

Supporting Information

Requirements for forming efficient 3-D charge transport pathway in Diketopyrrolopyrrole-Based Copolymers: Film Morphology vs. Molecular Packing

Gang-Young Lee,[§] A-Reum Han,[§] Taewan Kim, Hae Rang Lee, Joon Hak Oh, Taiho Park**

Department of Chemical Engineering, Pohang University of Science and Technology, San31,
Nam-gu, Pohang, Gyeongbuk, 790-780, South Korea

*Corresponding author: taihopark@postech.ac.kr, joonhoh@postech.ac.kr

[§]These authors contributed equally.

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Experimental sections

Materials

All the chemicals were purchased from Aldrich. Toluene was purified using the freeze-thaw method. 2-butyloctyl bromide, 2-octyldodecyl bromide and trimethyl(thieno[3,2-*b*]thiophen-2-yl)stannane were synthesized following procedures described in the literature.^{S1}

Material synthesis and characterization

Synthesis of 1,4-Dibromo-2,5-bis-(2-ethyl-hexyloxy)-benzene (1a)^{S2}

2,5-Dibromo-benzene-1,4-diol (5 g, 18 mmol) and 30 mL of DMF were put into a 100 mL flask and cooled to 0 °C. NaH (1.3 g, 56 mmol) was added in 1h and the mixture was stirred well for 1 hour at 0 °C. 2-Ethylhexy bromide (15 g, 56 mmol) was added, then the mixture was stirred under N₂ at 40 °C for 4 h. The reactant was poured into cold water and extracted with 100 mL of dichloromethane twice. The dichloromethane layer was dried over anhydrous MgSO₄. After removing the solvent, the crude product was purified by column chromatography on silica gel eluting with hexane/ethyl acetate = 8:2 (v:v) to give a white oil with a yield of 40 % (3.65 g). ¹H NMR (400 MHz, CDCl₃, δ): 7.10 (s, 1H), 3.85 (d, 2H), 1.76 (m, 1H), 1.50 (m, 4H), 1.30 (m, 4H), 0.9 (t, 6H).

Synthesis of 1,4-Dibromo-2,5-bis-(2-butyl-octyloxy)-benzene (1b)^{S2}

Following **1a** procedure, 3 g (yield = 50 %) of white oil (**1b**) was obtained. ¹H NMR (400 MHz, CDCl₃, δ) 7.09 (s, 1H), 3.83(d, 2H), 1.81 (m, 1H), 1.50-1.1 (m, 17H), 0.9 (t, 6H).

Synthesis of 1,4-Dibromo-2,5-bis-(2-octyl-dodecyloxy)-benzene (1c)^{S3}

Following **1a** procedure, 2.4 g (yield = 50 %) of white oil (**1c**) was obtained. ¹H NMR (400 MHz, CDCl₃, δ) 7.07 (s, 1H), 3.83 (d, 2H), 1.81 (m, 1H), 1.50-1.1 (m, 40H), 0.95 (t, 6H).

*Synthesis of 2,2'-(2,5-bis((2-ethylhexyl)oxy)-1,4-phenylene)dithieno[3,2-*b*]thiophene (2a)*

1a (3.4 g, 6.8 mmol), trimethyl(thieno[3,2-*b*]thiophen-2-yl)stannane (6.0 g 22 mmol), 20 mg of Pd(PPh₃)₄ and 30 ml of toluene were put into a 100 mL flask under N₂ atmosphere. The mixture was stirred under N₂ at 100 °C for 24 h. The reactant was poured into cold water and extracted with 100 mL of dichloromethane twice. The dichloromethane layer was dried over anhydrous MgSO₄. After removing the solvent, the crude product was purified by column chromatography on silica gel eluting with hexane/ethyl acetate = 8:2 (v:v) to give a pure yellow solid with a yield of 70 % (4.0 g). ¹H NMR (400 MHz, CDCl₃, δ): 7.76 (s, 1H), 7.38

(d, 2H) 7.28 (d, 2H), 4.03 (d, 2H), 1.89 (m, 1H), 1.50-1.1 (m, 10H), 0.95 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 149.8, 141.8, 139.7, 139.5, 126.9, 123.6, 119.6, 118.0, 112.9, 72.2, 39.7, 30.8, 29.3, 24.2, 23.2, 14.2, 11.3. MS (MALDI-TOF) m/z : Calcd for $\text{C}_{34}\text{H}_{44}\text{O}_2\text{S}_4$ [M^+] 610.21, found 609.20. Anal. calcd for $\text{C}_{34}\text{H}_{44}\text{O}_2\text{S}_4$: C, 70.28; H, 7.63; S, 22.08. Found: C, 70.01; H, 7.80; S, 22.10.

