Supporting Information

Molecular Stacking Structure and Field-Effect Transistor Characteristics of Crystalline Poly(3-hexylthiophene)-*block*-Syndiotactic Polypropylene through Solvent Selectivity

Chen-Tsyr Lo,[1] Chih-Jung Lin,[1] Jing-Yu Lee,[2] Shih-Huang Tung,[3]

Jing-Cherng Tsai,[2,] and Wen-Chang Chen[1,]**

[1]Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan.

[2]Department of Chemical Engineering, National Chung Cheng University, Chia-Yi 62142, Taiwan.

[3]Institute of Polymer Science and Engineering, National Taiwan university, Taipei 10617, Taiwan

*Author to whom all correspondence should be addressed: chenwc@ntu.edu.tw(W. C. Chen); chmjct@ccu.edu.tw (J. C. Tsai)

Table S1. Polymerization conditions, molecular weights, and thermal properties of azide-capped **sPP**, ethynyl-capped **P3HT** and the corresponding diblock copolymers, **P3HT**-*b*-**sPP**.

Entry	Polymer[a]	M_n[b] (g/mol)	PDI[b]	H-T ratio[c] (%)	[rrrr][d] (%)	T_d[e] (°C)	T_c[f] (°C)		T_m[f] (°C)	
							sPP	**P3HT**	**sPP**	**P3HT**
A1	**P3HT**$_1$	16,000	1.13	97.5	—	—	—	—	—	—
A2	**P3HT**$_2$	16,200	1.09	97.7	—	—	—	—	—	—
C1	**sPP$_{3k}$**	3,400	1.25		87.5	279.64	—	—	—	—
C2	**sPP$_{14k}$**	14,600	1.42		88.7	367.76	—	—	—	—
P1	**A1**-*b*-**C1**	19,000	1.13		—	418.35	58.16	190.16	118.62	223.12
P2	**A2**-*b*-**C2**	31,800	1.30		—	407.92	88.52	183.16	147.10	222.55

[a] Propylene polymerization condition: toluene 50 mL; [Zr]=2.5×10^{-6} mole; Al/Zr=2000; propylene pressure = 1 bar; time = 30 min; Temperature, T_p=25 °C.

[b] Molecular weight (M_n) and molecular weight distribution (M_w/M_n, PDI) were determined by high-temperature GPC at 110 °C with 1,2,4-chlorobenzene as solvent.

[c] Head-to-tail (H-T) ratio was determined by ^{1}H NMR analyses.

[d] Syndiotactity (rrrr) was determined by ^{13}C NMR analyses.

[e] Decomposed temperature (T_d) was obtained from TGA analyses.

[f] Crystallization temperature (T_c) and Melting point (T_m) were obtained from DSC analyses.

Table S2. The calculated results of Flory-Huggins interaction parameter between polymer and solvent ($\chi_{\text{polymer-solvent}}$).

CF content (vol %)	$\chi_{\textbf{P3HT}\text{-solvent}}$	$\chi_{\textbf{sPP}\text{-solvent}}$
100	0.031	0.394
70	0.097	0.282
30	0.262	0.146

The Flory-Huggins interaction parameter between the assigned polymer block and the solvent mixture, $\chi_{\text{polymer-solvent}}$, is generally employed to predict the microphase separation inside the block copolymers. Equation 1 is generally employed to calculate $\chi_{\text{polymer-solvent}}$, which is correlated to the solubility parameters δ of both the assigned polymer and the solvent mixture:

$$\chi_{\text{polymer-solvent}} = (\delta_{\text{polymer}} - \delta_{\text{solvent}})^2 \tilde{V}/RT \qquad (1)$$

where T is the temperature, R is the gas constant, and $\tilde{V}$ is the molar volume of the solvent mixture.

Moreover, the values of δ_{solvent} and $\tilde{V}$ may vary with the solvent ratios of solvent mixture. Therefore, the simple addition rule is commonly applied:

$$\delta_{\text{solvent}} = X_{\text{v},1}\delta_1 + X_{\text{v},2}\delta_2 \qquad (2)$$

where δ_{mixture} is the solubility parameter of a solvent mixture, $X_{\text{v},1}$ is the volume fraction of solvent 1 with solubility parameter δ_1, $X_{\text{v},2}$ is the volume fraction of solvent 2 with

solubility parameter δ_2. Same rule is applied to obtain the molar volume of the solvent mixture $\tilde{V}$:

$$\tilde{V} = X_{\mathrm{v},1}\tilde{V}_1 + X_{\mathrm{v},2}\tilde{V}_2 \quad (3)$$

In our case, the polymer 1 and 2 are CF and CH, respectively.[1-3]

References

[1] Y.-H. Lee, W.-C. Yen, W.-F. Su, C.-A. Dai, *Soft Matter* **2011**, *7*, 10429.

