Electronic Supplementary Information

One-Pot Synthesized ABA Tri-block Copolymers for High-Performance Organic Field-Effect Transistors

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Experimental Section

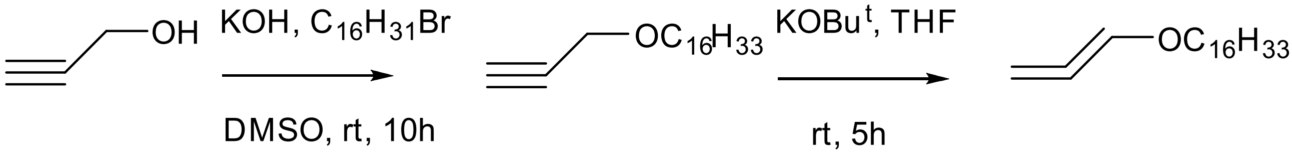
1. Materials

1-Bromohexadecane was obtained from Aladdin and used as received. 2,5-dibromo-3-hexylthiophene was obtained from Aladdin and passed through a silica gel column. Propargyl alcohol was purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. Ni(dppp)Cl_2 and t-BuMgCl in tetrahydrofuran (THF) (2 mol/L) was purchased from Aldrich and stored in glovebox at room temperature. Other reagents used in this work were purchased from Sinopharm Chemical Reagent Co, Ltd.. THF was dried over sodium benzophenone ketyl and further distilled just before use. DMF and CH_2Cl_2 were dried from calcium hydride prior to use. rr-P3HT 4002-EE purchased from Rieke Metals, Inc. used without further purification (regioregularity ≈ 91 ~ 94 % Mw ≈ 50 ~ 70 kDa).

2. Synthesis

2.1 Synthesis of monomer 2 hexadecyloxyallene

Scheme S1. Synthesis route of 1-(Prop-2-yn-1-yloxy) hexadecane.



1-(Prop-2-yn-1-yloxy)hexadecane: To a suspension of KOH (16.8 g, 0.30 mol) in 100 mL DMSO was added 5.4 mL propargyl alcohol (5.60 g, 0.10 mol) at 0 ºC. After stirring for 30 min, cetyl bromide (31.5 mL, 0.10 mol) was added at 0 oC. Stirring was continued for 10 h at room temperature. The resulting brown suspension was diluted with 200 mL water and extracted with diethyl ether (3 × 50 mL). The combined organic layer was washed with water (2 × 20 mL) and brine (2 × 20 mL), dried over Na2SO4, filtered and concentrated in *vacuo*. The yellowish, oily liquid was purified by flash chromatography (petroleum ether) gave 1-(prop-2-yn-1-yloxy)hexadecane as a colorless liquid (22.4 g, 80%). ^1H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 4.12 (s, 2H), 3.50 (t, 2H), 2.40 (s, 1H), 1.59 (t, 2H), 1.33 (m, 2H), 1.25 (m, 24H), 0.88 (t, 3H).

Hexadecyloxyallene: At room temperature, $KOBu^t$ (2.40 g, 21.4 mmol) was added batch-wise into a solution of 1-(prop-2-yn-1-yloxy)hexadecane (5.00 g 17.9 mmol) in 100 mL THF within 30 min. The suspension was stirred at room temperature for 5 h, then filtered through a celite pad and washed with Et_2O (50 mL). Combined solution was concentrated under reduced pressure and purified by flash chromatography (0.5~0.8% diethyl ether in petroleum ether) to afford 3 as a colorless oil (4.10 g, 82%). ^1H NMR (600 MHz, $CDCl_3$, 25 ºC): δ 6.72 (t, $J = 6.0$ Hz, CH, 1H), 5.41 (d, $J = 5.4$ Hz, CH_2, 2H), 3.54 (t, $J = 6.6$ Hz, OCH_2, 2H), 1.63 (m, OCH_2CH_2, 2H), 1.26 (m, 26H), 0.88 (t, $J = 7.2$ Hz, CH_3, 3H). 13C: δ 201.46, 121.63, 90.24, 68.91, 31.95, 29.72, 29.69, 29.62, 29.59, 29.43, 29.39, 29.19, 26.04, 22.71, 14.12.

2.2 Synthesis of a tri-block copolymer P3HT-PHA-P3HT

The general approaches to the preparation of the P3HT-PHA-P3HT rod-coil-rod tri-block copolymers are shown in Fig 1a, the copolymers were synthesized in one-pot via three sequential living polymerizations of 2,5-dibromo-3-hexylthiophene (1), hexadecyloxyallene (2) and 2,5-dibromo-3-hexylthiophene (1). A 50 mL flask was charged with monomer 1 (0.25 g, 0.80 mmol) and a stir bar. The flask was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure repeated this three times, dry THF (10.0 mL) and tert-butylmagnesium chloride (0.40 mL, 2.0 M solution in THF) were successively introduced by a syringe. The reaction mixture was allowed to stir at room temperature for 2 h, followed by the addition of Ni(dppp)Cl_2 (9.20 mL, 13.3 μmol, $[1]_0/[Ni]_0 = 60$) to generate macroinitiator Ni(Ⅱ)-terminated P3HT (poly-1_{60}). The polymerization process was monitored by gel permeation chromatography (GPC) analysis of small aliquots taken out from the reaction solution at appropriate time intervals. Subsequently, monomer 2 (0.40 g, 1.46 mmol) was dissolved in dry THF (5 mL) under nitrogen atmosphere and added into reaction mixture ($[2]_0/[Ni]_0 = 110$). After stirred at 50 °C for 10 h, the resulting mixture solution was subsequently cooled down to room temperature. A small aliquot was then taken out for analysis until the molecular weight of di-block copolymer Ni(Ⅱ)-terminated P3HT-PHA (poly(1_{60}-2_{110})) ceased to increase. After that, under nitrogen atmosphere, the solution which includes 1 (0.23 g, 0.73 mmol), t-BuMgCl (0.36 mL, 2.0 M solution in THF) and dry THF (10 mL) was added to the reaction mixture ($[1]_0/[Ni]_0 = 55$), the mixed solution was stirred at room temperature for another 2 h. the polymerization reaction was followed by GPC analysis. When the molecular weight was not increased, which was observed by GPC, that is, monomer 1 was completely consumed, the polymerization solution was quenched by methanol. That resulted in a dark purple solid to precipitate, the solid was then collected by filtration and washed with methanol and n-hexane to remove residual metal salts and unreacted monomers. The final purple solid was dried under vacuum to obtain 710 mg (yield: 81%) of the expected tri-block copolymers P3HT-PHA-P3HT (poly-(1_{60}-2_{110}-1_{55})). To illustrate the relationship between structure and performance of the material, we synthesized a series of tri-block copolymers same as above.

3. Fabrication and characterization of OFETs

3.1 Ordinary OFETs fabrication process

Heavily n-doped Si wafer with 300 nm thermally grown SiO_2 surface layer (capacitance of 10.8

nF cm^{-2}) was employed as the substrate for the fabrication of OFETs. The n-type Si wafer serves as the common gate electrode and the SiO_2 layer acts as the gate dielectric. The SiO_2/Si wafer was treated by octadecyltrichlorosilane (OTS). A chloroform solution containing the semiconductor polymer was dropped onto the wafer and spin-coated. The Au source-drain electrodes were prepared by thermal evaporation using shadow masks (W: L = 1000 μm : 100 μm). the electrical characteristics of the OFET devices were measured in accumulation mode using a Keithley 4200 instrument under ambient conditions. The mobility values were obtained by using the following equation used at saturation regime: $I_d = (W/2L)\ C_{i\mu}\ (V_g - V_{th})^2$, where W/L is the channel width/length, I_d is the drain current in the saturated regime, C_i is the capacitance of the SiO_2 gate dielectric, and V_{th} is the threshold voltage.

