEM sample preparation.

Dialysis method. 2 mL of $1 \times 10^{-2} \sim 1 \times 10^{-4}$ M of **BP26** solutions in THF were diluted slowly by adding 38 mL of anhydrous methanol. Resulting diluted polymer solutions ($5 \times 10^{-4} \sim 5 \times 10^{-6}$ M) were transferred into prewashed dialysis membrane tubes (3 kDa molecular weight cut-off) and dialyzed in copious anhydrous methanol for 12 h. After dialysis, samples were drop casted on Cu grid and dried at ambient temperature for TEM sample preparation. PS standards incorporated samples were prepared by including 1×10^{-3} M of PS (M_n = 9, 99, 395 kDa) in $1 \times 10^{-2} \sim 1 \times 10^{-4}$ M of **BP26** solutions in THF.

Sample preparation of XRD measurement. Non-transparent Si wafer (Boron doped Si, Siltron Inc. Korea) was washed with detergent, DI water, ethanol, and acetone for 15 minutes per each step and dried. 100 μ l of 20 mg/ml of polymer solutions in chloroform was spin-coated on the 1.5x 1.5 mm of Si wafer with 1000 rpm. Resulting thin films were annealed at 240 $^{\circ}$ C for 30 minute.

Synthesis of Monomers and Copolymers.

2-bromo-3-(3,6,9,12-tetraoxatridecanyl)thiophene. 3-(3,6,9,12-Tetraoxatridecanyl) thiophene (10.0g, 36.4mmol) were dissolved in 200ml of tetrahydrofuran (THF) and temperature of the solution was decreased to 0 $^{\circ}$ C. To this solution, N-bromosuccinimide (NBS) (6.49g, 36.4mmol) dissolved in 50ml of THF was dropwised and stirred overnight at 0 $^{\circ}$ C. The THF was removed under reduced pressure and residue was poured into water and extracted three times with ethyl acetate. The organic layer was washed with 10% NaHCO₃ aq. and dried by MgSO₄. Solvent was removed by evaporation under reduced pressure and remaining yellow colored liquid was purified by silica gel column chromatography (hexane : ethyl acetate (v/v) = 6:4) to give pure product (10.4g, yield : 80.9%). ¹H-NMR (300 MHz, CDCl₃, ppm) : δ 7.17 (d, *J*=5.7 Hz, 1H); 6.86 (d, *J*=5.7 Hz, 1H); 3.58-3.46 (m, 14H); 3.29 (s, 1H); 2.78 (t, *J*=6.9 Hz, 2H). ¹³C-NMR (75 MHz, CDCl₃, ppm): δ 138.74; 129.08; 125.69; 110.18; 72.31; 71.00; ; 70.95; 70.88; 70.62; 70.54; 59.36; 30.29. MS (EI+,*m/z*) [*M*]⁺ calcd for C₁₃H₂₁BrO₄S 353.27, found 353.29. Elemental analysis calcd (%) for C₁₃H₂₁BrO₄S : C 44.20, H 5.99, S 9.08 ; found : C 44.20, H 6.04, S 9.01.

2-bromo-5-iodo-3-(3,6,9,12-tetraoxatridecanyl)thiophene (9). 2-Bromo-3-(3,6,9,12-tetraoxatridecanyl)thiophene (7.21g, 20.4mmol) were dissolved in 200ml of dichloromethane and temperature of the solution was decreased to 0 $^{\circ}$ C. To this solution, iodine (2.69g, 10.6mmol) and iodobenzene diacetate (3.69g, 10.6mmol) were successively added and mixture was stirred overnight at room temperature. The reaction was quenched by adding Na₂S₂O₃ aq. and extracted three times with dichloromethane and washed with distilled water. Organic layer was dried by MgSO₄ and solvent was removed by evaporation under reduced pressure. Residue was purified by silica gel column chromatography (hexane : ethyl acetate (v/v) = 6:4) to give slightly yellow liquid (7.43g, yield : 76.0%). ¹H-NMR (300 MHz, CDCl₃, ppm) : δ 7.05 (s, 1H); 3.65-3.52 (m, 14H); 3.36 (s, 1H); 2.81 (t, *J*=6.6 Hz, 2H). ¹³C-NMR (75 MHz, CDCl₃, ppm): δ 141.17; 138.85; 113.12; 72.35; 71.55; 71.07; 71.05; 70.98; 70.93; 70.69; 70.34; 59.44; 30.05. MS (EI+,*m/z*) [*M*]⁺ calcd for C₁₃H₂₀BrIO₄S 479.17, found 479.19. Elemental analysis calcd (%) for C₁₃H₂₀BrIO₄S : C 32.59, H 4.21, S 6.69 ; found : C 32.48, H 4.19, S 6.71.

