*Supporting Information*

# Soft Poly(Butyl Acrylate) Side Chains Toward Intrinsically Stretchable Polymeric Semiconductors for Field-Effect Transistor Applications

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**Table S1**. Relevant crystallographic parameters of the studied polymer thin films under strain

| | | **PII2T** | | **PII2T-PBA5** | | **PII2T-PBA10** | | **PII2T-PBA20** | |
|---|---|---|---|---|---|---|---|---|---|
| Strain (%) | direction | d-spacing (Å) | π-π spacing (Å) | d-spacing (Å) | π-π spacing (Å) | d-spacing (Å) | π-π spacing (Å) | d-spacing (Å) | π-π spacing (Å) |
| 40 | Parallel | 24.8 | 3.5 | 25.5 | 3.5 | 26.0 | 3.6 | 26.6 | 3.6 |
| 40 | Perpendicular | 25.1 | 3.5 | 25.1 | 3.5 | 25.5 | - | 27.1 | - |
| 60 | Parallel | 25.2 | 3.5 | 25.5 | 3.5 | 26.0 | 3.6 | 26.5 | 3.6 |
| 60 | Perpendicular | 25.2 | 3.5 | 25.5 | 3.5 | 25.5 | - | 26.7 | - |
| 80 | Parallel | 25.5 | 3.5 | 25.5 | 3.5 | 25.5 | 3.6 | 26.7 | 3.6 |
| 80 | Perpendicular | 25.3 | 3.5 | 25.2 | 3.5 | 25.5 | - | 26.6 | - |

**Characterization**

Microwave polymerization was carried out using a Biotage microwave reactor in sealed vessels. $^{1}$H-NMR spectra was recorded with a Bruker Advance DRX-400 MHz spectrometer. Elemental analysis was performed by elementary Vario EL cube with sulfanilic acid as standard. Size exclusion chromatographic (SEC) analysis was performed on a Lab Alliance RI2000 instrument connected with a refractive index detector. A polymer/THF solution at a flow rate of 1 mL min$^{-1}$ under 40 °C was used, and the molecular weight was calibrated using polystyrene standards. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were probed under a nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$ using the TA instruments Q-50 and Q-100, respectively.

UV–Vis absorption spectrum was explored using a Hitachi U-4100 spectrophotometer. For the solid state spectra, polymers were firstly dissolved in chloroform (3-5 mg mL$^{-1}$) under 60 °C for 2 h, and then spin-coated at a speed rate of 1000 rpm for 60 s onto quartz substrate. A rotational polarizer was further introduced to measure the absorption intensity with the incident light polarized parallel ($A_{\parallel}$) or perpendicular ($A_{\perp}$) to the stretching direction, and then define the dichroic ratio ($R$) of the stretched polymer thin film as: $R = A_{\parallel}/A_{\perp}$. Cyclic voltammetry (CV) was performed on a CHI 611D electrochemical analyzer using a three-electrode cell in which ITO was used as a working electrode and a platinum wire was used as an auxiliary electrode. All cell potentials were taken with the usage of a homemade Ag/AgCl, KCl (sat.) reference electrode. The electrochemical properties of the polymer films were detected under 0.1 M dry acetonitrile solution containing tetrabutylammonium perchlorate as the electrolyte.

Grazing incidence X-ray diffraction (GIXD) measurements were carried out on beamline 17A1 in National Synchrotron Radiation Research Center (NSRRC) of Taiwan. An X-ray wavelength of 1.321 Å was used and the incident angle was set as 0.12°. The morphology of polymer film surface was obtained with a Nanoscope 3D Controller atomic force microscopy (AFM, Digital Instruments) operated under the tapping mode at room temperature. Note that the preparation parameters of polymer thin film samples were the same as that of the device fabrications for the measurements of

GIXD, UV, and AFM.

The electrical characterizations were carried out by a Keithley 4200-SCS semiconductor parameter analyzer (Keithley Instruments Inc.) in a $N_2$-filled glove box.

**Monomer synthesis**

**Synthesis of PBA homopolymer**

n-Butyl acrylate (BA) (5.0 mL, 32.0 mmol), anisole (5.0 mL) and ethyl 2-bromoisobutyrate (EBiB) (0.39 mL, 2.67 mol) were added to a dry schlenk flask and the mixture was degassed by three freeze-pump-thaw cycles. Then, CuBr (134 mg, 0.93 mmol), $CuBr_2$ (89.5 mg, 0.4 mmol) and PMDETA (279 μL, 1.34 mmol) were added to the flask. An initial sample was taken and the sealed flask was placed in an oil bath thermostated at 70 °C. The polymerization was monitored by SEC and the reaction was stopped after 1.5 h with 59% conversion by opening the flask and exposing the catalyst complex in the solution to air. The crude product was passed through an alumina column to remove catalysts. The molecular weight and polydispersity were estimated by analytical SEC, resulting a number-averaged molecular weight ($M_n$) of 1480 and a polydispersity index (PDI) of 1.09.

