Supporting information

Improved self-assembly of P3HT with pyrene functionalized methacrylates

Taniya M.S.K. Pathiranage,¹ Ziyuan Ma,¹ Chinthaka M. Udamulle Gedara,¹ Xiangcheng Pan,²

Youngmin Lee,³ Enrique D. Gomez,³,⁴ Michael C. Biewer,¹ Krzysztof Matyjaszewski,² and

Mihaela C. Stefan¹*

¹Department of Chemistry and Biochemistry, University of Texas at Dallas, 800 West Campbell

Road, Richardson, Texas 75080, United States

²Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon

University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, United States

³Department of Chemical Engineering, 404 Steidle Building, The Pennsylvania State University,

University Park, PA 16802

⁴Materials Research Institute, The Pennsylvania State University, University Park, PA 16802

General Characterization Methods
$^1$H NMR data for the monomers and the polymers were acquired in CDCl$_3$ on a Bruker Avance III 500 spectrometer under ambient conditions using tetramethylsilane (TMS) as the internal reference. GC-MS analyses were done on Agilent 6890–5973 GC/MS workstation with an injector and detector temperature of 250 °C. Temperature was programmed as; initial temperature 70 °C; final temperature, 280 °C with a temperature ramp of 10 °C min$^{-1}$. A Hewlett-Packard column with cross-linked phenyl methyl siloxane (5%) and fused silica as the stationary phase and Helium (flow rate = 1 mL min$^{-1}$) as the mobile phase were employed.

Molecular weight ($M_n$) and dispersity ($D$) determination was done with Size Exclusion Chromatography (SEC) with polystyrene standards on Viscotek VE 3580 separation module under the refractive index (RI) detector (flow rate = 1.0 mL min$^{-1}$, injector volume = 100 mL, detector temperature = 30 °C, column temperature = 35 °C). DSC thermograms were obtained with a Q100 differential scanning calorimeter (TA instruments) using hermetically sealed aluminum sample holders where the temperature was programmed from 20°C to 250°C for three cycles at the rate of 10°C/min.

The electrochemical analysis was done using a BAS CV-50W Voltammetric Analyzer from Bioanalytical Systems, Inc. with a cell comprised of a platinum electrode, a platinum wire
auxiliary electrode and an Ag/AgCl reference electrode. Acetonitrile (0.1 M tetra butylammonium perchlorate, TBAP) purged with Argon was used as the electrolyte. Standardizing all electrochemical shifts was done with ferrocene redox couple against Ag/AgCl reference electrode (0.471 V). HOMO and LUMO determination was done with the following equations: HOMO (eV) = -e (E_{ox} + 4.8 – 0.471); LUMO (eV) = -e (E_{red} + 4.8 – 0.471); where E_{ox} and E_{red} are the measured potentials relative to Ag/AgCl.

UV-Vis analysis in solution (chloroform) and thin films annealed at 120 °C was done using an Agilent 8453 UV-Vis spectroscopy system. Field-effect mobility of P3HT-Br and P3HT-b-poly(PyMA) was measured on OFETs in bottom-gate top-contact configuration. Highly doped n-type silicon wafers (0.001–0.003 Ω cm) with thermally grown SiO_2 (200 nm) dielectric were used. Common bottom-gate was created with e-beam evaporation of gold (100 nm) on the back side of the wafer after etching with buffered oxide etchant (7: 1 BOE from JT Baker). Cleaning of the wafer was done by sequential sonicating in acetone, isopropyl alcohol (IPA) and distilled water for 5 minutes in each solution and drying with nitrogen. After spin coating of the P3HT-Br and P3HT-b-poly(PyMA) from polymer solutions (5 mg mL^{-1}) in chlorobenzene, deposition of gold contacts (100 nm) was done by thermal evaporation for source and drain (channel width =
530 µm, channel length = 50 µm). Electrical characterization was done in Cascade Microtech Model Summit Microchamber using Keithley 4200-SCS semiconductor characterization system under ambient conditions. Surface treatment with FTS was done by keeping the devices immersed in a FTS solution (8 × 10⁻³ M in distilled toluene) for 48h (in the glove box) followed by cleaning with dry toluene.

Thin film TMAFM studies were executed with Nanoscope IV-Multimode Veeco instrument on OFET channel regions and polymer thin films drop casted on mica (0.2 mg mL⁻¹ chlorobenzene) under ambient conditions at 1 Hz scan frequency.

Thermotropic liquid crystalline mesophases were identified under a Meiji polarizing optical microscope (POM) with a Parker Daedal heating stage equipped with an Olympus digital camera and QCapture software. POM images were collected for a thin layer of polymer sample sandwiched between glass slides and heated from room temperature to isotropic state under cross polarizer at the rate of 5 °C/min and allowing to cool down to room temperature.