Synthesis of 2,2'-(2,5-bis((2-butyloctyl)oxy)-1,4-phenylene)dithieno[3,2-b]thiophene (2b)

Following **2a** procedure, 2.4 g (yield = 50 %) of yellow solid (**2b**) was obtained. ^1H NMR (400 MHz, CDCl_3 , δ): 7.76(s, 1H), 7.38 (d, 2H), 7.28 (d, 2H), 4.03 (d, 2H), 1.89 (m, 1H), 1.50-1.1 (m, 17H), 0.95 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3 , δ): 149.9, 145.3, 141.8, 141.1, 126.7, 123.9, 117.8, 113.0, 72.6, 38.4, 32.0, 31.7, 31.4, 29.9, 29.3, 27.1, 23.2, 22.9, 14.3. MALDI-TOF m/z : Calcd for $\text{C}_{42}\text{H}_{58}\text{O}_2\text{S}_4$ [M^+] 610.21, found 609.20. Anal. calcd for $\text{C}_{42}\text{H}_{58}\text{O}_2\text{S}_4$: C, 72.98; H, 8.45; S, 18.56. Found: C, 73.10; H, 8.34; S, 18.56.

Synthesis of 2,2'-(2,5-bis((2-octylododecyl)oxy)-1,4-phenylene)dithieno[3,2-b]thiophene (2c)

Following **2a** procedure, 2.0 g (yield= 60 %) of yellow solid (**2c**) was obtained. ^1H NMR (400MHz, CDCl_3 , δ): 7.76(s, 1H), 7.38(d, 2H) 7.28 (d,2H), 4.03(d, 2H), 1.89 (m, 1H), 1.50-1.1 (m, 40H), 0.95 (t, 6H) ^{13}C NMR (100 MHz, CDCl_3 , δ): 149.9, 141.8, 139.7, 139.6, 127.5, 126.9, 123.7, 119.6, 118.1, 113.1, 72.7, 38.3, 32.1, 31.7, 30.2, 29.8, 29.5, 27,1, 22.9, 14.3 MALDI-TOF m/z : Calcd for $\text{C}_{58}\text{H}_{90}\text{O}_2\text{S}_4$ [M^+] 946.6, found 946.5. Anal. calcd for $\text{C}_{58}\text{H}_{90}\text{O}_2\text{S}_4$: C, 76.08; H, 9.90; S, 14.01. Found: C, 75.95; H, 9.97; S, 14.08.

Synthesis of (5,5'-(2,5-bis((2-ethylhexyl)oxy)-1,4-phenylene)bis(thieno[3,2-b]thiophene-5,2-diyl))bis(trimethylstannane) (3a)

Under N_2 atmosphere, compound **2a** (2.0 g, 3.12 mmol) was dissolved in dry THF (20 mL), then cooled to $-78\text{ }^\circ\text{C}$ and *n*-butyllithium (1.2 mL, 2.0 mmol, 1.6 M in hexane) was added dropwise manner. The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h, then brought to room temperature. The stirring was continued for 20 min and then the reaction mixture was cooled to $-78\text{ }^\circ\text{C}$ again. A solution of trimethyltinchloride (2.41 g, 2.62 mmol) was added. The mixture was slowly brought to room temperature and stirred overnight. Water was added to the reaction mixture and the aqueous phase extracted with ethyl acetate three times. The organic layer was separated and dried with anhydrous MgSO_4 , and the resulting solution was then concentrated by evaporation. A yellowish solid (**3a**) was obtained with yield 65% (3.15g).

^1H NMR (400 MHz, CDCl_3 , δ): 7.76 (s, 1H), 7.38 (s, 1H) 7.28 (s, 1H), 4.03 (d, 2H), 1.89 (m, 1H), 1.50-1.1 (m, 10H), 0.95 (t, 6H), 0.5 (t, 9). ^{13}C NMR (100 MHz, CDCl_3 , δ): 149.9, 145.3, 141.8, 141.1, 126.7, 123.8, 117.7, 112.9, 72.1, 39.8, 30.9, 29.2, 24.3, 23.2, 14.3, 11.4, -7.96. MALDI-TOF m/z: Calcd for $\text{C}_{40}\text{H}_{58}\text{O}_2\text{S}_4\text{Sn}_2$ [M^+] 936.10, Found 936.14. Anal. Calcd for $\text{C}_{40}\text{H}_{58}\text{O}_2\text{S}_4\text{Sn}_2$: C 72.02, H 8.76, S 19.21. Found: C 71.95, H 8.80 S 19.25.

Synthesis of (5,5'-(2,5-bis((2-butyloctyl)oxy)-1,4-phenylene)bis(thieno[3,2-b]thiophene-5,2-diyl))bis(trimethylstannane) (3b)

Following **3a** procedure, 1.4 g (yield = 70 %) of bright yellow solid (**3b**) was obtained. ^1H NMR (400 MHz, CDCl_3 , δ): 7.76(s, 1H), 7.38 (s, 1H) 7.28 (s, 1H), 4.03 (d, 2H), 1.89 (m, 1H), 1.50-1.1 (m, 17H), 0.95 (t, 6H), 0.5 (t, 9). ^{13}C NMR (100 MHz, CDCl_3 , δ): 149.9, 145.3, 141.8, 141.1, 126.7, 123.9, 117.8, 113.0, 72.6, 38.4, 32.0, 31.7, 31.4, 29.9, 29.3, 27.1, 23.2, 22.9, 14.3, -7.96. MALDI-TOF m/z: Calcd for $\text{C}_{48}\text{H}_{74}\text{O}_2\text{S}_4\text{Sn}_2$ [M^+] 1048.26, Found 1048.20. Anal. Calcd for $\text{C}_{48}\text{H}_{74}\text{O}_2\text{S}_4\text{Sn}_2$: C, 73.97; H, 9.56; S, 16.45. Found: C, 74.00; H, 9.60; S, 16.40.