3.2 OFETs fabrication process via blending method

P3HT-PHA-P3HT and PMMA were separately dissolved in chlorobenzene, and mixed at ultimate concentration of P3HT (3.0 mg/ml) and PMMA (3 wt. %). The films were spin coated on silicon substrate (dealt with piranha solution, washed in deionized water, and dried with nitrogen flow) at 2000 rpm for 60 s in glovebox, and dry in vacuum oven overnight to remove solvent without heating. The films were immersed in deionized water to strip itself from silicon substrate, and transferred with Cytop-treated SiO_2/Si substrates (300 nm-thick SiO_2) followed by a washing step with acetone. Thermally evaporated gold source/drain electrodes (30 nm) were prepared on P3HT-PHA-P3HT films using shadow masks (W: L = 1000 μm : 100 μm).

4. Instrumentation

Nuclear magnetic resonance (NMR) spectra were performed on a Mercury plus 600 MHz machine. FT-IR spectra were obtained using a Thermo Nicolet Spectrum Nicolet 67 system using KBr pellets. Gel permeation chromatography (GPC) analyses were recorded on a Waters Series 1525 gel coupled with a UV-vis detector using 1,2,4-trichlorobenzene as eluent with polystyrene as standard. Polystyrene standards in the range of 4100 to 422000 g mol^{-1} were used to calibrate the GPC. The flow rate for the GPC system was 1 mL min^{-1}. UV-vis absorption spectra were recorded on a Perkin Elmer model λ 20 UV-vis spectrophotometer. Atomic force microscopy (AFM) images were obtained using tapping-mode atomic force microscopy (Nanoscope, Veeco Instrument Inc.). The OFET electrical characteristics were measured using a Keithley 4200-SCS instrument in air ambient. 2D GIXD were measured at Pohang Accelerator Laboratory (PAL), 11.07 keV photons (1.12 Å) with a grazing angle of 0.12° were directed onto the sample.

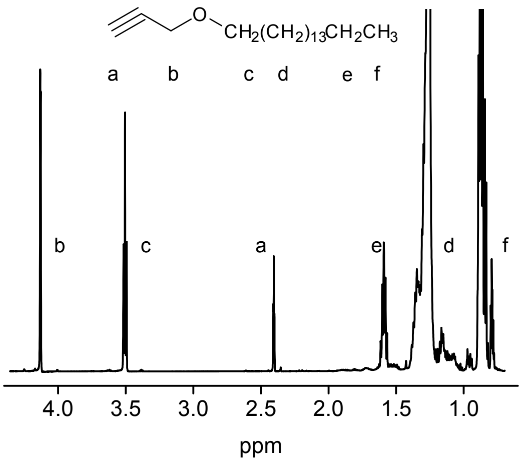


Fig S1. ^{1}H NMR of 1-(Prop-2-yn-1-yloxy) hexadecane.

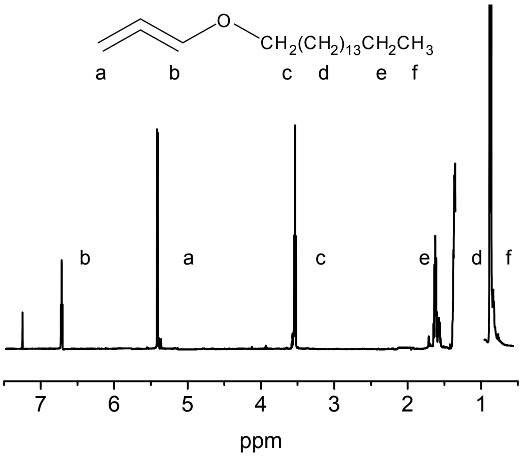


Fig S2. ^{1}H NMR of hexadecyloxyallene.

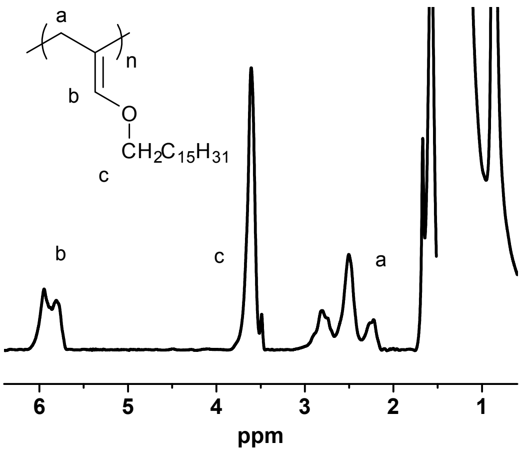


Fig S3. ^{1}H NMR of poly (hexadecyloxyallene).

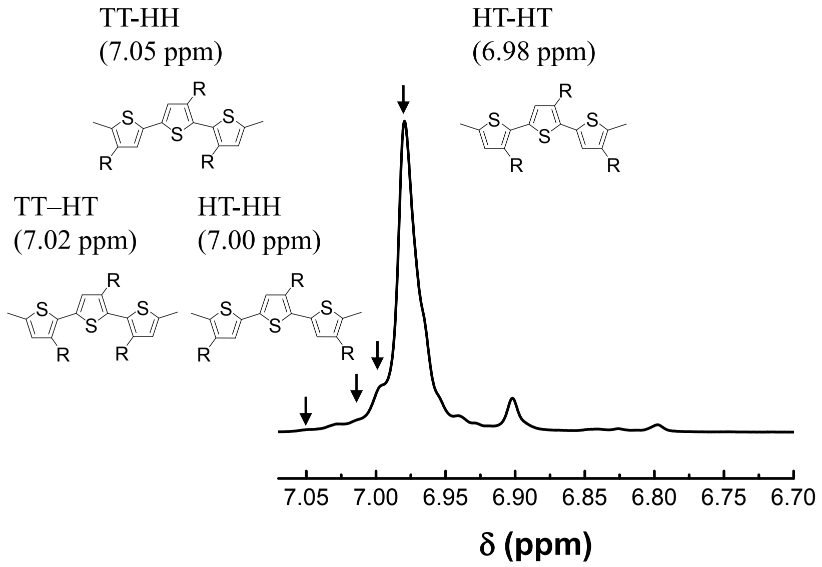


Fig S4. ^{1}H NMR of tri-block copolymer poly(1_{60}-2_{110}-1_{55}) indicating the regioregularity of P3HT segments.[1]