Grazing-incidence wide angle X-ray scattering (GIWAXS) measurements were carried out at beamline 7.3.3 of Advanced Light Source in Lawrence Berkeley National Laboratory. Beamline
7.3.3 operates at energy of 10.0 keV with $\lambda = 1.2398$ Å. Scattering data were acquired at an incident angle of 0.15°. In-plane data was extracted as line cuts from the 2D images and is presented as a function of the scattering vector, $q$ ($q = [4\pi \sin \theta] / \lambda$). GIWAXS intensities were also azimuthally averaged and presented versus $q$.

Thin film XRD for drop casted polymer films on a silicon wafer (5.0 mg mL$^{-1}$ in chlorobenzene) was performed on a RIGAKU Ultima III diffractometer with Cu-Kα ($\lambda = 1.54$ Å) radiation source. Data collection was done from 1° to 40° ($2\theta$) at a rate of 2° per min.

**Synthesis of allyl-terminated P3HT**

A 250 mL three neck flask with stir bar was flushed with nitrogen for 5 minutes. Tetrahydrofuran (THF) (10 mL) and 2, 5-dibromo-3-hexylthiophene (1.63 g, 5.0 mmol) were injected into the flask via syringe. t-Butylmagnesium chloride (2.5 mL, 5.0 mmol) was added into the reaction mixture and stirred for 90 minutes. Samples from the reaction mixture were taken and analyzed with GC-MS to monitor the monomer conversion. Catalyst, Ni(dppp)Cl$_2$ (0.04 g) (0.07 mmol) was added into the reaction mixture and stirred for 8 minutes followed by injection of allyl magnesium bromide (3 mL), (3.0 mmol) into the reaction mixture. The polymer
was quenched in methanol and purified by the Soxhlet extraction with methanol, hexane and chloroform. (\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \textit{\delta} H 0.9 (t, 3H), 1.35-1.43 (m, 6H), 1.69 (t, 2H), 2.80 (t, 2H), 3.49 (d, 2H), 5.11 (m, 2H), 5.98 (m, 1H), 6.98 (s, 1H), SEC: \textit{M}_n = 13000 \text{ g mol}^{-1}; \text{PDI} = 1.6)

**Synthesis of hydroxypropyl-terminated P3HT**

Allyl-terminated poly(3-hexylthiophene) [0.5 g, 0.04 mmol) was dissolved in anhydrous THF (50 mL) under nitrogen. To this reaction mixture, a 0.5 M solution of 9-BBN (1 mL, 1 mmol) in anhydrous THF was added via a syringe and the reaction mixture was stirred for 24 hours at 40 °C. Then 6 M NaOH (2 mL) was added to the reaction flask. The reaction mixture was stirred for another 15 min under ambient temperature. The reaction mixture was allowed to cool down to room temperature followed by addition of a 33% aqueous solution of hydrogen peroxide (2 mL), and the reaction was allowed to proceed for additional 12 hr at 40 °C. The hydroxy-terminated polymer was precipitated in methanol. The polymer was purified by a Soxhlet extraction with methanol, hexane and chloroform and was characterized by \textsuperscript{1}H NMR. (\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \textit{\delta} H 0.9 (t, 3H), 1.35-1.43 (m, 6H), 1.69 (t, 2H), 2.80 (t, 2H), 3.78 (t, 2H), 6.98 (s, 1H), SEC: \textit{M}_n = 13000 \text{ g mol}^{-1}; \text{PDI} = 1.6)
**Scheme S1.** Synthesis of hydroxypropyl-terminated P3HT

**Synthesis of the P3HT macroinitiator (P3HT-Br)**

Hydroxypropyl-terminated P3HT (2 g, 0.15 mmol) was dissolved in anhydrous THF (100 mL) under inert gas, followed by stirring for 15 min at 40 °C. Then sequential addition of triethylamine (3 mL, 22 mmol) and 2-bromoisobutyryl bromide (2.5 mL, 20 mmol) was added drop wise. The reaction mixture was stirred for another 8 hr at 40 °C. The resulting monobromoester-terminated P3HT macroinitiator (P3HT-Br) was precipitated in methanol and washed with cold methanol (300 mL), followed by drying under vacuum for 24 hr. Polymer was characterized by SEC and $^1$H NMR. (Figure S3 in supporting information). ($^1$H NMR (500 MHz, CDCl$_3$): $\delta$ H 0.9 (t, 3H), 1.35-1.43 (m, 6H), 1.69 (t, 2H), 1.95 (s, 6H), 2.80 (t, 2H), 4.28 (m, 2H), 6.98 (s, 1H), SEC: $M_n = 13000$ g mol$^{-1}$; PDI = 1.6)
Figure S1. $^1$H NMR spectrum of allyl-terminated P3HT

