

Supporting information

Poly(3-hexylthiophene) Block Copolymer with Macroscopically Aligned Hierarchical Nanostructure Induced by Mechanical Rubbing

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Materials

Toluene (Malinckdrot, 99.5%) for anionic polymerization was purified with sodium/benzophenone and living polystyryl anions. Tetrahydrofuran (Malinckdrot, 99%) was dried with calcium hydride and sodium/benzophenone prior to use. Hexane (Echo, 95%), ethyl acetate (Echo, 99.5%) and dichloromethane (Malinckdrot, 99.5%) was used as received. Styrene (Aldrich, 99%), and isoprene (Acros, 98%) were degassed and distilled from dibutylmagnesium (Aldrich, 1.0 M solution in heptane) prior to use. 3-hexylthiophene was synthesized according to the literature¹ and purified by vacuum distillation. N-bromosuccinimide (Aldrich, 99%), Na₂S₂O₃ (Aldrich, 98%), kalium hydroxyde (Aldrich, 90%), anhydrous magnesium sulfate (Aldrich, 99%), iodine (Aldrich, 99.8%), iodobenzene diacetate (Aldrich, 98%), sodium-benzophenone, 4-formylphenyl boronic acid (Acros, 97%) and Pd(PPh₃)₄ (Acros, 99%) were used as received.

Syntheses of P3HT-b-PI

1. Synthesis of 2-bromo-3-hexylthiophene

3-hexylthiophene (30 g, 0.1782 mol) was charged into 500 ml reaction flask equipped with a stir bar. 200 ml THF was freshly distilled from sodium-benzophenone followed by addition of N-bromosuccinimide (33.29 g, 0.1872 mol) at 0°C. Reaction was carried out for at least 1 hour in ice bath and terminated with 10 wt% Na₂S₂O₃(aq). Most of THF was evaporated by rotavapor before the mixture was extracted with ether and washed subsequently with 10 wt% Na₂S₂O₃(aq) and 10 wt%

KOH(aq). The product was dried with anhydrous magnesium sulfate, rotavaporated and subjected to vacuum distillation (oil bath $T = 120^{\circ}\text{C}$, 3.10^{-3} Torr). ^1H NMR: ^1H NMR (400 MHz, CDCl_3) ppm 7.18 (d, $J = 5.59$ Hz, 1H), 6.78 (dd, $J = 7.88, 4.23$ Hz, 1H), 2.54 (m, 2H), 1.56 (m, 3H), 1.33 (m, 7H), 0.89 (td, $J = 15.40, 7.67$ Hz, 3H)

2. Synthesis of 2-bromo-3-hexyl-5-iodothiophene

2-bromo-3-hexylthiophene (30 g, 0.1213 mol) was put into a 500 ml reaction flask followed by the addition of 300 ml dichloromethane. Iodine (14.63g, 0.057 mol) and iodobenzene diacetate (19.496 g, 0.060) were added subsequently at 0°C and the mixture was stirred for overnight at room temperature. Reaction was quenched by addition of 10 wt% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution. Dichloromethane was evaporated and the crude product was extracted with ether and washed several times with 10 wt% $\text{Na}_2\text{S}_2\text{O}_3$ (aq). ^1H NMR (400 MHz, CDCl_3) ppm 6.97 (m, 1H), 2.51 (m, 2H), 1.52 (m, 4H), 1.30 (m, 7H), 0.89 (t, $J = 6.76$ Hz, 3H)

3. Synthesis of P3HT-H/CHO

P3HT with bromine at one terminal and hydrogen at other terminal (P3HT-H/Br) was synthesized using Yokozawa method² and purified with Soxhlet extraction using methanol. $M_n = 7464$, PDI = 1.13. P3HT-H/Br (1 g), 4-formylphenyl boronic acid (0.3749 g, 2.5mmol), K_2CO_3 (0.3455 g, 2.5mmol) were charge into a reaction flask and filled with N_2 . 250 ml dried THF was added and stirred until the mixture became clear solution. $\text{Pd}(\text{PPh}_3)_4$ was added and then the mixture was reflux at 70°C and finally 2.5 ml water was added. The coupling reaction was performed for 24 h under N_2 flow. The crude product was precipitated and Soxhlet with methanol. MALDI-TOF and ^1H -NMR spectra were obtained to check the completeness of end-capping reaction. (yield: 97%)