**Synthesis of IID-PBA**

To a suspension of 6,6'-dibromoisoindigo (0.234 g, 0.559 mmol) and potassium carbonate (0.386 g, 2.79 mmol) in 12 mL of dimethylformaldehyde (DMF), PBA homopolymer (1.834 g, 1.23 mmol) was added through a septum under nitrogen. The mixture was heated up to 100 °C and stirred for 12 h. Afterward the mixture was poured into methanol (200 mL), and the precipitates were collected by vacuum filtration and extracted using methylene chloride and water. The crude products were further purified by chromatography using methylene chloride and ethyl acetate (v:v = 5:1) as eluent to obtain IID-PBA (yield: 60%) as a viscous red oil. $^1$H-NMR (400 MHz, $CD_2Cl_2$), δ

(ppm): 9.11-9.07 (dd, Ar-*H*), 7.23-7.21 (dd, Ar-*H*), 6.95 (s, Ar-*H*), 4.07-4.04 (br, $OCH_2CH_2$), 2.34-2.30 (br, $CH_2CH_2CH$), 1.91.1.58 (br, $NCH_2CH_2$) 1.42-1.37 (t, $CH_2CH_2CH_3$), 1.28-1.22 (m, $CH_2CH_3$), 1.14-1.11 (m, $CH_3CH$), 0.97-0.93 (m, $CH_3CH$), 0.85-0.83 (br, $CH_2CH_3$).