[2] Y. Lee, J. K. Kim, C.-H. Chiu, Y.-K. Lan, C.-I. Huang, *Polymer* **2009**, *50*, 4944.

[3] D. Pospiech, A. Gottwald, D. Jehnichen, P. Friedel, A. John, C. Harnisch, D. Voigt, G. Khimich, A. Bilibin, *Colloid. Polym. Sci.* **2002**, *280*, 1027.

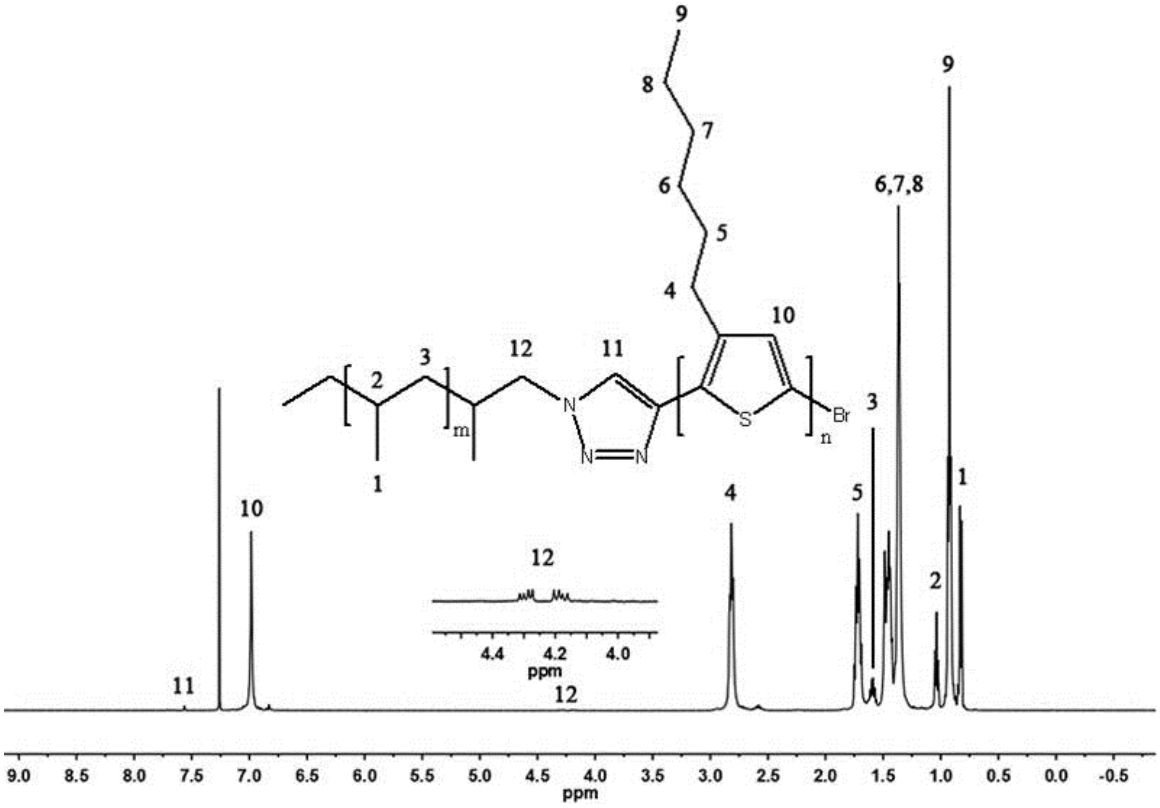

Figure S1. ^{1}H NMR Spectra (500 MHz) of P1 ($P3HT_{16K}$-*b*-sPP_{3K}) (M_n = 19000 g/mol; PDI = 1.14; P3HT H-T ratio = 97.5 %) in $CDCl_3$ (temperature = 50°C).

