

Supporting Information for:

# **Solution Self-Assembly and Phase Transformations of Form II Crystals in Nanoconfined Poly (3-hexyl thiophene) Based Rod-Coil Block Copolymers**

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## Detailed Synthesis Procedure

### Materials.

All reagents and chemicals were purchased from Aldrich Chemical Co. and carried out under purified nitrogen.

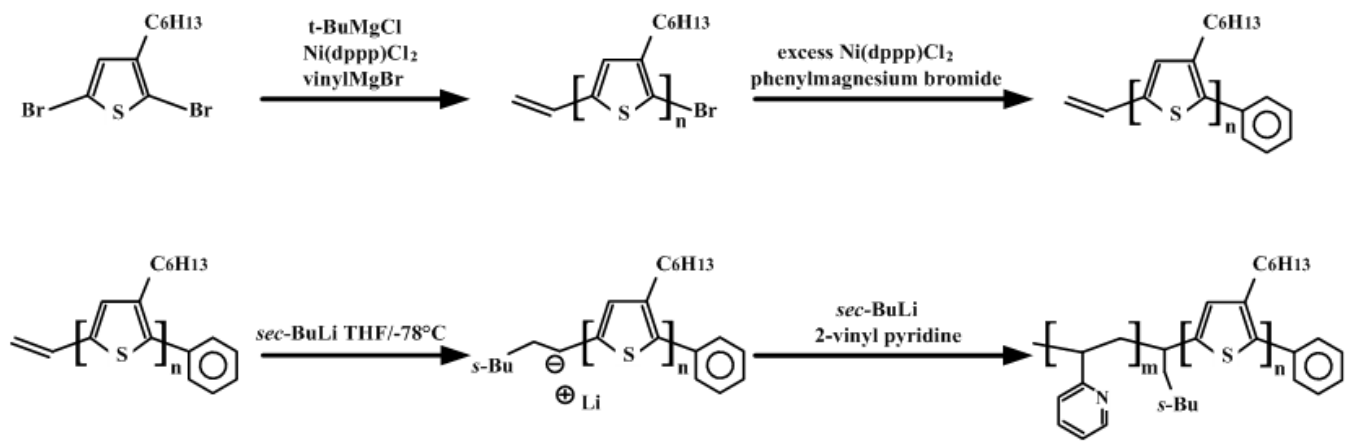
### Synthesis of P3HT-P2VP block copolymers.

The schematic procedure for synthesizing P3HT-P2VP block copolymer is shown in Figure S1. First, a  $\alpha$ -vinyl- $\omega$ -(bromo) end functional P3HT was synthesized. The vinyl modified P3HT with high capping yield (~90%) was conducted according to the described procedure in a previously published work. Then,  $\alpha$ -vinyl- $\omega$ -(phenyl) end functionalized P3HT was further prepared via an end-capping reaction with Grignard reagent phenylmagnesium bromide. This  $\omega$ -phenyl end-capping reaction was performed in order to prevent lithium-halogen exchange of  $\alpha$ -vinyl- $\omega$ -(bromo) end functional P3HT with *sec*-butyllithium added for the subsequent anionic polymerization. For the synthesis of P3HT-P2VP sample, the as-synthesized  $\alpha$ -vinyl- $\omega$ -(phenyl) end-functional P3HT was first dissolved in dry THF solvent. After mixing, the solution was cooled down to  $-78^{\circ}\text{C}$ , followed by adding an excess amount of *sec*-butyllithium in hexane in one portion via a gas-tight syringe. After 1 hr waiting period for the lithiation reaction on the vinyl terminated P3HT at  $-78^{\circ}\text{C}$ , the excess unreacted *sec*-butyllithium was removed by heating the solution to  $40^{\circ}\text{C}$  for 20mins. Subsequently, the solution was re-cooled to  $-78^{\circ}\text{C}$  followed by adding 2-vinylpyridine monomer into the reaction solution for the anionic macroinitiation of 2-vinylpyridine. Upon stirring for 3 hrs of polymerization reaction, a degassed methanol was added to terminate the reaction, and the resulting solution was concentrated and precipitated into hexane. The unreacted P3HT homopolymer in the anionic macroinitiation procedure was removed by using MeOH/water as an extraction solvent from the THF/hexane solution. Finally, the purified P3HT-P2VP block copolymer sample was dried in a vacuum oven at  $50^{\circ}\text{C}$  for 3 days.