4. Synthesis of P3HT-b-PI

Polyisoprene anions was synthesized by anionic polymerization in toluene at room temperature under nitrogen using *sec*-butyl lithium as initiator and the polymerization was allowed to perform for 24 hours. A portion of toluene solution of P3HT-H/CHO in designated equivalents was then transferred into the above toluene solution of living polyisoprene anions and the resulting mixture was allow to react for 3 hours before anhydrous methanol was injected to terminate the reaction. The

solvent was removed by rotavaporation and a ethyl acetate/hexane mixture (4:1) was charged into the residual to dissolve excess polyisoprene homopolymer. The above two-phase mixture was subjected to centrifugation and the liquid part was removed to afford pure P3HT-b-PI after the following redissolution, precipitation and vacuum dry. $M_n = 10731$, $PDI = 1.10$ are determined from GPC for P3HT-b-PI and the weight percentage of PI was 19.4% as calculated from $^1\text{H-NMR}$. (yield = 90 %).

Rubbing procedure

The setup for rubbing is illustrated in **Figure S1**. P3HT-b-PI was deposited onto a glass substrate coated with Kapton® using a spatula. Rubbing was performed by engaging a Kapton®-coated rotating drum with the surface of the substrate. The gap between the two was adjusted to about 0.1 mm. Rubbing was performed for a duration of 1 hour before the rubbed material was detached from the substrate along with the Kapton® tape. The rubbed Kapton® tape shows no obvious scattering signals in 2-D SAXS and WAXS patterns (similar to pristine Kapton®), which indicates neither crystallization nor orientational order could be induced on Kapton® from rubbing. (**Figure S2**)

Rubbing experiment setup

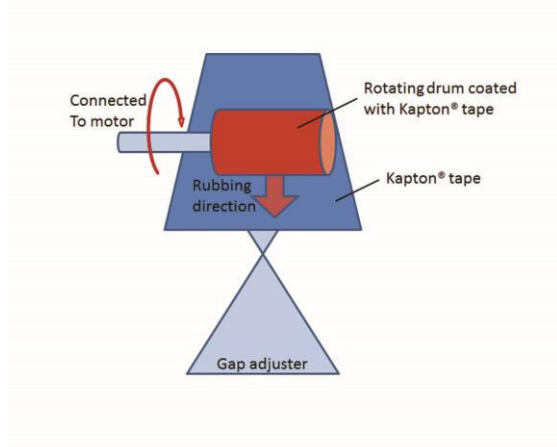


Figure S1. Rubbing experiment setup

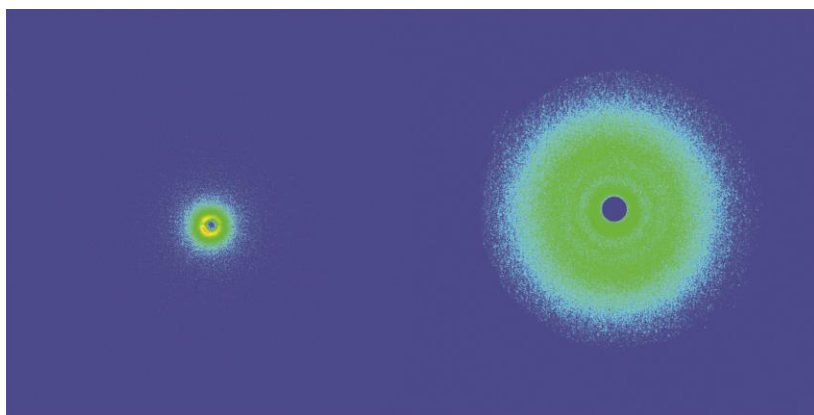


Figure S2. 2-D SAXS (left) and WAXS (right) patterns of rubbed kapton.