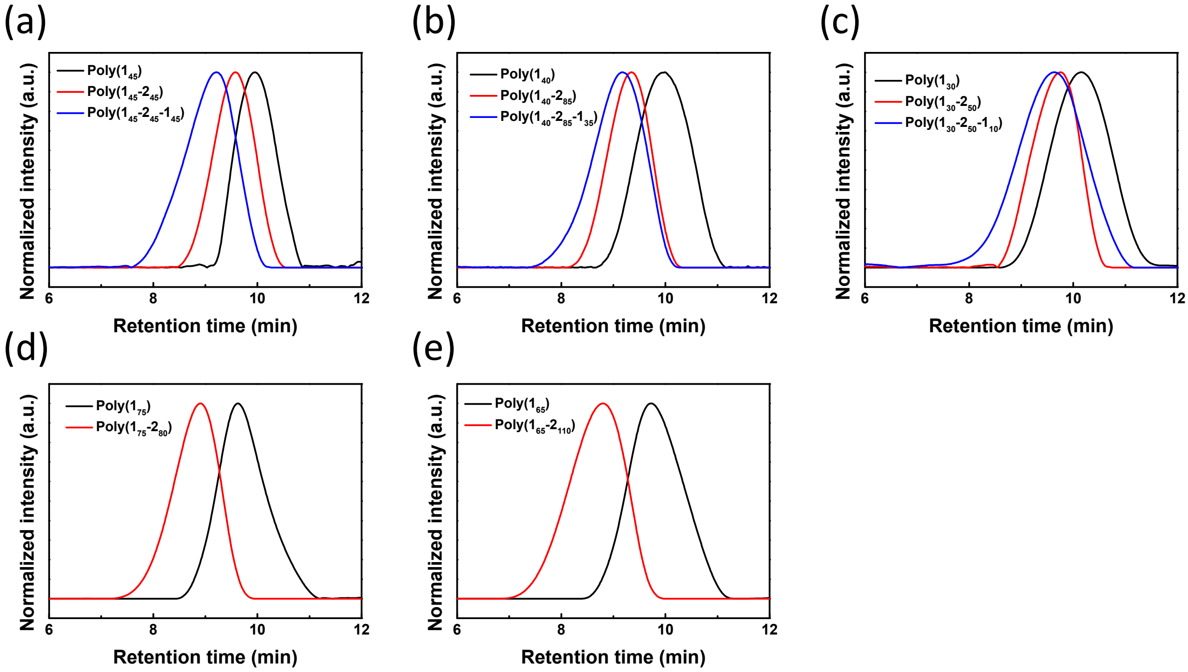


Fig S5. (a-e) GPC trace of P3HT, corresponding di-block copolymer P3HT-PHA and corresponding tri-block copolymer P3HT-b-PHA-b-P3HT, the molecular weight of these block copolymer are shown as insert.

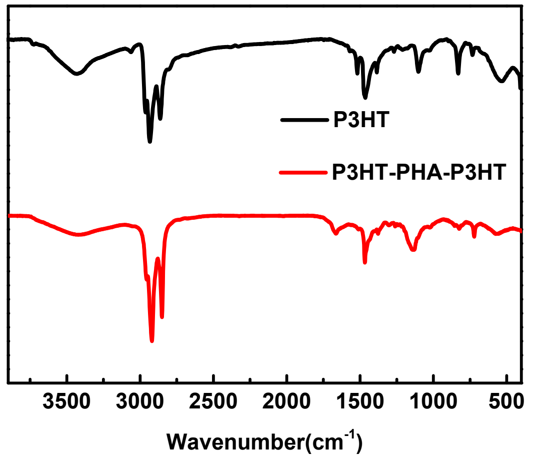


Fig S6. FT-IR spectrum (KBr) of P3HT homopolymer and tri-block copolymer P3HT-b-PHA-b-P3HT.

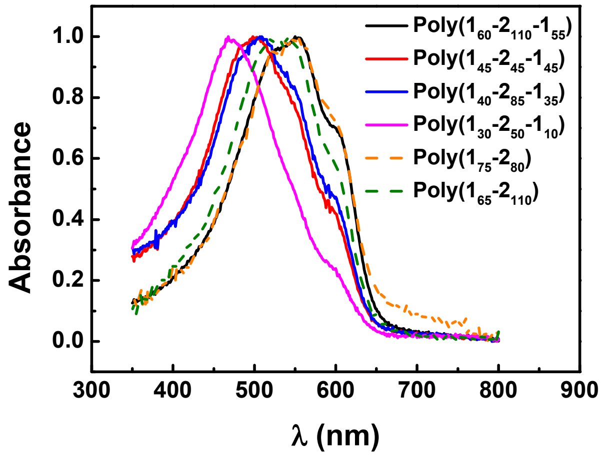


Fig S7. UV-Vis spectra of tri-block polymer P3HT-b-PHA-b-P3HT (solid line) and di-block polymer P3HT-b-PHA (dash line) films with different block ratio.

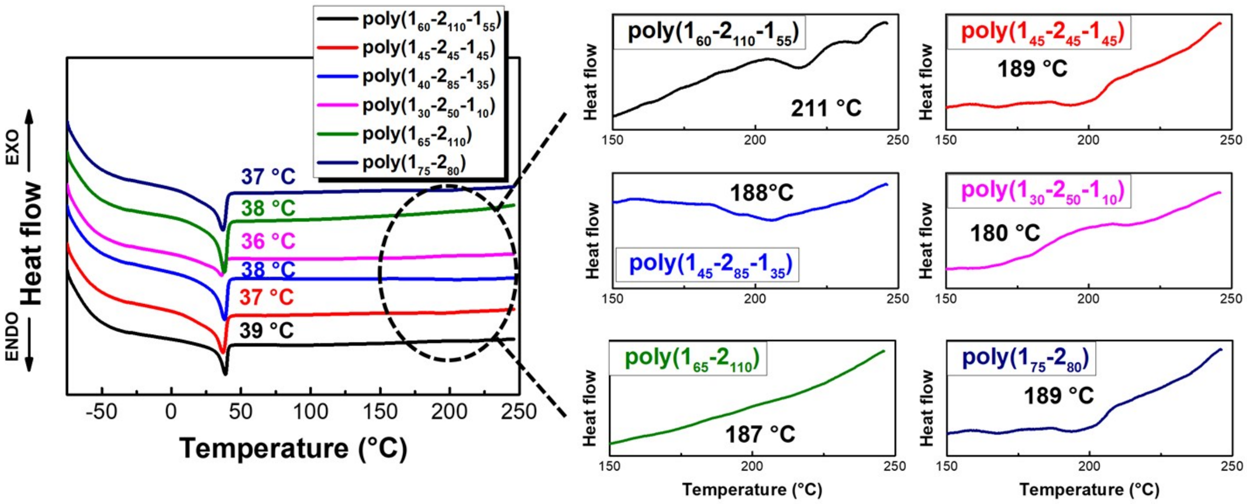


Fig S8. DSC curves of tri-block polymer P3HT-b-PHA-b-P3HT and di-block polymer P3HT-b-PHA films with different block ratio.