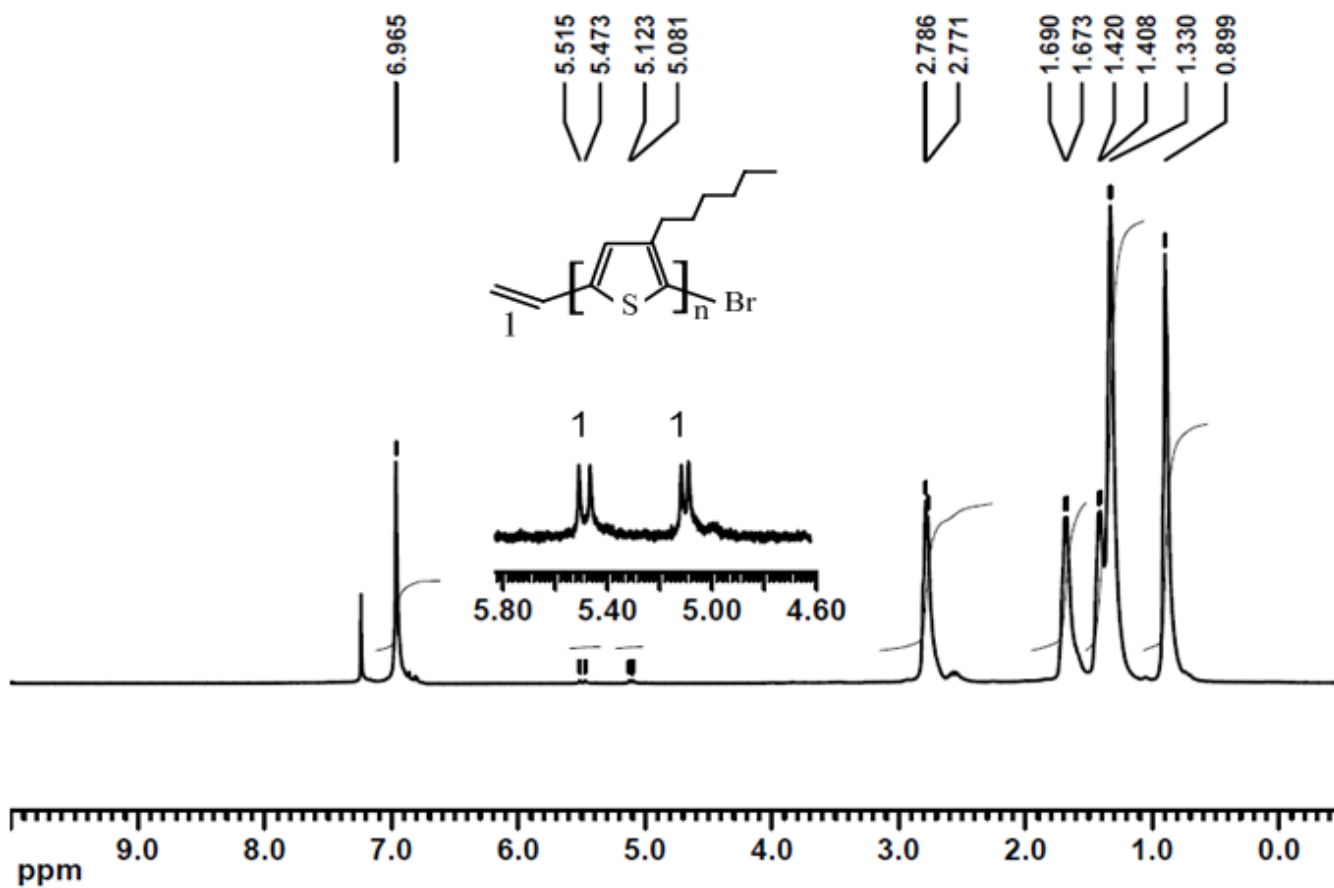
**<sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H NMR).** The chemical structures of the synthesized P3HT precursor and P3HT-P2VP block copolymer samples were identified by using a Bruker NMR spectrometer operating at 400MHz, and CDCl<sub>3</sub> was used as solvent. First, the synthesis of the α-vinyl end-functionalized P3HT was confirmed by the presence of vinyl signals (δ5.12 and δ5.51) shown in the NMR spectrum (Figure S2). Subsequently, the α-vinyl-ω-(phenyl) end functionalized P3HT was synthesized by using a Grignard reagent phenylmagnesium bromide. The success of the ω end-capping reaction was confirmed by the appearance of additional phenyl signals (δ7.43 ~δ7.47) shown in Figure S3. It should be noted that both α-vinyl and ω end-capping modifications were found to give high end-capping conversion efficiency (>90%) by the comparison of the NMR peak-area between the end vinylic hydrogen, the end benzylic hydrogen and the thienyl hydrogen in Figure S2 and S3. The as-synthesized α-vinyl-ω-(phenyl) end functionalized P3HT were further used as a macroinitiator for the following anionic macroinitiation reaction to synthesize P3HT-P2VP block copolymer sample. Based on the <sup>1</sup>H NMR spectrum in Figure S4, the disappearance of the vinyl signals (δ5.12 and δ5.51) indicates the completion of the anionic macroinitiation reaction. On the other hand, the NMR signals for the end-phenyl group (δ7.43 ~δ7.47) remain unchanged, indicating that the anionic initiation in the α-vinyl-ω-(phenyl) end functionalized P3HT occurs only from the vinylic chain end. The weight fraction of P3HT in copolymer sample (~46%) was calculated by integrated area ratio between the α-methylene-H (δ= 2.4~2.9 ppm) signal of the hexyl side-chain of P3HT and H-6 resonance signal (δ= 8.0~8.4 ppm) of P2VP. Then, volume fraction of P3HT in copolymers calculated by utilizing density values 1.10 g/cm<sup>3</sup> for P3HT and 1.14 g/cm<sup>3</sup> for P2VP. The volume fraction of P3HT in the synthesized sample was calculated as 48%. Therefore, The P3HT-P2VP block copolymer was denoted as TP48.