Characterization

GPC was performed on a Viscotek HTGPC module 350 equipped with a RI detector and an UV detector at room temperature using THF as the eluent with 1 ml/minute flow rate. Calibration was performed using polystyrene standards from Viscotek. ^1H NMR spectra were obtained from Bruker Avance 400 MHz spectrometer with d-chloroform as solvent. MALDI-TOF MS spectra were obtained using Voyager DE-PRO MALDI-TOF MS (Applied Biosystems, Texas, USA) equipped with a N_2 laser (337 nm). SAXS and WAXS measurements were conducted on Bruker Nanostar and on NSRRC (Hsinchu, R.O.C) beamline 23A and 17A. Ultrathin sections (around 100 nm) was obtained with Leica Ultracut UCT6 and then deposited onto grid and subjected to Transmission Electron Microscopy analysis on JEOL JEM-1400 operating at 100 kV. The POM was done with Zeiss Axiophot microscope equipped with cross-polarizers and a digital camera (Canon PowerShot A640).

Integrated WAXS spectra

The integrated spectra of the 2-D WAXS pattern of the pristine copolymer and the rubbed sample were presented in **Figure S3**. The pristine copolymer shows very low crystallinity as suggested by the absence of integrated peaks, while the crystallinity was remarkably enhanced in the rubbed film.