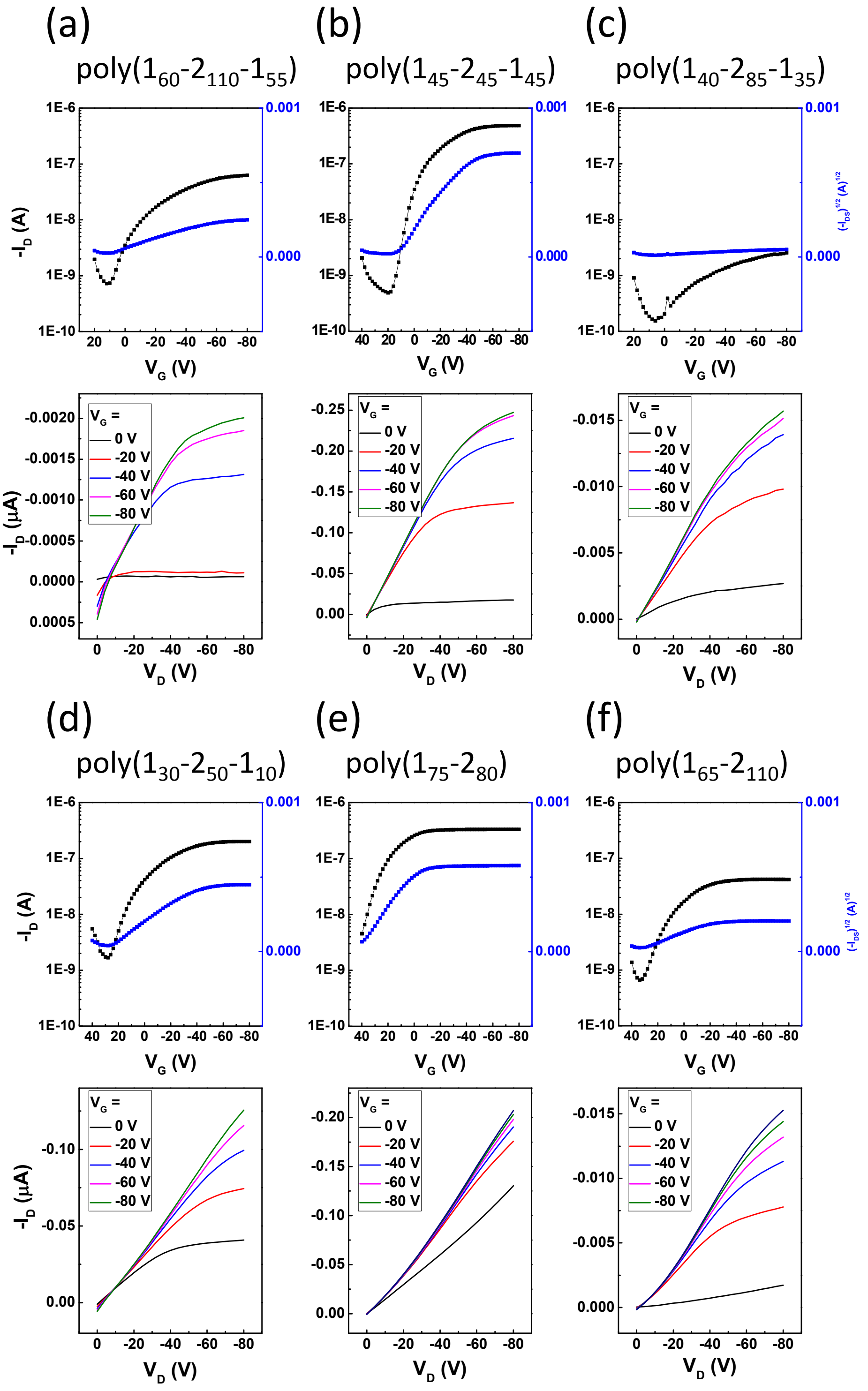


Fig S9. (a-f) Transfer and output characters of block copolymers with different block ratio fabricated by ordinary device-fabrication process.

Table S1. The OFET performance of tri- and di-block copolymers with different block ratio fabricated by ordinary device-fabrication process.

Polymers	**Annealing temperature**	**μ_{avg} (cm²/V·s)**	**μ_{max} (cm²/V·s)**	**Threshold Voltage (V)**
poly(1_{60}-2_{110}-1_{55})	RT	2.00×10^{-5}	3.59×10^{-5}	17.5
	100 °C	2.57×10^{-5}	7.02×10^{-5}	14.7
	150 °C	1.11×10^{-4}	1.44×10^{-4}	16.3
	200 °C	2.32×10^{-4}	3.53×10^{-4}	17.5
poly(1_{45}-2_{45}-1_{45})	RT	9.61×10^{-7}	1.10×10^{-6}	41.6
	100 °C	2.58×10^{-5}	3.11×10^{-5}	16.6
	150 °C	9.69×10^{-4}	1.91×10^{-3}	19.6
	200 °C	3.16×10^{-4}	4.16×10^{-4}	30.8
poly(1_{40}-2_{85}-1_{35})	RT	5.09×10^{-7}	7.26×10^{-7}	22.1
	100 °C	7.05×10^{-5}	8.66×10^{-5}	19.6
	150 °C	4.15×10^{-5}	6.83×10^{-5}	24.5
	200 °C	2.72×10^{-4}	4.14×10^{-4}	30.9
poly(1_{30}-2_{50}-1_{10})	RT	1.36×10^{-6}	4.27×10^{-6}	-43.1
	100 ℃	2.58×10^{-5}	3.11×10^{-5}	16.6
	150 ℃	5.34×10^{-4}	7.43×10^{-4}	45.8
	200 ℃	3.16×10^{-4}	4.16×10^{-4}	30.8
poly(1_{75}-2_{80})	RT	—	6.81×10^{-5}	33.3
	100 °C	—	3.17×10^{-4}	32.0
	150 °C	—	7.87×10^{-4}	79.4
	200 °C	—	1.64×10^{-3}	57.1
poly(1_{65}-2_{110})	RT	—	1.66×10^{-7}	44.1
	100 °C	—	4.58×10^{-6}	46.5
	150 °C	—	4.28×10^{-5}	31.5
	200 °C	—	8.91×10^{-4}	26.7

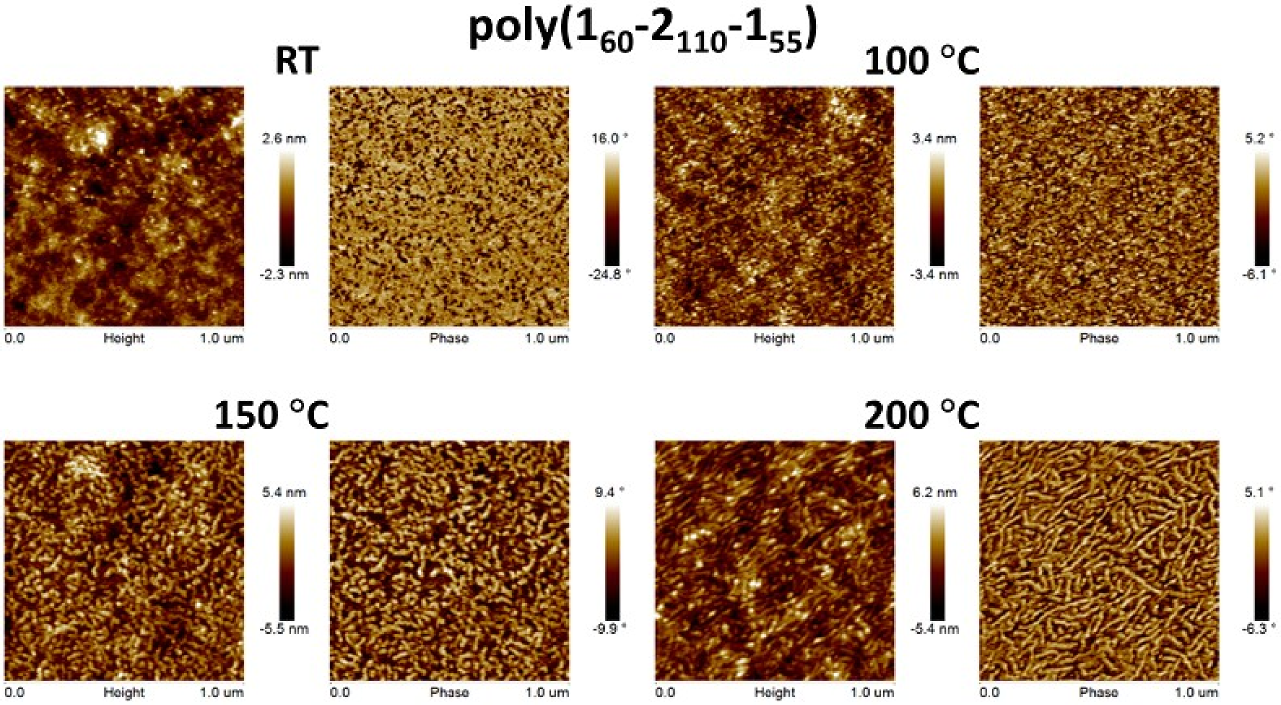


Fig S10. AFM height and phase images of poly(1_{60}-2_{110}-1_{55}).