**Gel Permeation Chromatography (GPC).** In addition, the anionic macroinitiation reaction for synthesizing P3HT-P2VP sample was also monitored by using a GPC (Waters 2695) equipped with two

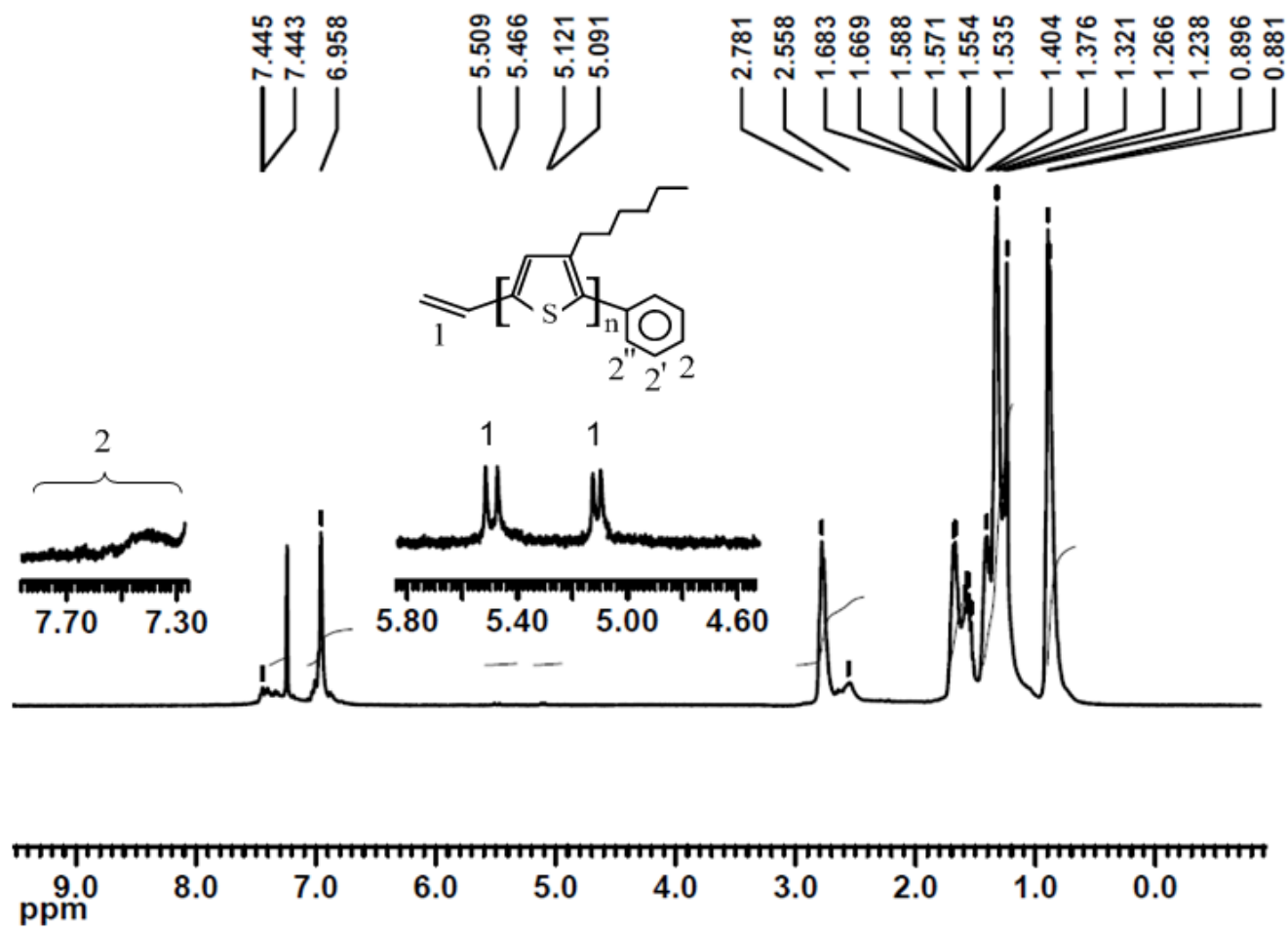
Styragel columns (HR3 and HR4E), a refractive index detector (Waters 2414) and a photodiode array absorbance detector (Waters 2996). THF was used as the mobile phase at a flow rate of 1 mL/min and monodispersed polystyrene standards (Pressure Chemicals) were used for the system calibration. Figure S5 shows the GPC results in which the measured trace of P3HT precursor, crude P3HT-P2VP product, and purified P3HT-P2VP sample are denoted as a solid line, a dashed line and a dotted line, respectively. According to the GPC data, it can be observed that the  $\alpha$ -vinyl- $\omega$ -(phenyl) end-functionalized P3HT has a number-average molecular weight of 4500 g/mol and reveals a narrow molecular weight distribution. After the addition of 2-vinyl pyridine monomers, it can be observed that there is an obvious shift in the GPC trace from the original molecular weight of 4500 g/mol towards a higher molecular weight, indicating the formation of P3HT-P2VP block copolymer via anionic macroinitiation reaction. However, the GPC trace of the crude product exhibited a shoulder corresponding to unreacted P3HT homopolymer (~15% of initial P3HT). This excess P3HT precursor was easily removed by a solvent extraction procedure with mixed solvents. Therefore, the GPC trace of the purified P3HT-P2VP block copolymers shows a monomodal molecular weight distribution, indicating that almost all of the uninitiated or terminated P3HTs were removed after the extraction.