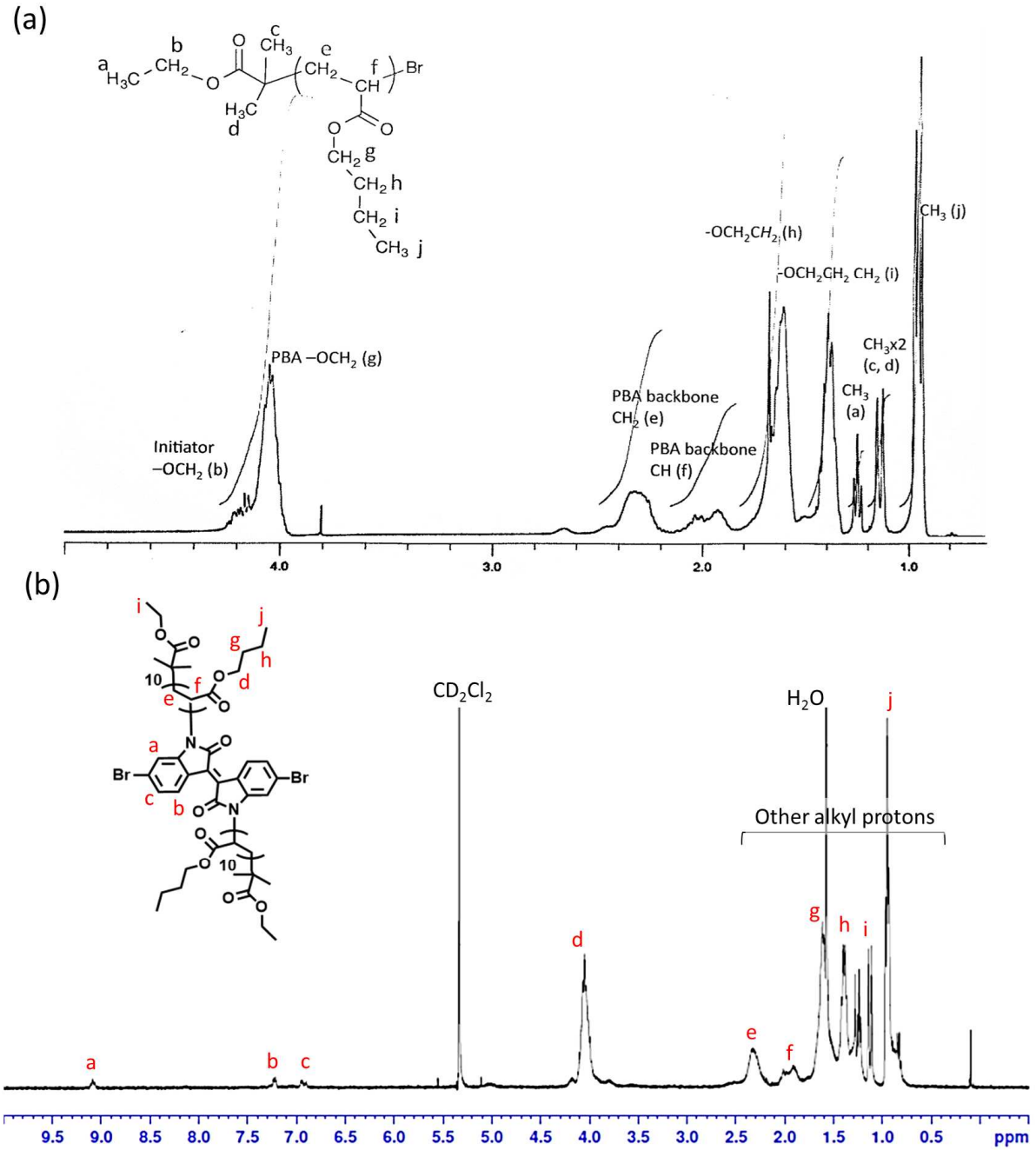


**Figure S1**. $^1$H-NMR spectra of (a) PBA homopolymer and (b) IID-PBA, respectively.

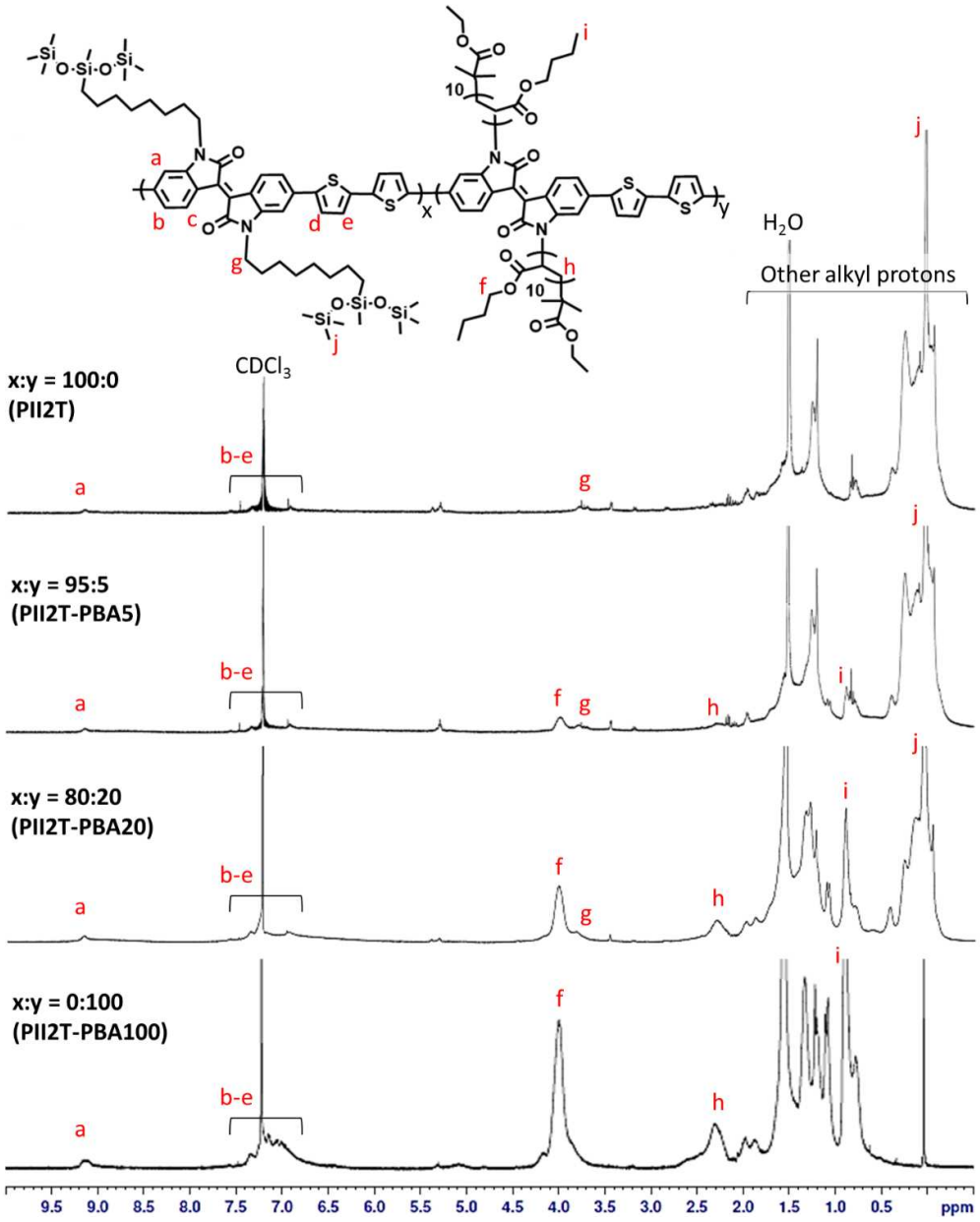


**Figure S2**. $^{1}$H-NMR spectra of the studied polymers in $CDCl_3$.

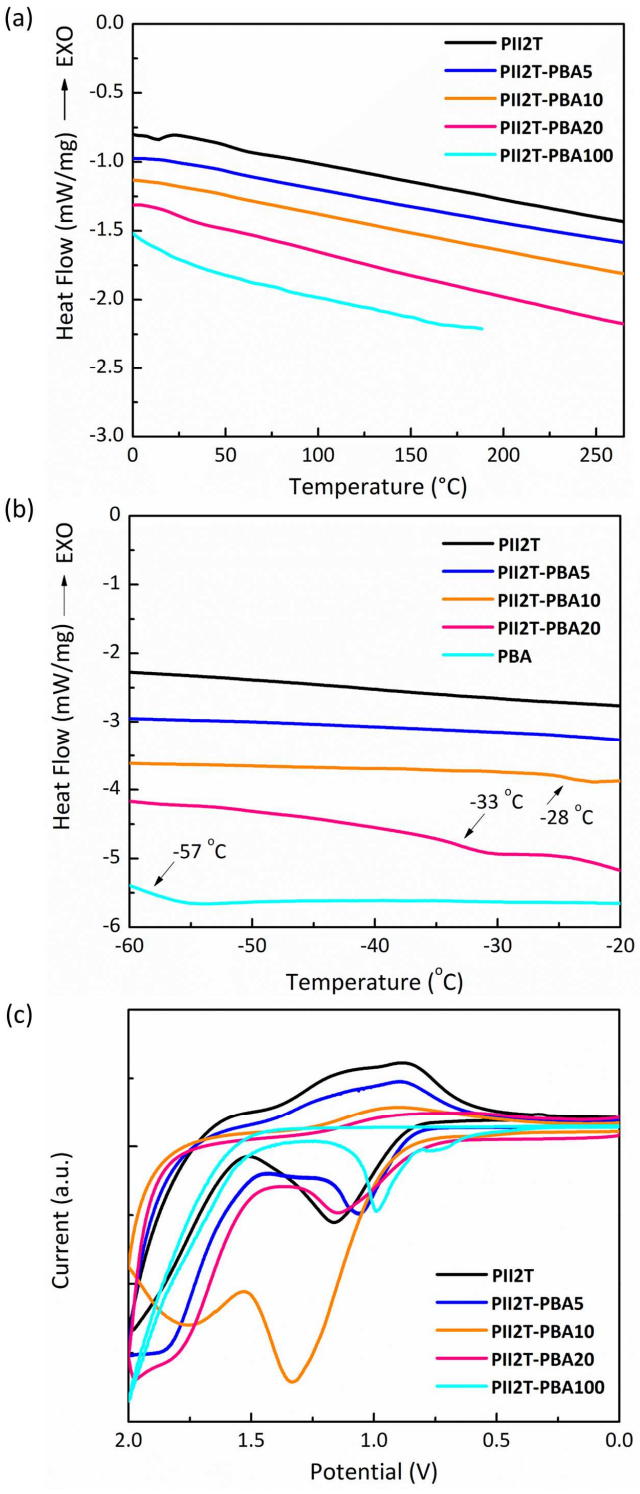