Synthesis of (5,5'-(2,5-bis((2-octyldodecyl)oxy)-1,4-phenylene)bis(thieno[3,2-b]thiophene-5,2-diyl))bis(trimethylstannane) (3c)

Following **3a** procedure, 2.4 g (yield = 50 %) of bright yellow solid was obtained. ^1H NMR (400 MHz, CDCl_3 , δ) 7.76(s, 1H), 7.38(d, 2H) 7.28 (d,2H), 4.03(d, 2H), 1.89 (m, 1H), 1.50-1.1 (m, 40H), 0.95 (t, 6H), 0.5(t, 9). ^{13}C NMR (100 MHz, CDCl_3 , δ): 149.9, 145.3, 141.8, 141.0, 126.7, 123.8, 117.7, 113.0, 72.6, 38.3, 32.1, 31.7, 30.2, 29.8, 29.5, 27.1,0 22.8, 14.3, -8.0. MALDI-TOF m/z: Calcd $\text{C}_{64}\text{H}_{106}\text{O}_2\text{S}_4\text{Sn}_2$ [M^+] 1271.50, Found 1272.50. Anal. Calcd for $\text{C}_{64}\text{H}_{106}\text{O}_2\text{S}_4\text{Sn}_2$: C, 76.58; H, 10.64; S, 12.77. Found: C, 76.80; H, 10.25; S, 12.95.

Synthesis of poly[2,2'-(2,5-bis((2-ethylhexyl)oxy)-1,4-phenylene)dithieno[3,2-b]thiophene-alt-2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione] (P1)

To a microwave reactor vial containing **3a** (150 mg, 0.1 mmol), and 2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (42.3 mg, 0.1 mmol) in a mixture of degassed toluene (3 mL), a catalyst of tris(dibenzylideneacetone)dipalladium (10 mg, 2.6 mol) and tri-*o*-tolylphosphine (17 mg, 10.4 mol) The mixture was allowed to stir for 5 min at 120 °C, 10 min at 150 °C, 30 min at 170 °C. The reaction solution was cooled to room temperature then poured into methanol (200 mL). The precipitated solid was recovered by filtration in a Soxhlet thimble and extracted with acetone, hexane and chloroform for 24 h

each. The chloroform fraction was added ethylenediaminetetraacetate (EDTA) (150 mg, 0.403 mmol) and stirred for 6 h. The organic fraction was washed three times with demineralized water (200 mL) and concentrated under reduced pressure. The residue was precipitated in a vigorously stirred methanol (200 mL) and the desired dark violet polymers were obtained: (160 mg, 61%). GPC (CB, 40 °C): $M_n = 52.0$ kDa, PDI = 2.0, $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ) : 8.66 (d, 2H), 8.16 (br, 2H), 7.95 (s, 1H), 7.72 (s, 1H), 7.69 (br, 2H), 7.60 (br, 2H), 4.71 (br, 1H), 4.26 (br, 4H), 2.50 (br, 2H), 2.11 (br, 6H), 1.50 – 1.12 (br, 44H), 0.91 (s, 6H), 0.78 (t, 6H).

Synthesis of poly[2,2'-(2,5-bis((2-butyloctyl)oxy)-1,4-phenylene)dithieno[3,2-b]thiophene-alt-2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione] (P2)

Following **P1** procedure, 150 mg (yield = 55 %) of purple solid was obtained. GPC (CB, 40 °C): $M_n = 86.0$ kDa, PDI = 1.8, $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ) : 8.66 (d, 2H), 8.16 (br, 2H), 7.95 (s, 1H), 7.72 (s, 1H), 7.69 (br, 2H), 7.60 (br, 2H), 4.71 (br, 1H), 4.26 (br, 4H), 2.50 (br, 2H), 2.11 (br, 6H), 1.50 – 1.12 (br, 44H), 0.91 (s, 6H), 0.78 (t, 6H).

Synthesis of poly[2,2'-(2,5-bis((2-butyloctyl)oxy)-1,4-phenylene)dithieno[3,2-b]thiophene-alt-2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione]

Following **P1** procedure, 130 mg (yield = 60 %) of purple solid was obtained. GPC (CB, 40 °C): $M_n = 66.0$ kDa, PDI = 2.0 $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ) : 8.66 (d, 2H), 8.16 (br, 2H), 7.95 (s, 1H), 7.72 (s, 1H), 7.69 (br, 2H), 7.60 (br, 2H), 4.71 (br, 1H), 4.26 (br, 4H), 2.50 (br, 2H), 2.11 (br, 6H), 1.50 – 1.12 (br, 44H), 0.91 (s, 6H), 0.78 (t, 6H).