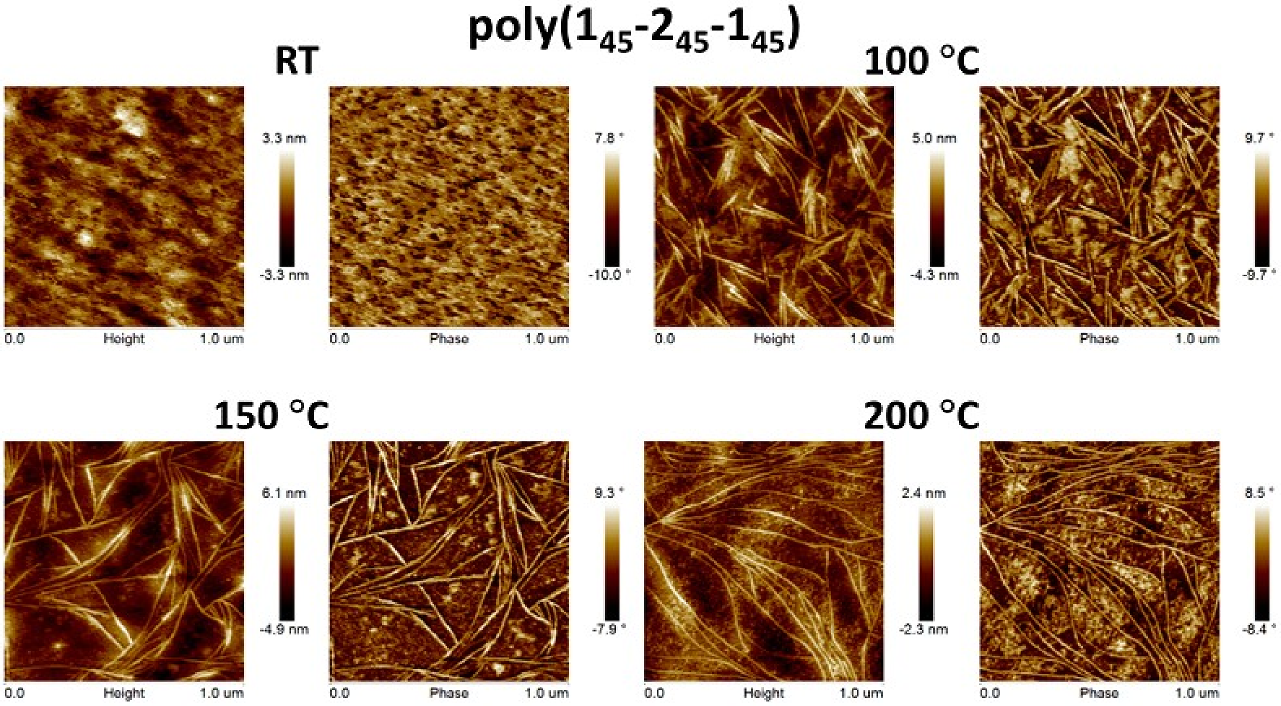


Fig S11. AFM height and phase images of poly(1_{45}-2_{45}-1_{45}).

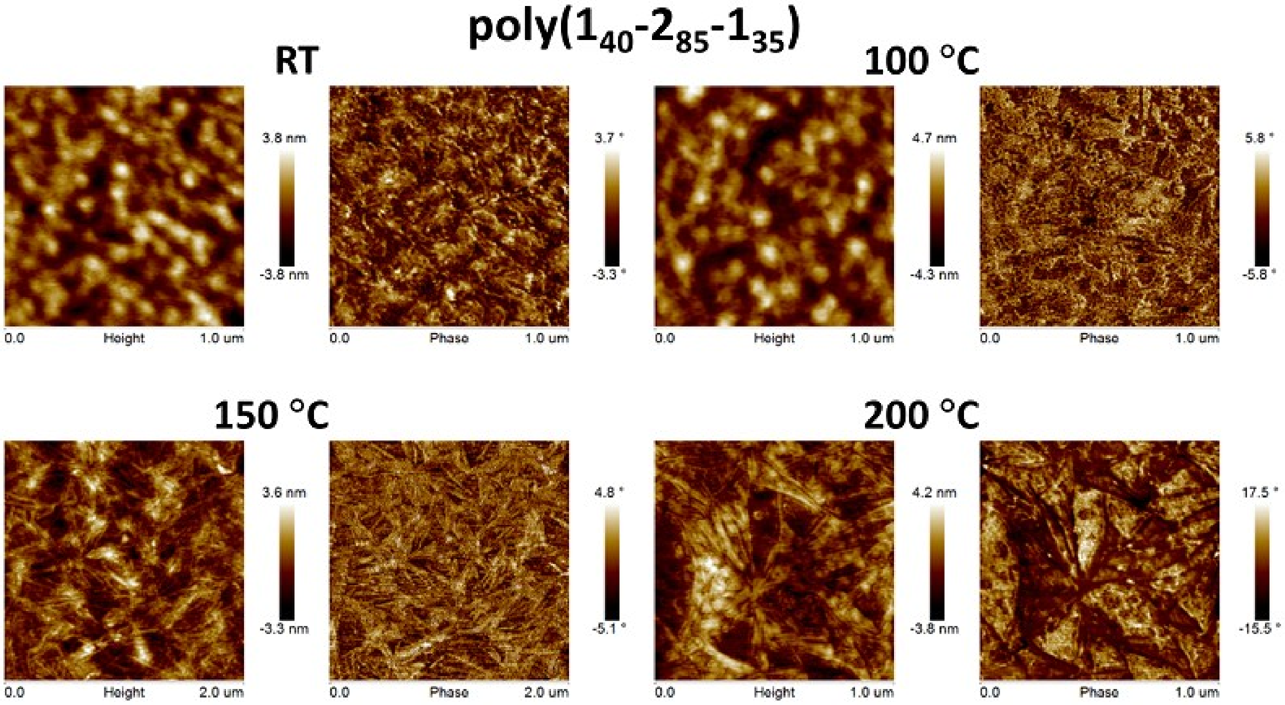


Fig S12. AFM height and phase images of poly(1_{40}-2_{85}-1_{35}).