General procedure of GRIM polymerization (P3HTs). To a 50 mL one-neck flask containing monomer (**1** or **3**) (2 mmol) and lithium chloride (2 mmol) in anhydrous THF (20 mL), was added 2M isopropyl magnesium chloride in THF(1 mL, 2mmol) and the mixture was stirred at room temperature. After 1h, Ni(dppp)Cl₂ catalyst following specific conditions(0.01 ~ 0.05 mmol) dispersed in THF (20 mL) was added in one portion and mixture was stirred for 12h. All this procedures were performed in a glove box filled with N₂ atmosphere. The reaction was quenched by adding 5M of HCl aq. and extracted three times with chloroform. The organic layer was dried by MgSO₄ and solvent was removed by evaporation under reduced pressure. Concentrates were precipitated in methanol and filtered. Resulting polymers were dried in vacuum oven for 24 h at an ambient temperature to give purple solid (P3HT). Yields were 68.9 %. ¹H-NMR (300 MHz, CDCl₃, ppm) : δ 6.98 (s, 1H); 2.81 (t, *J*=7.5 Hz, 2H); 1.71 (br, 2H); 1.36 (br, 6H); 0.91 (t, *J*=6.6 Hz, 3H).

PEGT. Following the polymerization procedure with **9** (0.958 mg, 2 mmol) described above. Resulting concentrates was washed with cold hexane and dried in vacuum oven for 24 h to given the sticky purple solid. (201 mg, 36.6%). ¹H-NMR (300 MHz, CDCl₃, ppm) : δ 7.07 (s, 1H); 3.65 (br, 12H); 3.55 (br, 2H); 3.35 (br, 3H); 3.10 (br, 2H).

RP. Following general procedure of GRIM polymerization, monomers (**3** and **9**) was used initially with following Ni(dppp)Cl₂ catalyst (10.8mg, 0.02mmol) and feed ratios; 75:25, 50:50, 25:75 mol % of **3** and **9**. Purple solids (yield, 44.4%) were obtained. Representative ¹H-NMR (300 MHz, CDCl₃, ppm) for **RP32**: δ 7.07-6.98 (m, 2H); 3.77 (br, 2.63H); 3.67-3.60 (br, 15.0H); 3.52 (br, 3.03H); 3.35 (br, 4.40H), 3.11 (br, 2.25H); 2.79 (br, 1.33H); 1.69 (br, 1.39H); 1.48-1.30 (br, 4.13H); 0.91 (br, 2.08H).

General procedure of GRIM polymerization for diblock copolymers. To 50 mL one-neck flasks containing compound **3** (187 mg, 0.500 mmol) and lithium chloride (21.2 mg, 0.500 mmol) in anhydrous THF (5 mL), was added 2 M isopropyl magnesium chloride in THF(0.250 mL, 0.500mmol) and the mixture was stirred at room temperature for 1h (solution A). In the other flask, **9** (719mg, 1.50 mmol) was reacted with 2 M isopropyl magnesium chloride in THF (0.750mL, 1.50mmol)

following the same means with solution A (solution B). Ni(dppp)Cl₂ catalyst (10.8mg, 0.02mmol) dispersed in THF (20 mL) was added in one portion to solution A and mixture was stirred for 1h. Prepared solution B was added into solution A with each ratios against solution A (75:25, 50:50, 25:75 mol % , **9** against **3**) through syringe and resulting solution was stirred for 12h. All this procedures were performed in a glove box filled with N₂ atmosphere. The reaction was quenched by adding 5M of HCl aq. and extracted three times with chloroform. The organic layer was dried by MgSO₄ and solvent was removed by evaporation under reduced pressure. Resulting concentrates were precipitated in methanol or cold hexane.

BP93. Purple solid (187 mg, 37.4%). ¹H-NMR (300 MHz, CDCl₃, ppm) : (based on integral of proton at 4-position of P3HT block = 1) δ 7.07 (s, 0.08H); 6.98 (s, 1H); 3.67 (br, 0.86H); 3.54 (br, 0.16H); 3.35 (br, 0.25H); 3.10 (br, 0.09H); 2.81 (t, *J*=7.5 Hz, 2H); 1.71 (br, 2H); 1.36 (br, 6H); 0.91 (t, *J*=6.6 Hz, 3H).