Polymer Characterization

Microwave irradiation experiments were performed using a “Monowave 300” single-mode microwave reactor with a maximum of 850 W magnetron output power. ^1H and ^{13}C NMR spectra were recorded on a Bruker BioSpin AG system operated at 400 MHz. Number-average (M_n) and weight-average (M_w) molecular weights were determined by gel-permeation chromatography (GPC) using the Shimadzu LC solution, chlorobenzene as an eluent with a flow rate of 1.0 mL/min, and polystyrenes as standards to calibrate. UV-vis absorption were obtained using an OPTIZEN POP UV-vis-near-IR single beam spectrophotometer. Cyclic voltammetry was performed using a PowerLab/AD instrument model system in 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in anhydrous acetonitrile as supporting electrolyte at a scan rate of 50 mV s^{-1} . A glassy carbon disk ($\sim 0.05 \text{ cm}^2$) coated with a thin polymer film, an Ag/AgNO₃ electrode, and a platinum wire were used as working electrode, reference electrode, and counter electrode, respectively. The atomic force microscopy (AFM) (Multimode IIIa, Digital Instruments) was operated in tapping mode to acquire images of the surfaces of polymers films. Films were prepared by drop-casting from chlorobenzene solutions on *n*-octadecyltrimethoxysilane (OTS)-modified SiO₂/Si substrates. The prepared samples were annealed at optimal temperature on a hot plate under nitrogen. Grazing incidence X-ray diffraction (GIXD) measurements were performed at 3C SAXS and 5A MS-XRS beamline of Pohang Accelerator Laboratory (PAL) in Korea. The incidence angle (α_i) was set at 0.15° to allow for complete penetration of X-rays into the sample. The crystallographic parameters are calculated from GIXD diffractogram profiles obtained at $E = 11.10 \text{ keV}$, $\text{SDD} = 226 \text{ mm}$.

FET Fabrication and Measurement

FETs with bottom-gate top-contact configuration were prepared to characterize the electrical performance of **P1**, **P2**, and **P3** copolymers. A highly *n*-doped (100) Si wafer ($< 0.004 \Omega\cdot\text{cm}$) with a thermally grown SiO₂ (300 nm, $C_i = 10 \text{ nF cm}^{-2}$) was used as the substrate and gate dielectrics; the SiO₂ surface was modified with *n*-octadecyltrimethoxysilane (OTS) as a self-assembled monolayer (SAM) according to a previously reported method.^{S4} First, 3 mM of OTS solution in trichloroethylene was spin-coated on the piranha-treated wafer at 3000 rpm for 30 s. Then, the wafer was exposed to ammonia vapor for $\sim 12 \text{ h}$ to facilitate formation of the SAM, then cleaned by sonication, sequential washing (toluene, acetone, and isopropyl

alcohol, consecutively), and drying. The contact angle (droplet of DI water) on the hydrophobic OTS-modified wafer was $\sim 110^\circ$.

All polymers were dissolved in anhydrous chlorobenzene ($\sim 2 \text{ mg mL}^{-1}$) and the polymer films were prepared onto the substrate by spin-coating, drop-casting, and solution-shearing methods, and then annealed at the optimal temperature. In the solution-shearing method, the polymer solution was placed onto an OTS-treated SiO_2/Si substrate on a preheated plate at 65°C to facilitate wetting solutions and generation of nuclei on the hydrophobic substrate. Then, another OTS-treated substrate was put down on the solution-deposited substrate as a shearing tool and moved at a shearing rate of 0.1 mms^{-1} by a digital syringe pump. Au contacts (40 nm) were thermally evaporated onto the polymer films to form source and drain electrodes with channel length $L = 50 \mu\text{m}$ and width $W = 1000 \mu\text{m}$ using a shadow mask.

The electrical performance of FETs was tested in N_2 atmosphere using a Keithley 4200 semiconductor parametric analyzer. μ was calculated in the saturation regime using the following equation:

$$I_{DS} = \frac{1}{2} \frac{W}{L} \mu C_i (V_G - V_T)^2$$

where I_{DS} is drain-to-source current, V_G is gate voltage and V_T is threshold voltage.

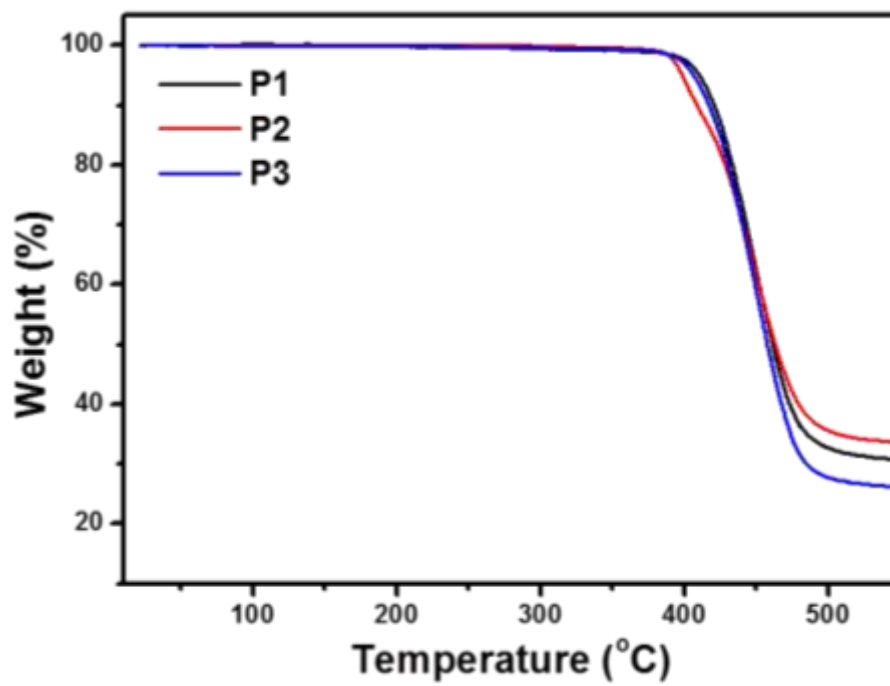


Fig. S1 TGA plots of copolymers with a heating rate $10\text{ }^{\circ}\text{C min}^{-1}$.