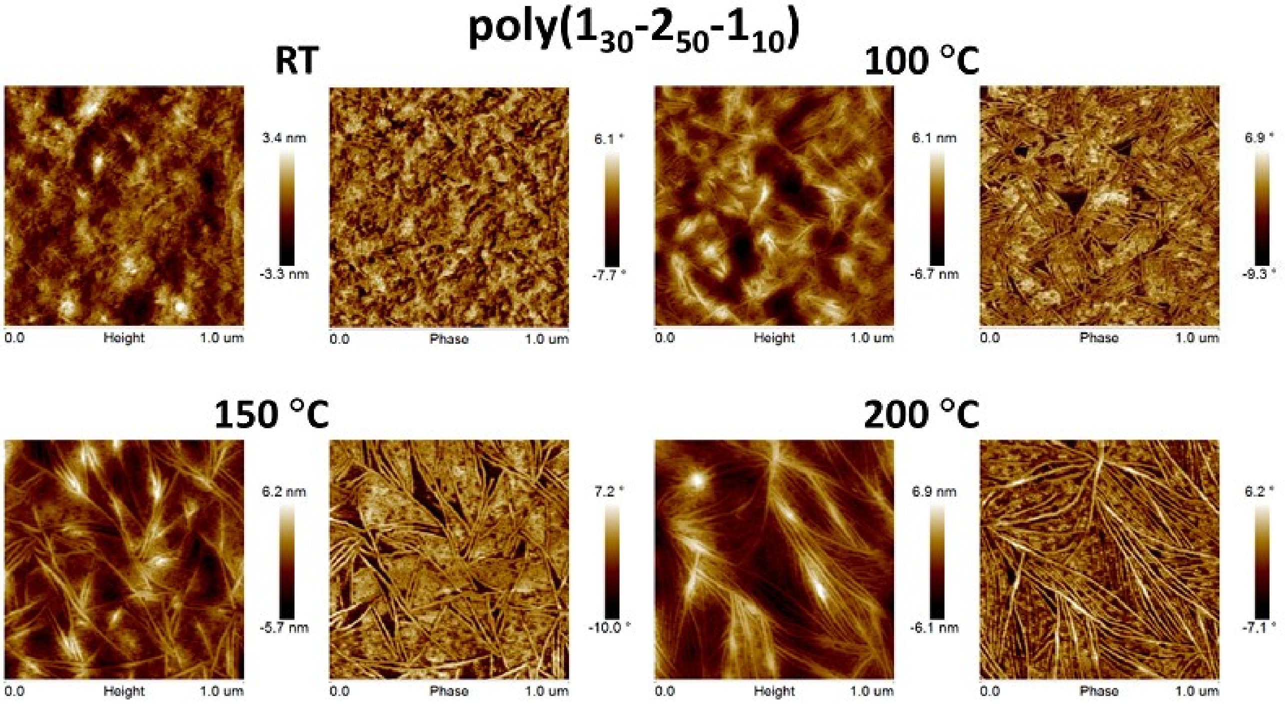


Fig S13. AFM height and phase images of poly(1_{30}-2_{50}-1_{10}).

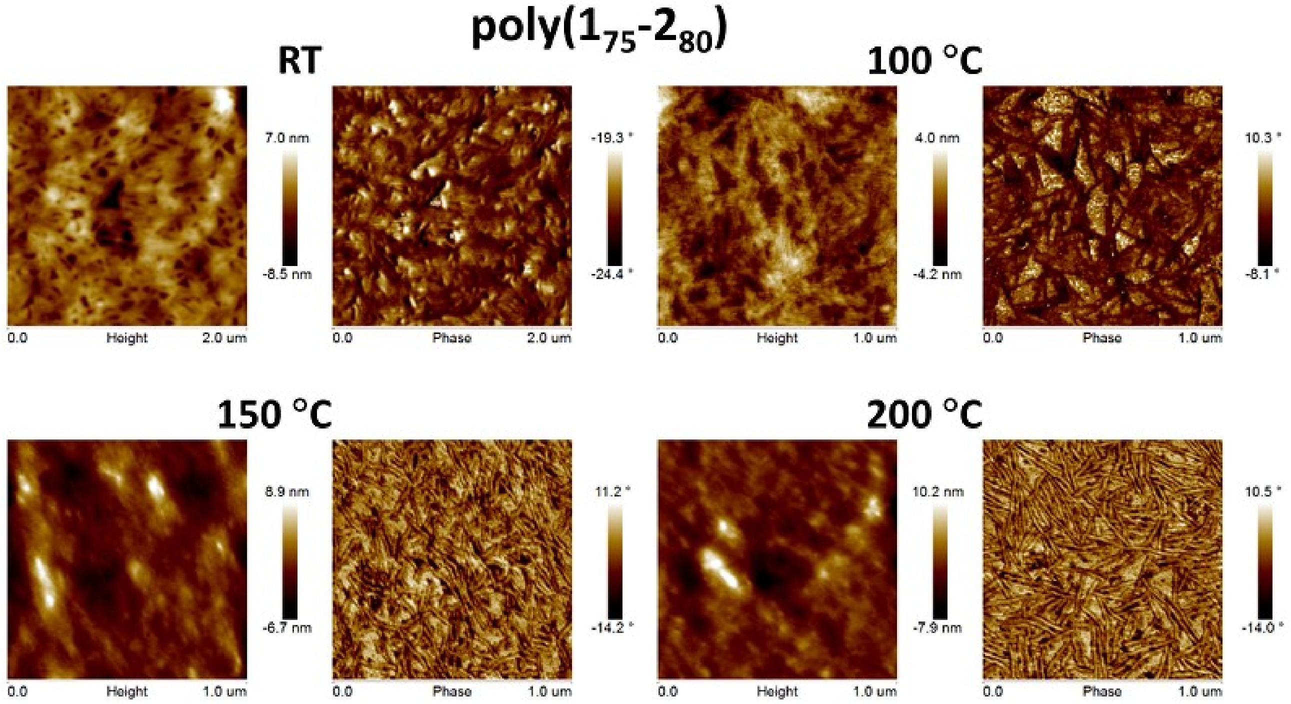


Fig S14. AFM height and phase images of poly(1_{75}-2_{80}).

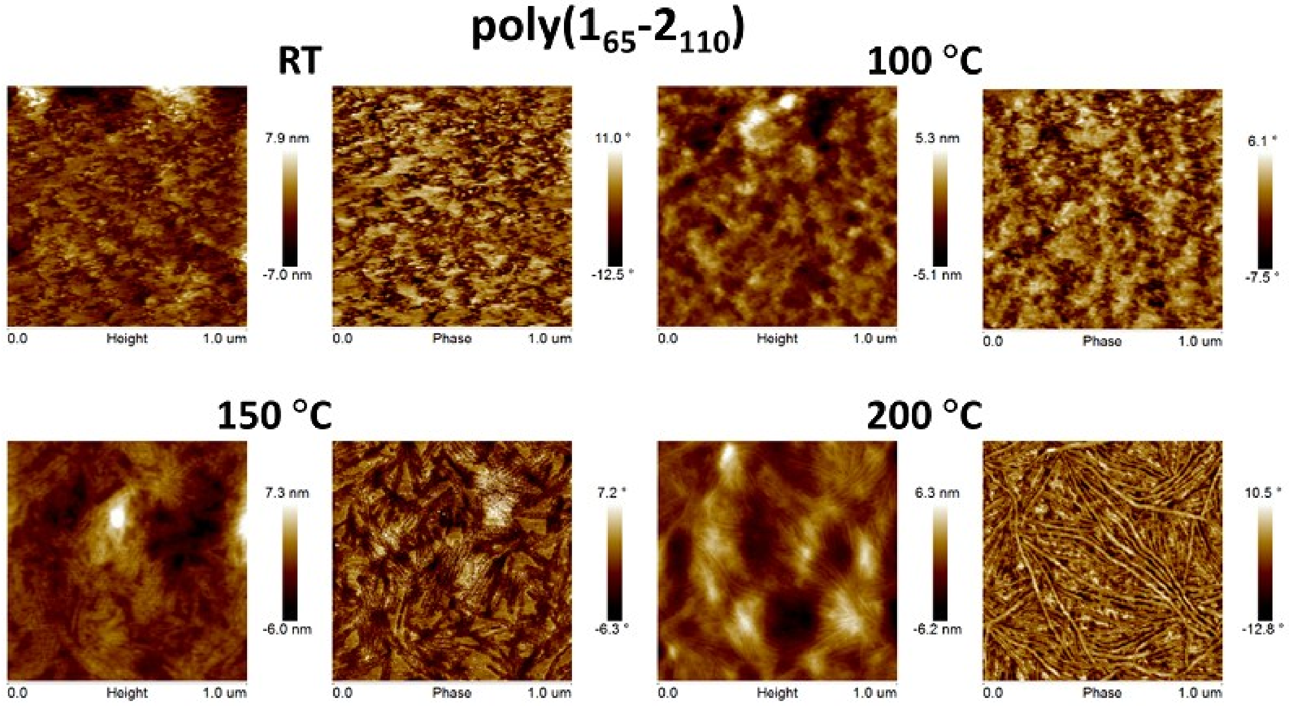


Fig S15. AFM height and phase images of poly(1_{65}-2_{110}).