**Figure S3**. DSC traces in (a) high and (b) low temperature range and (c) CV curves of the studied polymers, respectively.

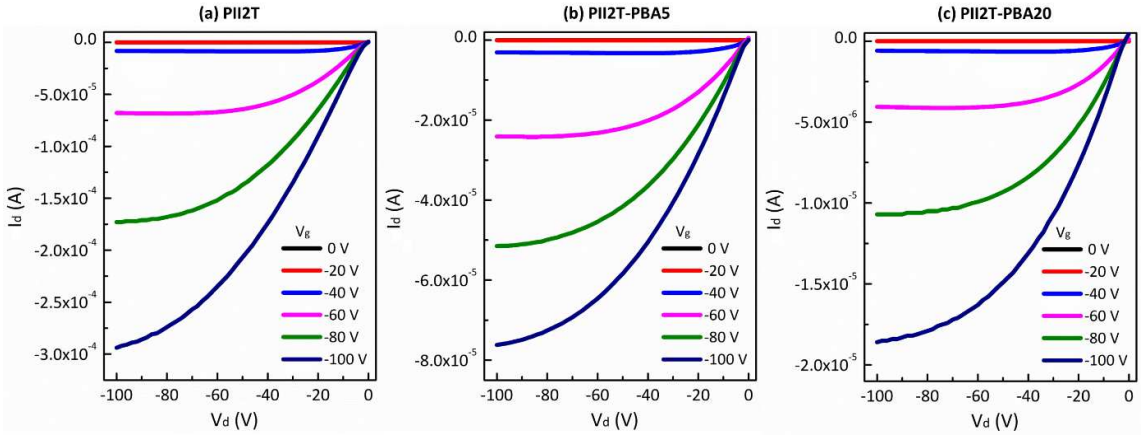


**Figure S4**. FET output characteristics of (a) **PII2T-**, (b) **PII2T-PBA5-** and (c) **PII2T-PBA20**-based device, respectively.