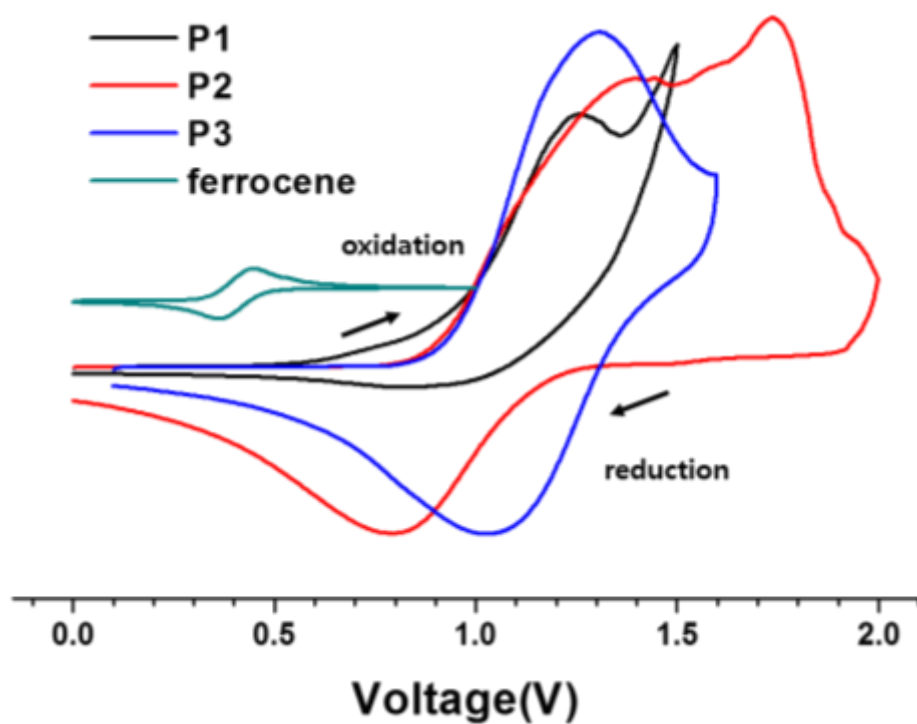


Fig. S2 Cyclic voltammetry of **P1**, **P2**, and **P3** performed in 0.1 M TBAPF₆ in acetonitrile and referenced to an internal Fc/Fc⁺ standard.

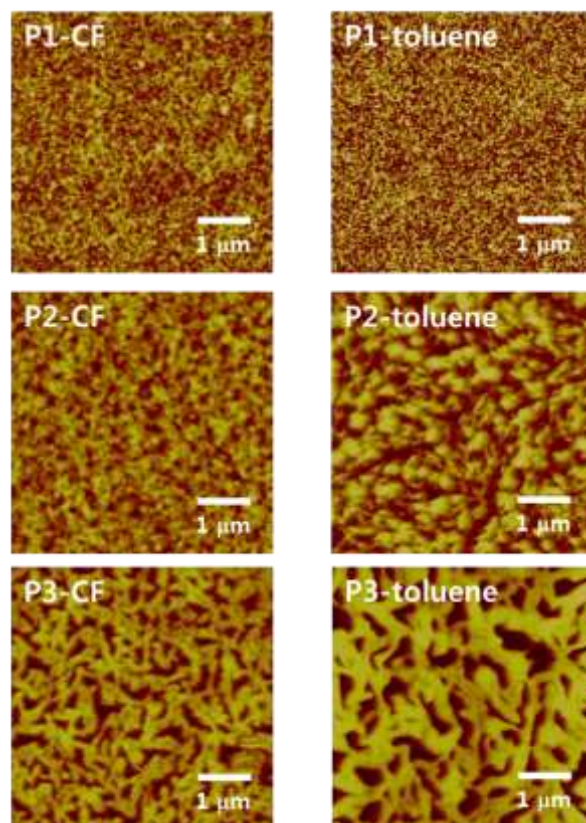


Fig. S3. AFM height image of copolymers in chloroform and toluene solution system.