Figure S2. $^1$H NMR spectrum of hydroxypropyl-terminated P3HT
Scheme S2. Synthesis of monobromoester-terminated P3HT (P3HT-Br)

Figure S3. $^1$H NMR spectrum of P3HT macroinitiator (P3HT-Br)
Figure S4. $^1$H NMR spectrum of pyren-1-ol
Figure S5. $^1$H NMR spectrum of 1-((6-bromohexyl)oxy)pyrene

Figure S6. $^1$H NMR spectrum of 6-(pyren-1-yloxy)hexyl methacrylate (PyMA)
Figure S7. $^1$H NMR spectrum of P3HT-$b$-poly(PyMA)
Figure S8. $^1$H NMR spectrum of poly(PyMA) (P2)
**Figure S9:** UV-Vis absorption spectra of P3HT-Br in chloroform solution and as thin films drop cast from chloroform solution.

**Figure S10:** Cyclic voltammograms of P3HT-Br and P3HT-$b$-PyMA
Figure S11. Complete absorbance spectra of the solvatochromism study with H$_2$O and THF mixture.

Table S1: Maximum absorbance values of absorbance spectra of the solvatochromism study with H$_2$O and THF mixtures.

| Solvent mixture       | $\lambda$ max (nm) |
|-----------------------|---------------------|
| THF                   | 447                 |
| 10% H$_2$O in THF     | 512                 |
| 20% H$_2$O in THF     | 511                 |
| 30% H$_2$O in THF     | 514                 |
| H₂O in THF | Intensity |
|------------|-----------|
| 40%        | 515       |
| 50%        | 515       |
| 60%        | 514       |
| 70%        | 515       |
| 80%        | 515       |

**Figure S12**: GISAXS data of P3HT-\(b\)-poly(PyMA) a) before annealing and b) after annealing at 150 °C. c) Horizontal line cuts of GISAXS data of P3HT-\(b\)-poly(PyMA) under annealed and non-annealed conditions.
Figure S13: Thin film XRD spectra of P3HT-\(b\)-poly(PyMA) on SiO\(_2\) substrate deposited from chlorobenzene.

Table S2: Thin film XRD data obtained for P3HT-Br and P3HT-\(b\)-poly(PyMA) on SiO\(_2\) surface.

| Polymer     | q (Å\(^{-1}\)) | d spacing (Å) | Packing                      |
|-------------|----------------|---------------|------------------------------|
| P3HT-Br     | 0.37           | 16.97         | Lamella stacking (100)       |
|             | 0.76           | 8.26          | Lamella stacking (200)       |
|                  | Value 1  | Value 2  | Description                   |
|------------------|----------|----------|-------------------------------|
| Lamella stacking (300) | 1.16     | 5.41     |                               |
| π-π stacking     |          |          |                               |
| Lamella stacking (100) | 0.46     | 13.65    |                               |
| Lamella stacking (200) | 0.84     | 7.41     |                               |
| Lamella stacking (300) | 1.24     | 5.06     |                               |
| π-π stacking     |          |          |                               |
| P3HT-\textit{b}- |          |          | poly(PyMA)                    |
| Molecular weight (g/ mol) |          |          |                               |

**Figure S14**: GPS traces of polymer P3HT-Br and P3HT-\textit{b}-poly(PyMA)
**Figure S15.** Transfer curves of a) P3HT-Br non-treated OFETs and b) P3HT-Br FTS-treated OFETs and output curves of c) P3HT-Br non-treated OFETs and d) P3HT-Br FTS-treated OFETs at $V_{DS} = -100$ V ($W = 530 \, \mu m$, $L = 45 \, \mu m$).
Figure S16. 3D TMAFM images of a) P3HT-Br ($R_q=0.8$); b) P3HT-$b$-poly(PyMA) ($R_q=1.1$) on mica; c) P3HT-$b$-poly(PyMA) on non-treated OFET devices ($R_q=1.7$) and d) P3HT-$b$-poly(PyMA) on FTS treated OFET devices ($R_q=1.5$).
**Figure S17.** DSC thermograms for the heating cycle of P3HT-\(b\)-poly(PyMA)

**Figure S18:** DSC thermograms for the cooling cycles of a) P3HT-\(b\)-poly(PyMA) and b) P3HT-Br