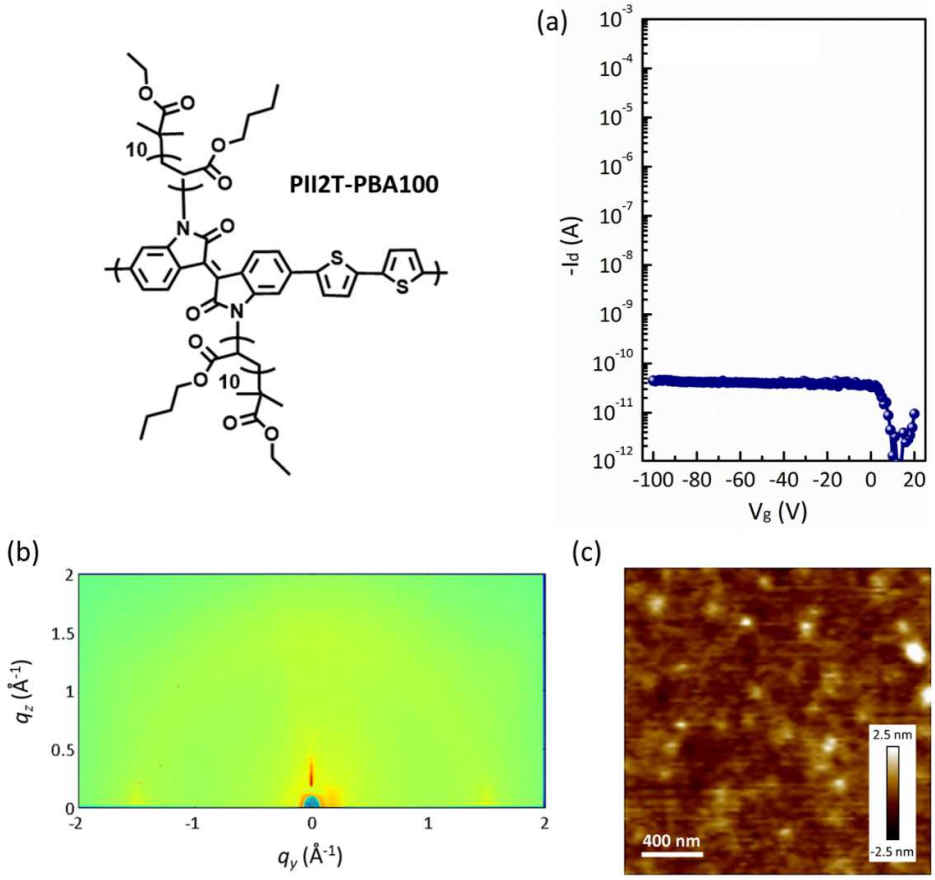


**Figure S5**. (a) FET transfer curve, (b) 2D GIXD pattern and (c) AFM topography of **PII2T-PBA100**, respectively.

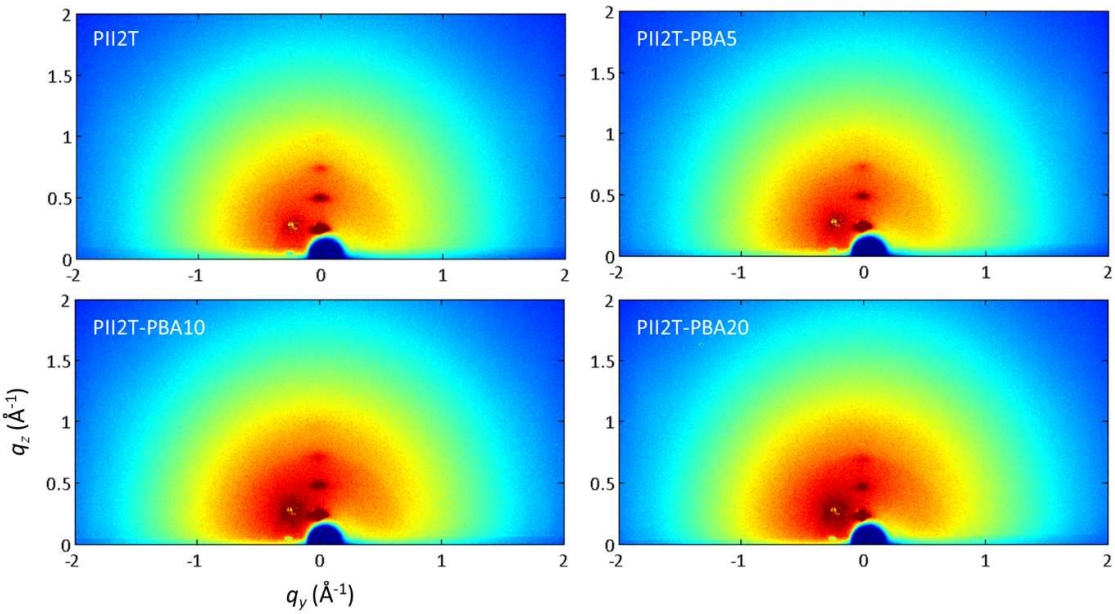


**Figure S6**. 