BP73. Dark black solid was obtained (190 mg, 48.2%). ¹H-NMR (300 MHz, CDCl₃, ppm) : (based on integral of proton at 4-position of P3HT block = 1) δ 7.07(s, 0.32H); 6.98 (s, 1H); 3.67 (br, 4.00H); 3.54 (br, 0.83H); 3.35 (br, 1.17H); 3.10 (br, 0.57H); 2.81 (t, *J*=7.5 Hz, 2H); 1.71 (br, 2H); 1.36 (br, 6H); 0.91 (t, *J*=6.6 Hz, 3H).

BP26. In resulting concentrated solution, the cold hexane was added and the insoluble residue was collected to give dark brown sticky solid (187 mg, 37.4%). ¹H-NMR (300 MHz, CDCl₃, ppm) : (based on integral of proton at 4-position of P3HT block = 1) δ 7.07 (br, 3.07H); 6.98 (br, 1H); 3.67 (br, 37.96H); 3.54 (br, 7.54H); 3.35 (br, 9.83H); 3.10 (br, 5.687H); 2.81 (t, *J*=7.5 Hz, 2H); 1.71 (br, 2H); 1.36 (br, 6H); 0.91 (t, *J*=6.6 Hz, 3H).

3. Normalized photoluminescence spectra and their dependency on solvent polarity

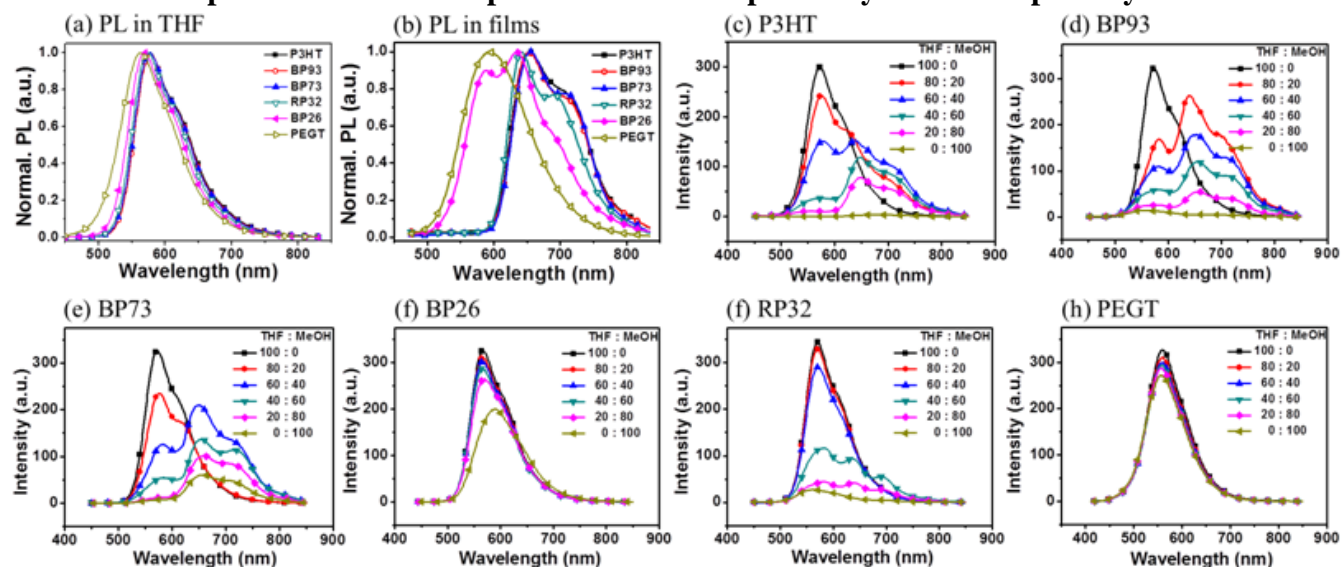


Figure S1. Optical properties of polymers of normalized photoluminescence (PL) spectra in THF (a) and normalized photoluminescence (PL) spectra spectra of films (b). PL emissions dependency in various ratios of THF and methanol for P3HT (c), **BP93** (d), **BP73** (e), **BP26** (f), **RP32** (g), and **PEGT** (h).

4. References

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