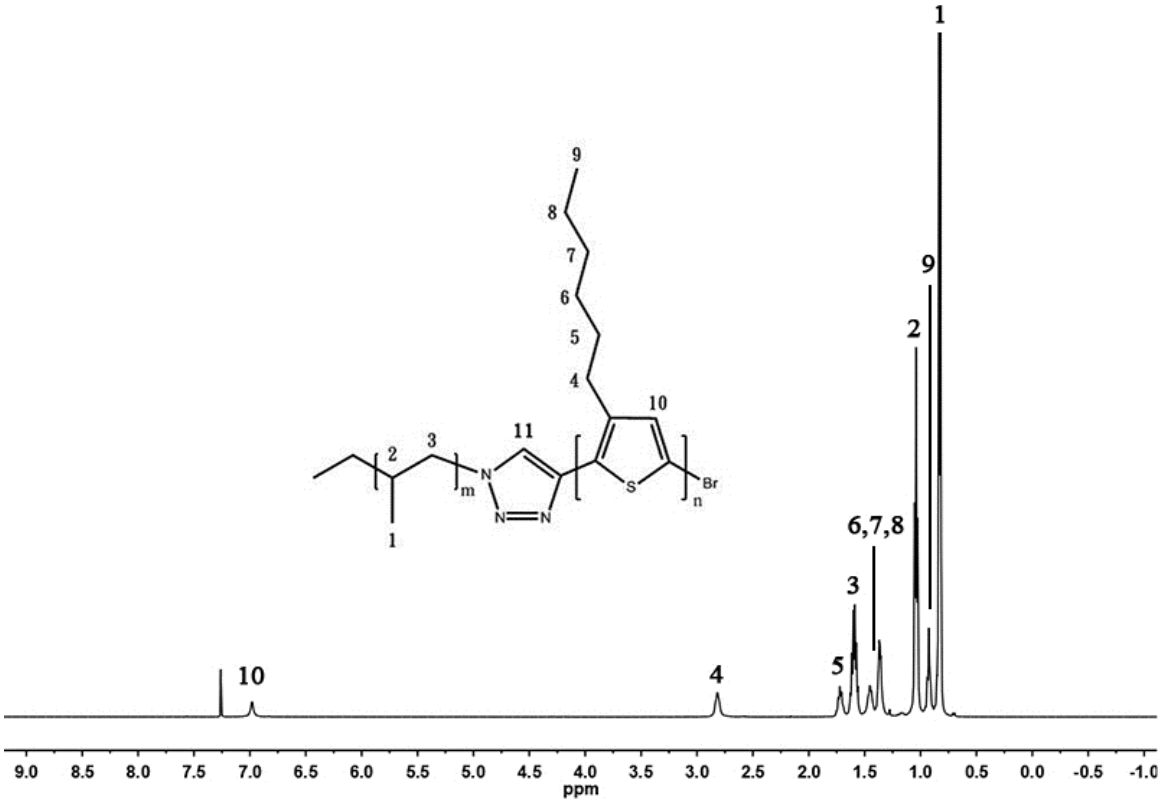

Figure S2. ^{1}H NMR Spectra (500 MHz) of P2 ($P3HT_{16K}$-*b*-sPP_{14K}) (M_n = 31800 g/mol; PDI = 1.30; P3HT H-T ratio = 97.7 %) in $CDCl_3$ (temperature = 50°C).