2D GIXD patterns of **PII2T**, **PII2T-PBA5**, **PII2T-PBA10** and **PII2T-PBA20**, respectively.

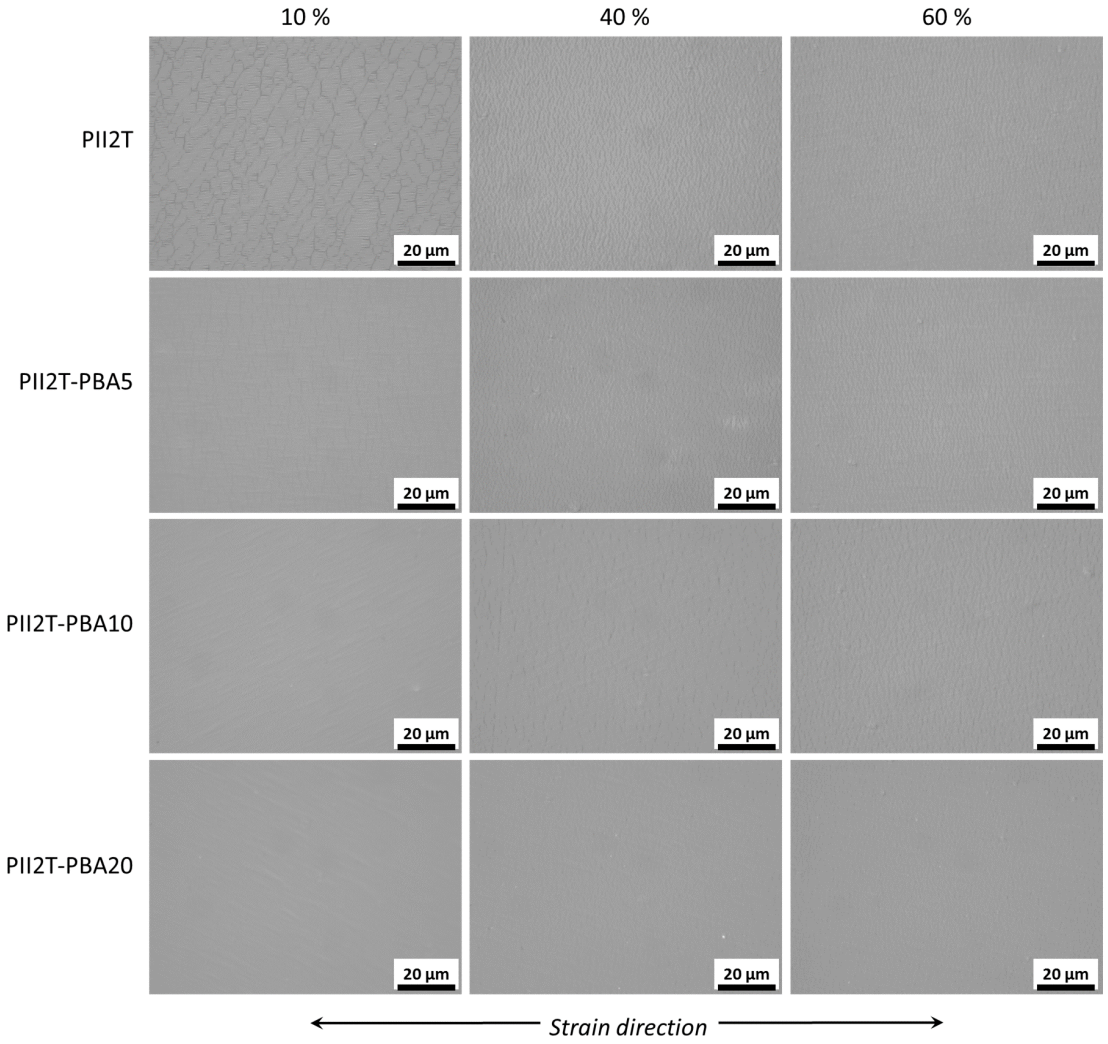


**Figure S7**. Optical microscopy images of **PII2T**, **PII2T-PBA5**, **PII2T-PBA10** and **PII2T-PBA20** thin films under 10, 40 and 60% strain.