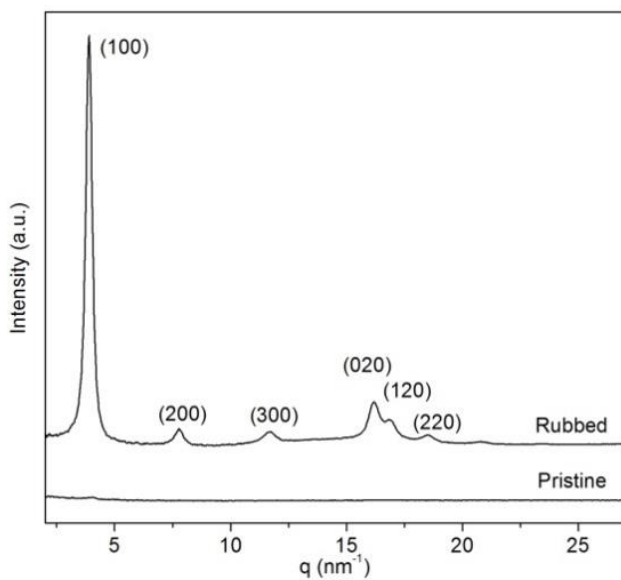


Figure S3. WAXS plot of rubbed and pristine copolymer

Differential Scanning Calorimetry

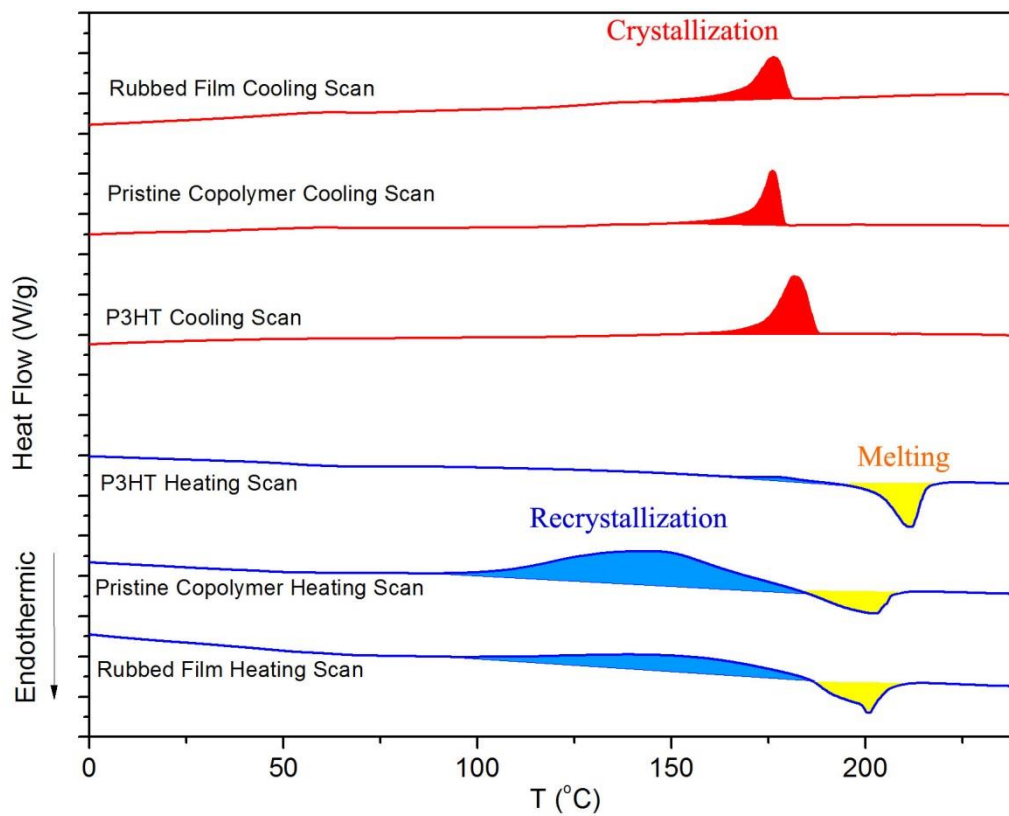


Figure S4. DSC trace of rubbed and pristine copolymer

The DSC traces of the pristine precipitate and the rubbed sample of the P3HT-b-PI copolymer as well as the pristine precipitate of the P3HT homopolymer are depicted in Figure S4. For the samples of block copolymer, and the values were close to the crystallization enthalpy (pristine = 15.93 J/g; rubbed = 15.17 J/g). Re-crystallization was obviously occurred during the heating scan for both the untreated and rubbed block copolymers; therefore, the melting enthalpy should be contributed from both the already existed crystallites and those formed by re-crystallization. As the melting enthalpy for both samples were comparable (pristine = 12.74 J/g; rubbed = 13.43 J/g) and the enthalpy of re-crystallization for the rubbed film is much smaller than that for the pristine precipitate, we could rationally suggest a much improved degree of crystallization in the rubbed sample. In addition, the recrystallization could not be observed in the pristine precipitate of the P3HT homopolymer, indicating the lack of chain mobility of P3HT homopolymer to rearrange during heating to support the comment in the first point.

Calculation of Herman's Orientation

The azimuthal plot of the (100) reflection extracted from the 2-D WAXS pattern of the rubbed P3HT-b-PI was presented in **Figure S5**. The degree of orientation was quantified with Herman's orientation factor f as defined in equation (1). f ranges from 0 to 1, suggesting random orientation to complete alignment parallel to the rubbing direction.

$$f = \frac{3\langle \cos^2 \varphi \rangle - 1}{2} \quad (1)$$

and

$$\langle \cos^2 \varphi \rangle = \frac{\int_0^\pi \cos^2 \varphi \sin \varphi \, d\varphi}{\int_0^\pi \sin \varphi \, d\varphi} \quad (2)$$