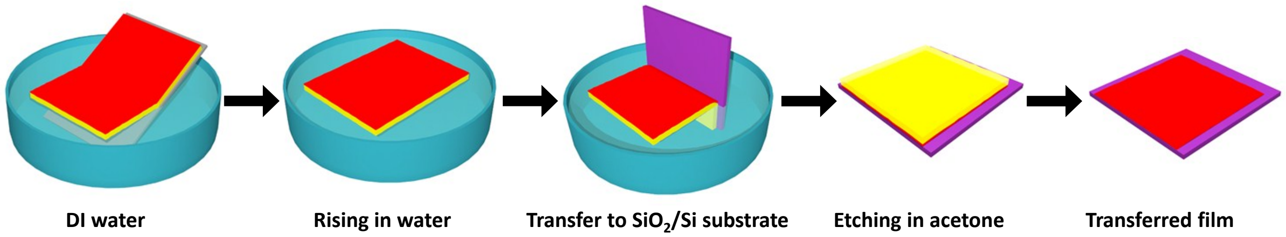


Fig S16. The transfer and etching processes of vertical phase separated P3HT-b-PHA-b-P3HT/PMMA film.

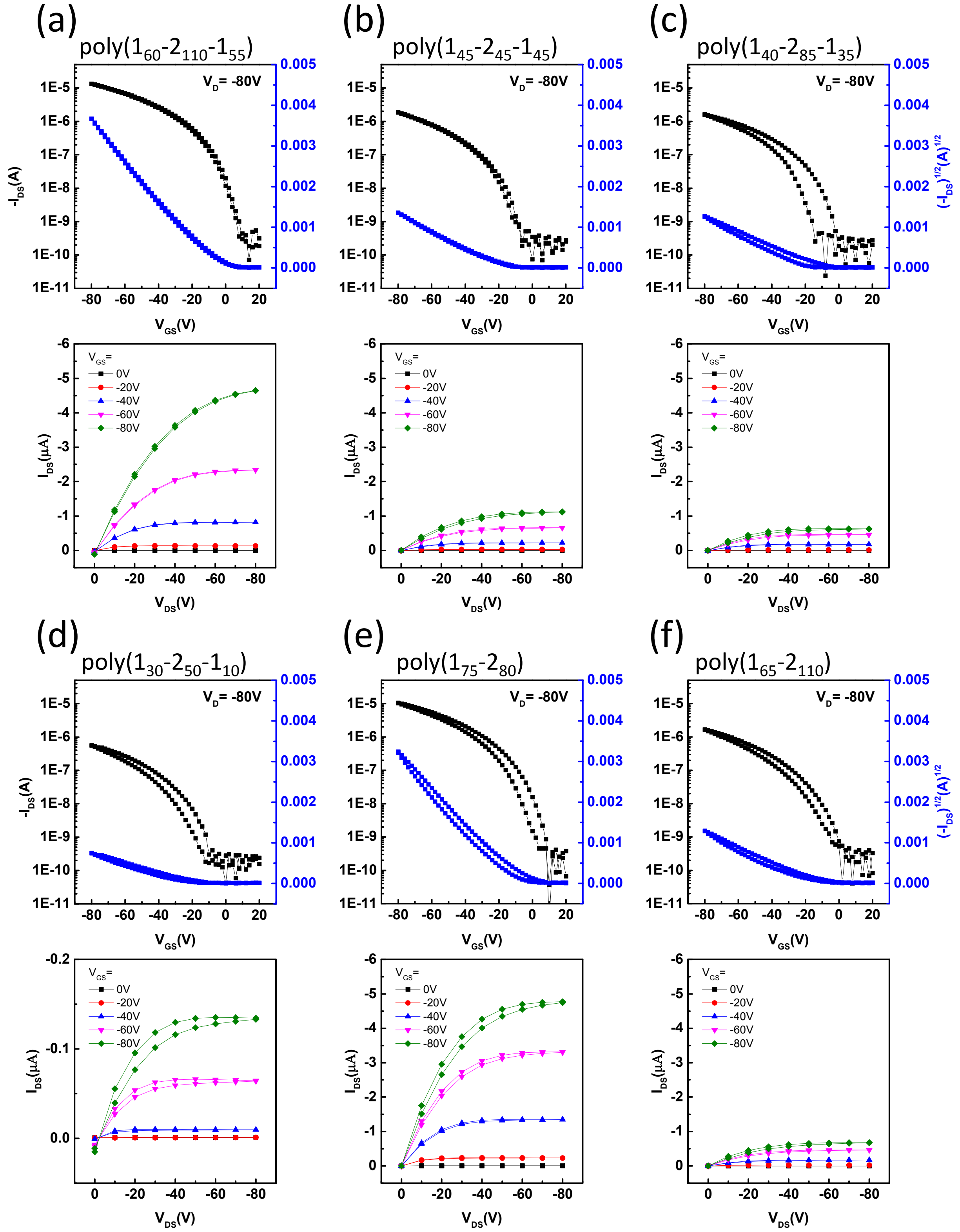


Fig S17. (a-f) Transfer and output characters of block copolymers with different block ratio fabricated by transfer and etching process.