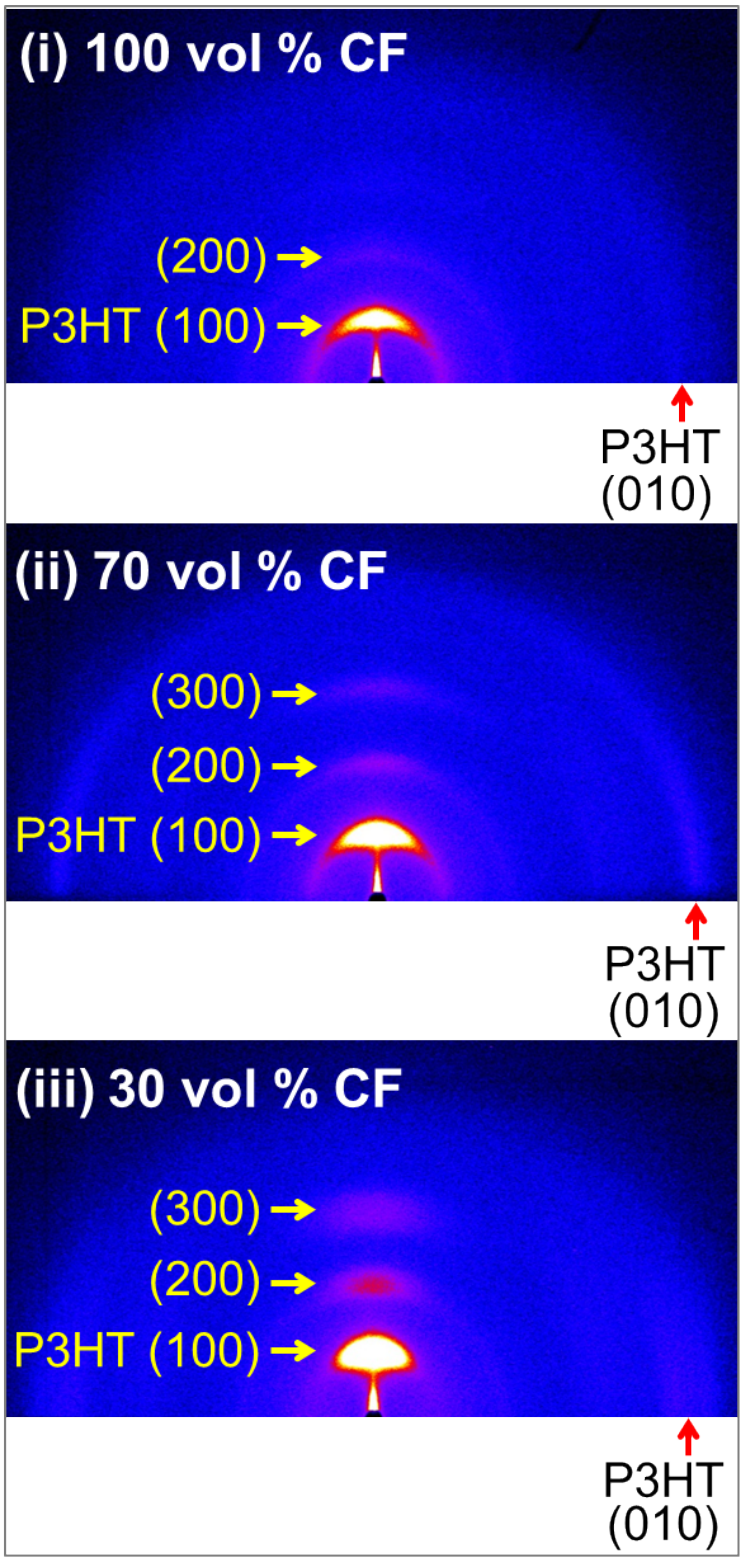

Figure S3. Two-dimensional GIWAXS patterns of **P3HT** homopolymer prepared from

solvent mixtures with different CF content (vol. %).

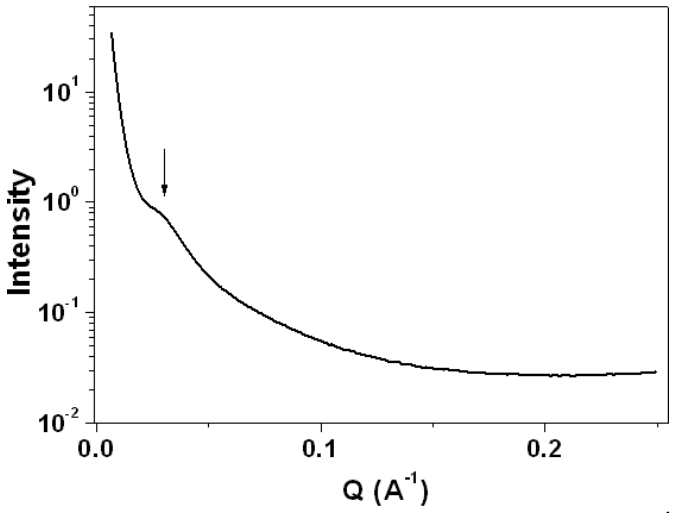

Figure S4. SAXS measurements on the P1 sample prepared from pure chloroform (CF) without further annealing