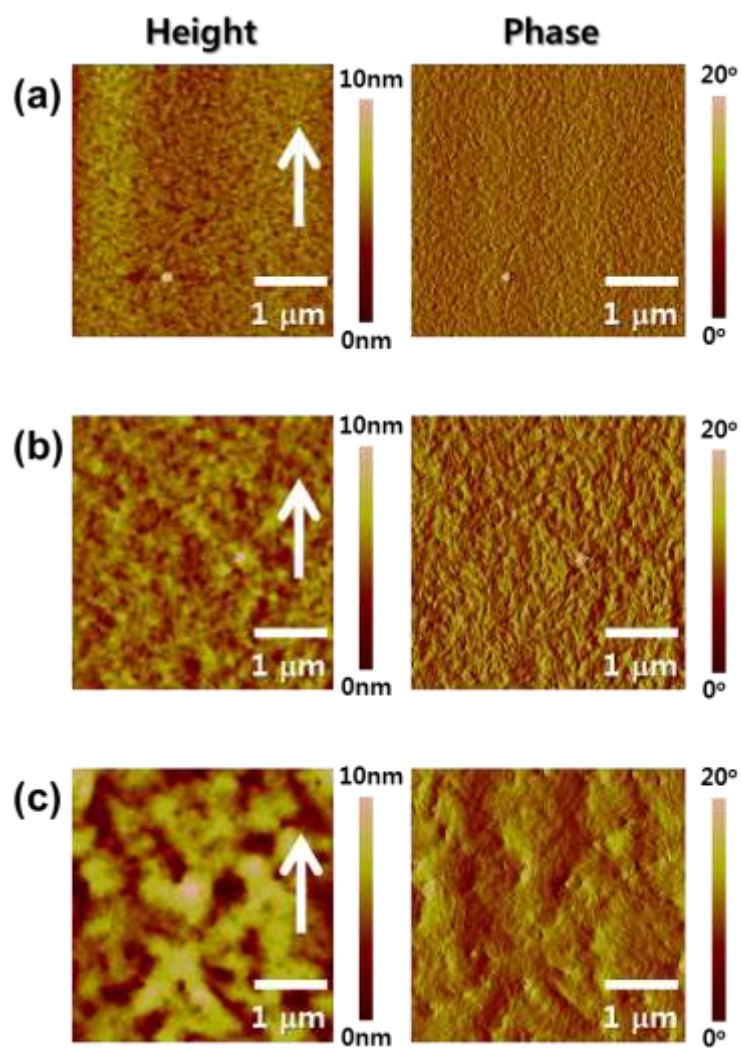


Fig. S4 AFM height (left) and phase (right) images of (a) **P1**, (b) **P2**, and (c) **P3** films prepared by solution-shearing methods after annealing at optimal temperature. Arrow: direction of shearing.

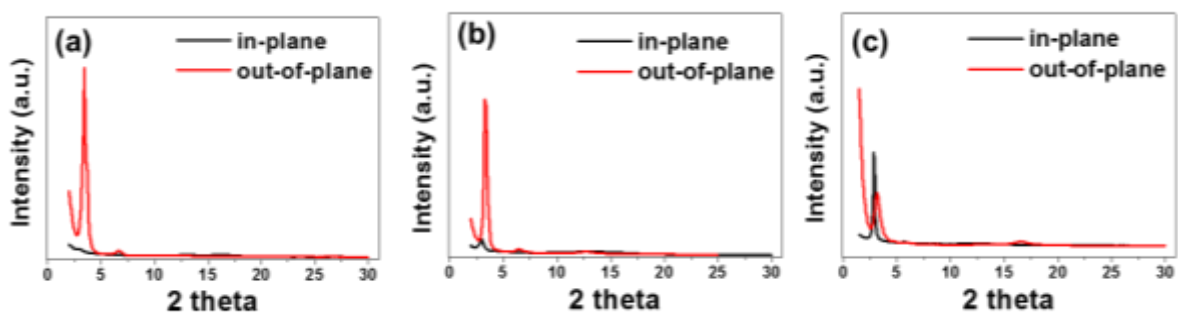


Fig. S5 GIXD patterns of (a) **P1**, (b) **P2**, and (c) **P3** in thin film state thermally annealed at optimal temperature.

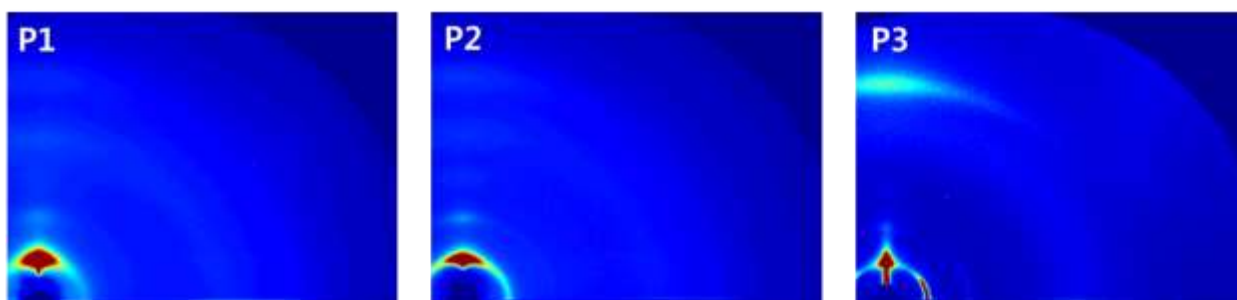


Fig. S6 2D GIXD patterns of the copolymer thin films as spun.