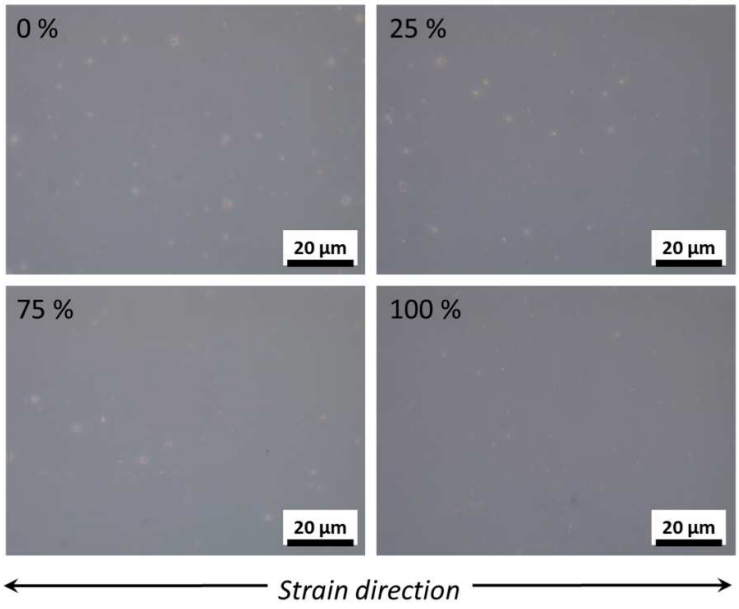


**Figure S8**. Optical microscopy images of **PII2T-PBA100** thin films under various strain ratios. Crack-free surface can be observed upon 100% strain in general.

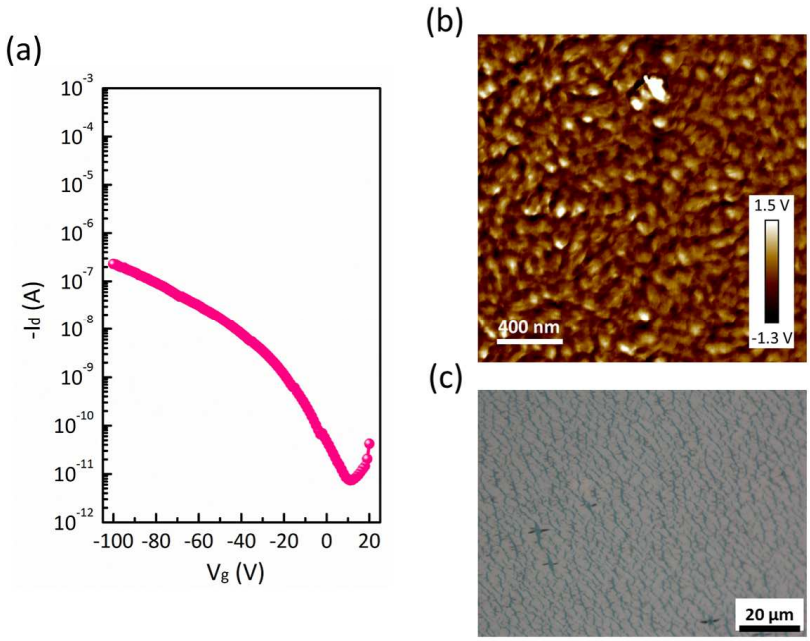


**Figure S9**. (a) FET transfer characteristics, (b) AFM phase image and (c) OM image at 60% strain of the thin film based on PII2T/PBA blend (90:10 w/w). Low mobility of $2\times10^{-4}$ $cm^2V^{-1}s^{-1}$ is detected due to the large phase separation. In addition, the phase separation and non-uniform thin film morphology also lead to the poor film deformability and ductility, resulting in lots of cracks form on the thin film surface.