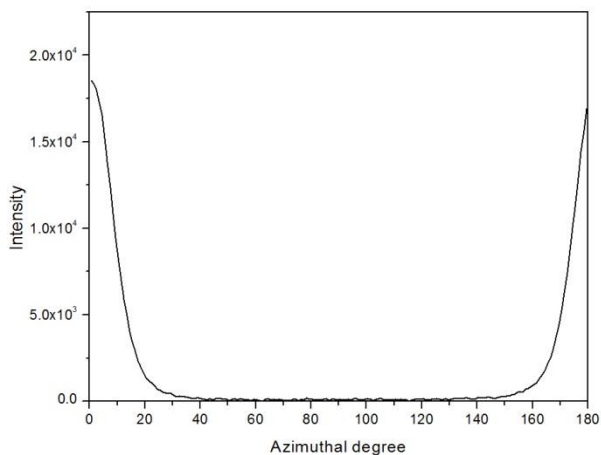


Figure S5. Azimuthal plot of (100) reflection of P3HT-b-PI

Determination of domain spacing from TEM and SAXS

The domain spacing, i.e. the periodicity or the thickness of the lamellae containing one P3HT and one PI, of the rubbed film of P3HT-b-PI was calculated to be 14 nm from $d = 2\pi/q$ with q corresponding to the position of the strongest scattering signal in the SAXS spectra (**Figure S6**). From the line plot of the TEM image (**Figure S7**) with the y-axis representing the brightness of the image, the distance between two next P3HT domains were measured and the average was 13.3 nm, which was close to the domain spacing obtained from the SAXS study.

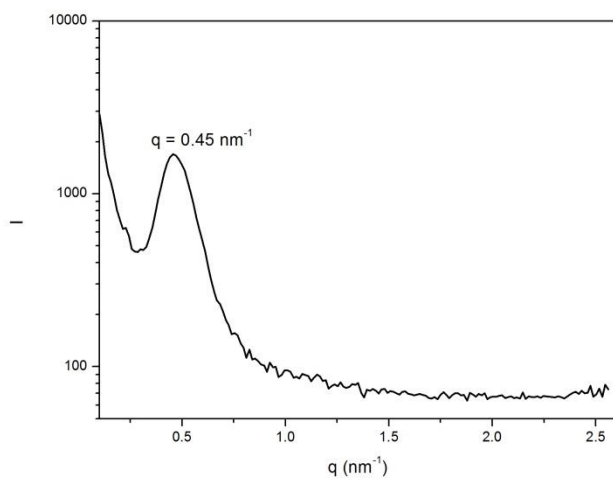


Figure S6. SAXS profile of P3HT-b-PI rubbed film. The domain spacing that measured from the scattering peak is 14 nm

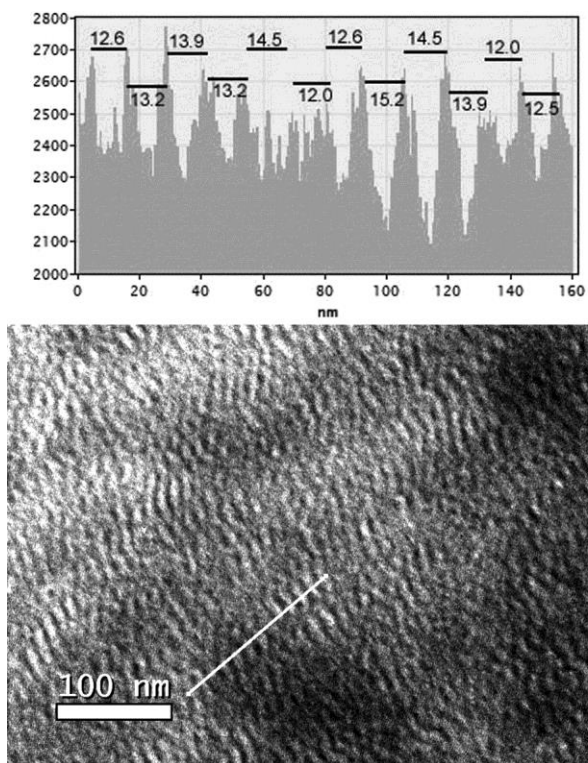


Figure S7. Line plot of TEM profile showing the domain spacing which is closed to the domain spacing obtained from SAXS profile.

References

1. B. Pal, W.C. Yen, J.S. Yang, W.F. Su, *Macromolecules* 2007, 40, 8189–8194.
2. R. Miyakoshi, A. Yokoyama and T. Yokozawa, *Journal of the American Chemical Society*, 2005, 127, 17542-17547.