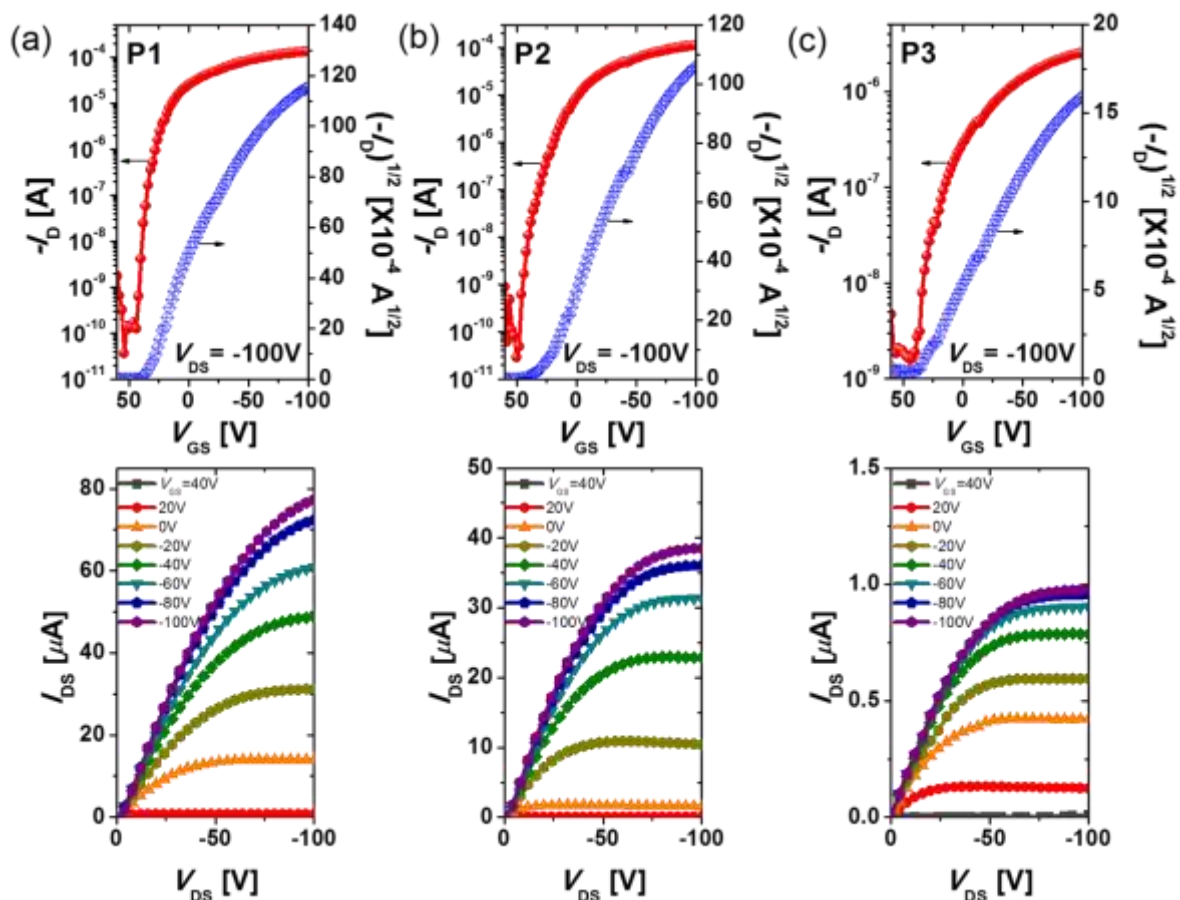


Fig. S7 I - V curves of the polymer FETs based on as-cast solution-sheared films. Transfer (top) and output characteristics (bottom) for (a) **P1**, (b) **P2**, and (c) **P3** films at hole-enhancement operation.

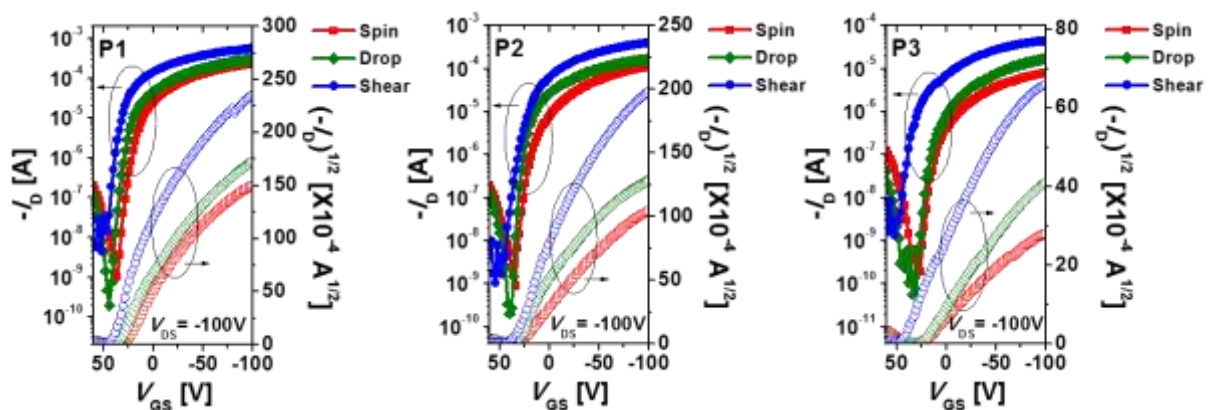


Fig. S8 I - V curves of optimized OFETs based on solution-processed copolymer films: spin-coated, drop-cast, and solution-sheared films of **P1** (left), **P2** (middle), and **P3** (right).