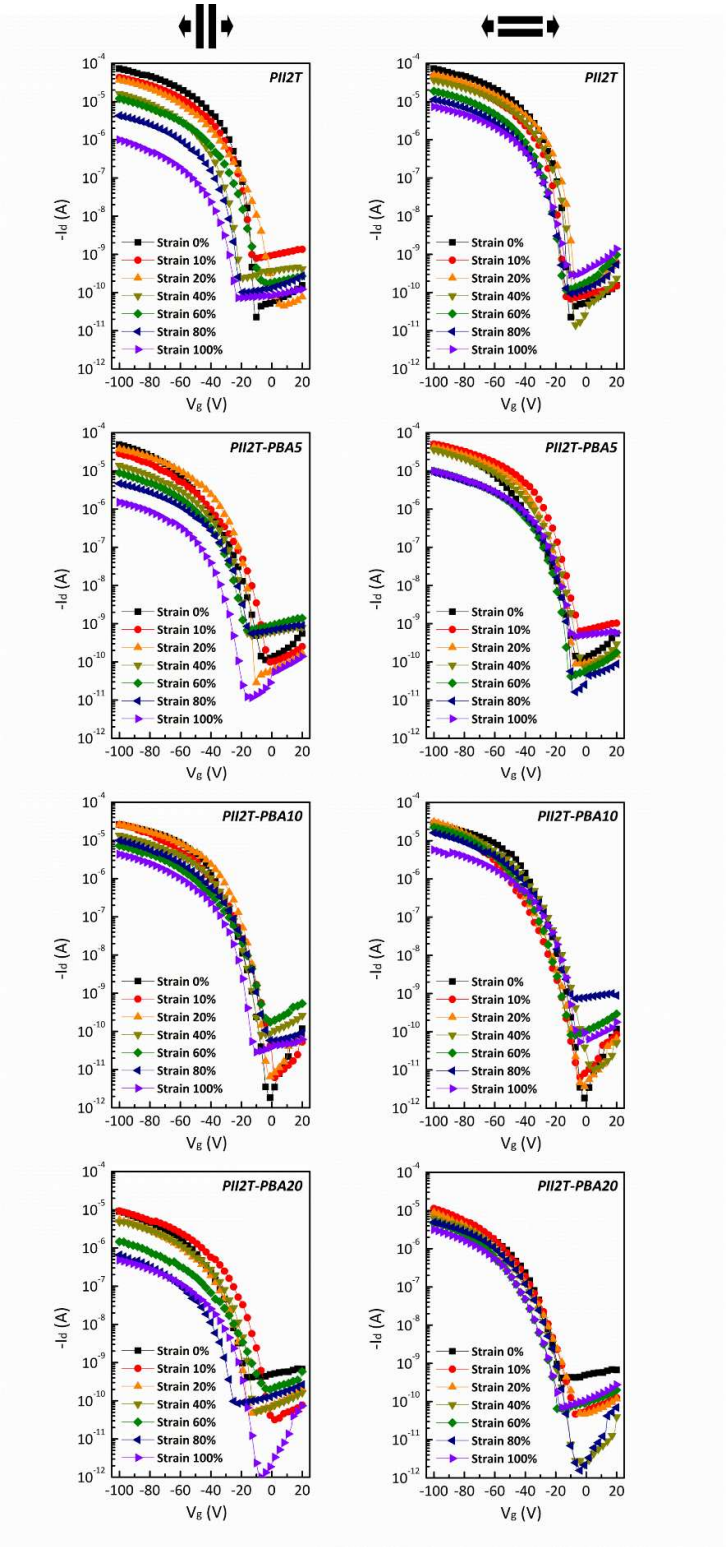


**Figure S10**. FET transfer characteristics of the studied polymer under different applied strain ratios and stretching directions.

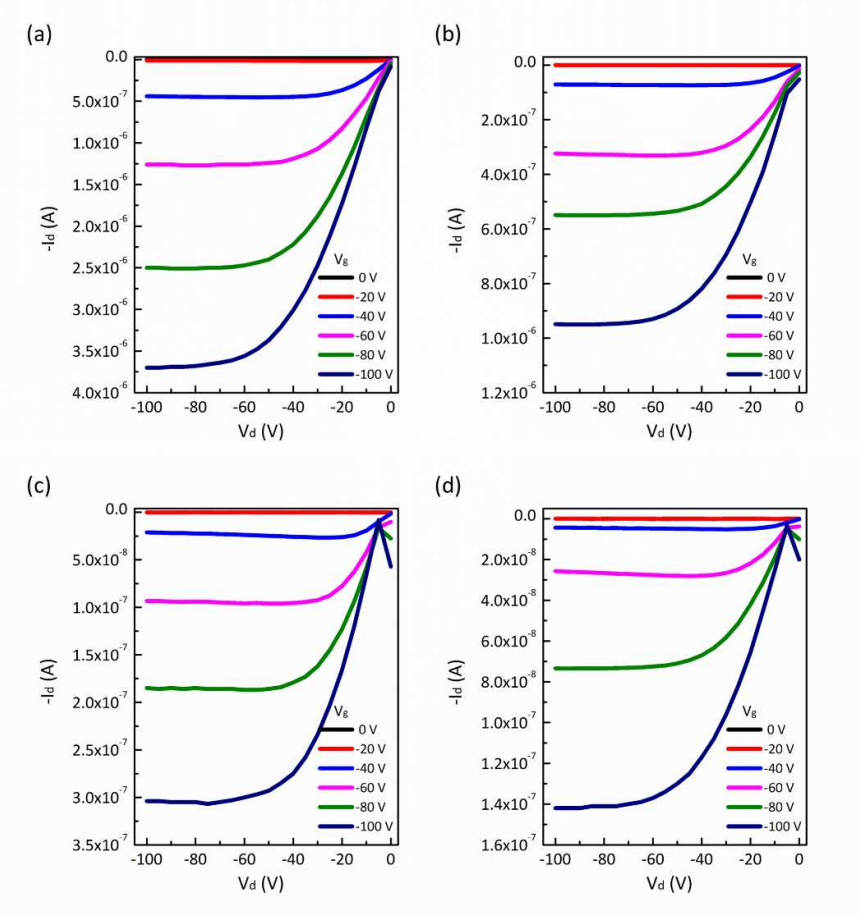


**Figure S11**. Output characteristics of (a) **PII2T**, (b) **PII2T-PBA5**, (c) **PII2T-PBA10** and (d) **PII2T-PBA20**-based FET devices under a 100% strain.