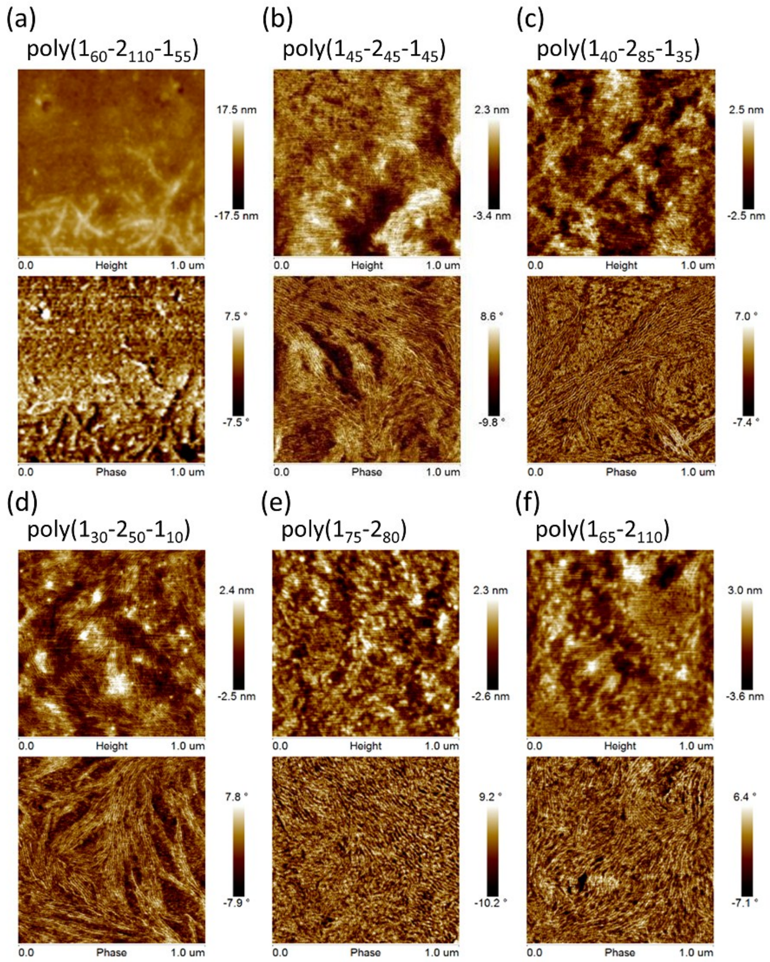


Fig S18. (a-f) AFM height and phase images of block copolymers with different block ratio fabricated by blending method.

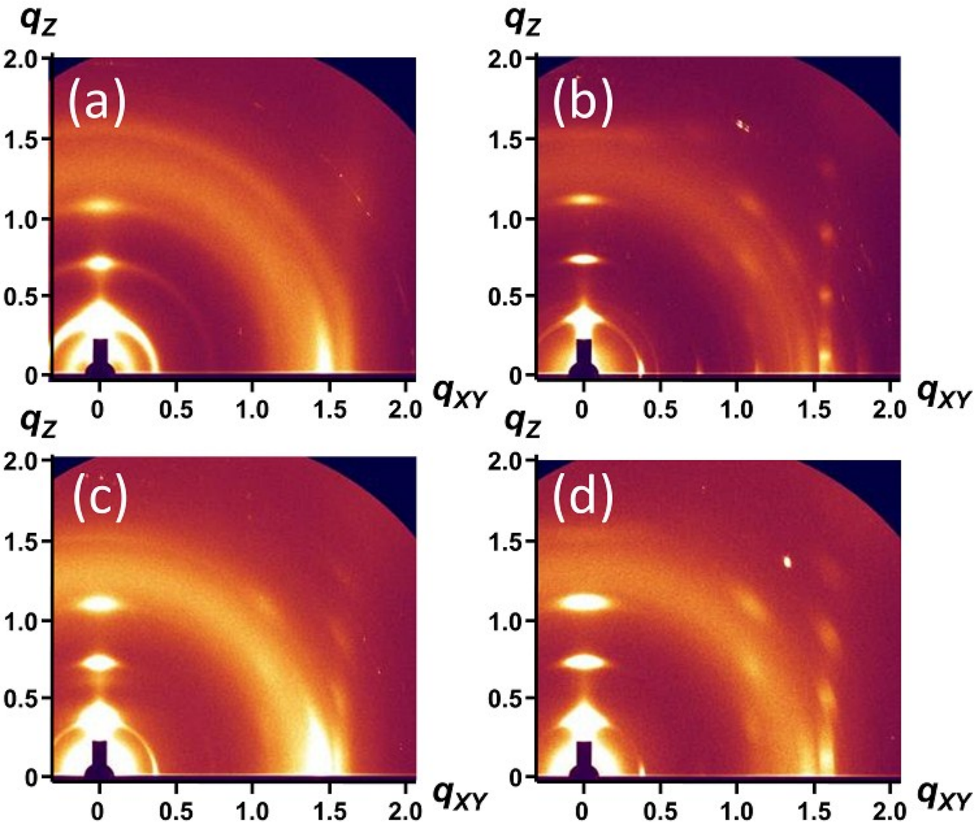


Fig S19. 2D GIXD scattering patterns of four tri-block copolymers films with different block ratio (a) poly(1_{60}-2_{110}-1_{55}), (b) poly(1_{45}-2_{45}-1_{45}), (c) poly(1_{40}-2_{85}-1_{35}), (d) poly-(1_{30}-2_{50}-1_{10}).

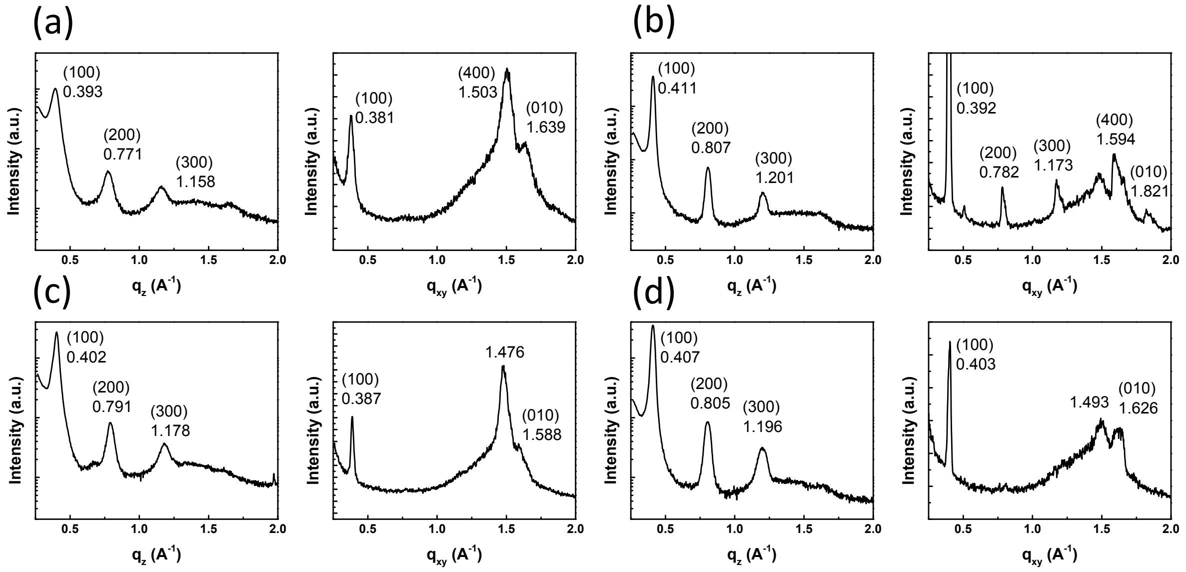


Fig S20. 1D GIXD profiles of out-of-plane (left) and in-plane (right) directions of four tri-block copolymers films with different block ratio, (a) poly(1_{60}-2_{110}-1_{55}); (b) poly(1_{45}-2_{45}-1_{45}); (c) poly(1_{40}-2_{85}-1_{35}); (d) poly(1_{30}-2_{50}-1_{10}).

Table S2. Peak position and molecular stacking distance of tri-block copolymer films.

Polymers	Qxy (Å^{-1})	π-staking (Å)	Qz (Å^{-1})	*d*-spacing (Å)
poly(1_{60}-2_{110}-1_{55})	1.639	3.83	0.393	15.99
poly(1_{45}-2_{45}-1_{45})	1.594	3.94	0.411	15.29
poly(1_{40}-2_{85}-1_{35})	1.588	3.96	0.402	15.63
poly(1_{30}-2_{50}-1_{10})	1.626	3.86	0.407	15.44

References

1. T.A. Chen, R.D. Rieke, *J. Am. Chem. Soc.* 1992, **114,** 10087.