Table S1. FET performance of drop-cast polymer films after thermal annealing treatment

| Polymer ^a | T_a [°C] | μ_{\max}^b [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$] | μ_{avg}^c [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$] | $I_{\text{on}}/I_{\text{off}}$ |
|----------------------|------------|--|--|--------------------------------|
| P1 | 220 | 0.49 | 0.41 (± 0.05) ^d | $10^3 - 10^4$ |
| | 260 | 0.55 | 0.50 (± 0.05) | $10^3 - 10^4$ |
| P2 | 220 | 0.41 | 0.37 (± 0.02) | $10^5 - 10^6$ |
| | 260 | 0.32 | 0.27 (± 0.03) | $10^4 - 10^5$ |
| P3 | 220 | 7.6×10^{-3} | 6.7×10^{-3} ($\pm 8.3 \times 10^{-4}$) | $10^4 - 10^5$ |
| | 260 | 3.0×10^{-2} | 2.4×10^{-2} ($\pm 3.3 \times 10^{-3}$) | $10^5 - 10^6$ |

^aThe FET performance of more than 5 devices was tested in nitrogen atmosphere; ^bThe maximum and ^caverage mobility of the FET devices ($L = 50 \mu\text{m}$ and $W = 1000 \mu\text{m}$); ^dThe standard deviation.

Table S2. Summary of solution-processed FET performance depending on the film preparations at the thermally optimized annealing condition

| Polymer ^a | Condition | | <i>p</i> -channel | | |
|----------------------|-------------------|--------------|--|--|--------------------------------|
| | Film preparation | T_a^b [°C] | μ_{\max}^c [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$] | μ_{avg}^d [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$] | $I_{\text{on}}/I_{\text{off}}$ |
| P1 | Spin-coating | | 0.85 | 0.58 (± 0.158) ^e | $10^5 - 10^6$ |
| | Drop-casting | 260 | 1.66 | 0.99 (± 0.291) | $10^7 - 10^8$ |
| | Solution-shearing | | 2.27 | 1.86 (± 0.161) | $10^5 - 10^6$ |
| P2 | Spin-coating | | 0.52 | 0.35 (± 0.102) | $10^7 - 10^8$ |
| | Drop-casting | 220 | 0.70 | 0.51 (± 0.082) | $10^7 - 10^8$ |
| | Solution-shearing | | 1.14 | 0.88 (± 0.074) | $10^5 - 10^6$ |
| P3 | Spin-coating | | 1.66×10^{-2} | 1.38×10^{-2} (± 0.002) | $10^6 - 10^7$ |
| | Drop-casting | 260 | 2.80×10^{-2} | 2.32×10^{-2} (± 0.004) | $10^6 - 10^7$ |
| | Solution-shearing | | 7.03×10^{-2} | 5.19×10^{-2} (± 0.012) | $10^4 - 10^5$ |

^aThe FET performance of more than 15 devices was tested in nitrogen atmosphere; ^bThe optimized annealing temperature; ^cmaximum and ^daverage mobility of the FET devices ($L = 50 \mu\text{m}$ and $W = 1000 \mu\text{m}$); ^eThe standard deviation.

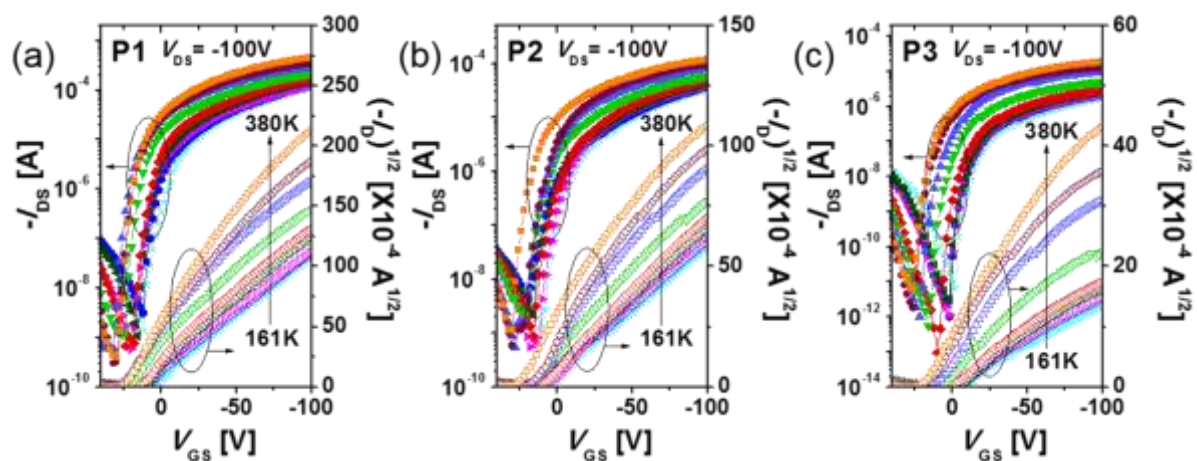


Fig. S9 Transfer characteristics of the optimized FETs at temperatures 161–380 K with $V_{DS} = -100$ V at 1×10^{-5} Torr: (a) **P1**, (b) **P2**, and (c) **P3**.

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