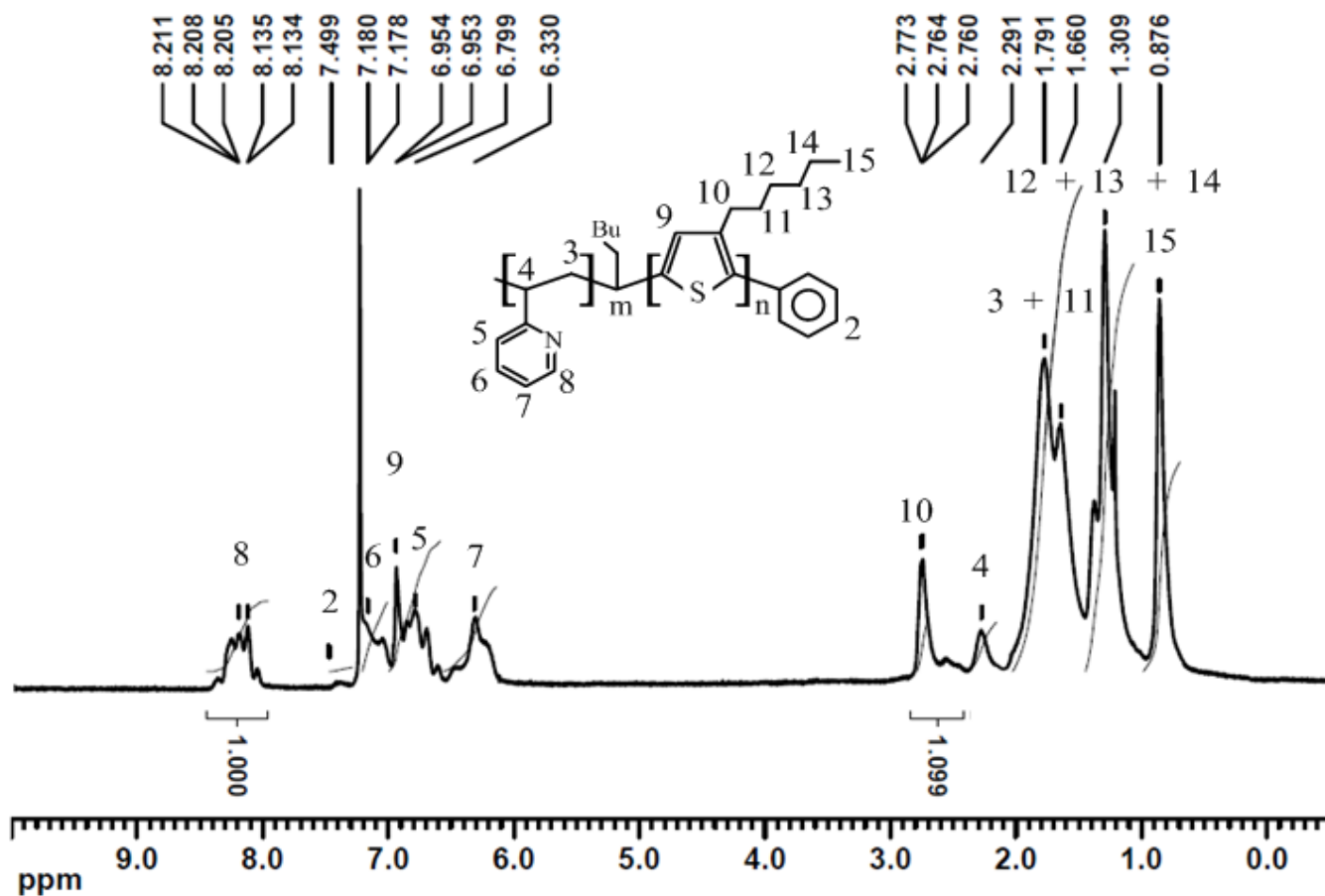
**Figure S1.** Synthesis scheme of P3HT-P2VP block copolymers using anionic macroinitiation method.



**Figure S2.** <sup>1</sup>H NMR spectra showing the structural assignments of α-vinyl-ω-(bromo) end functional P3HT.

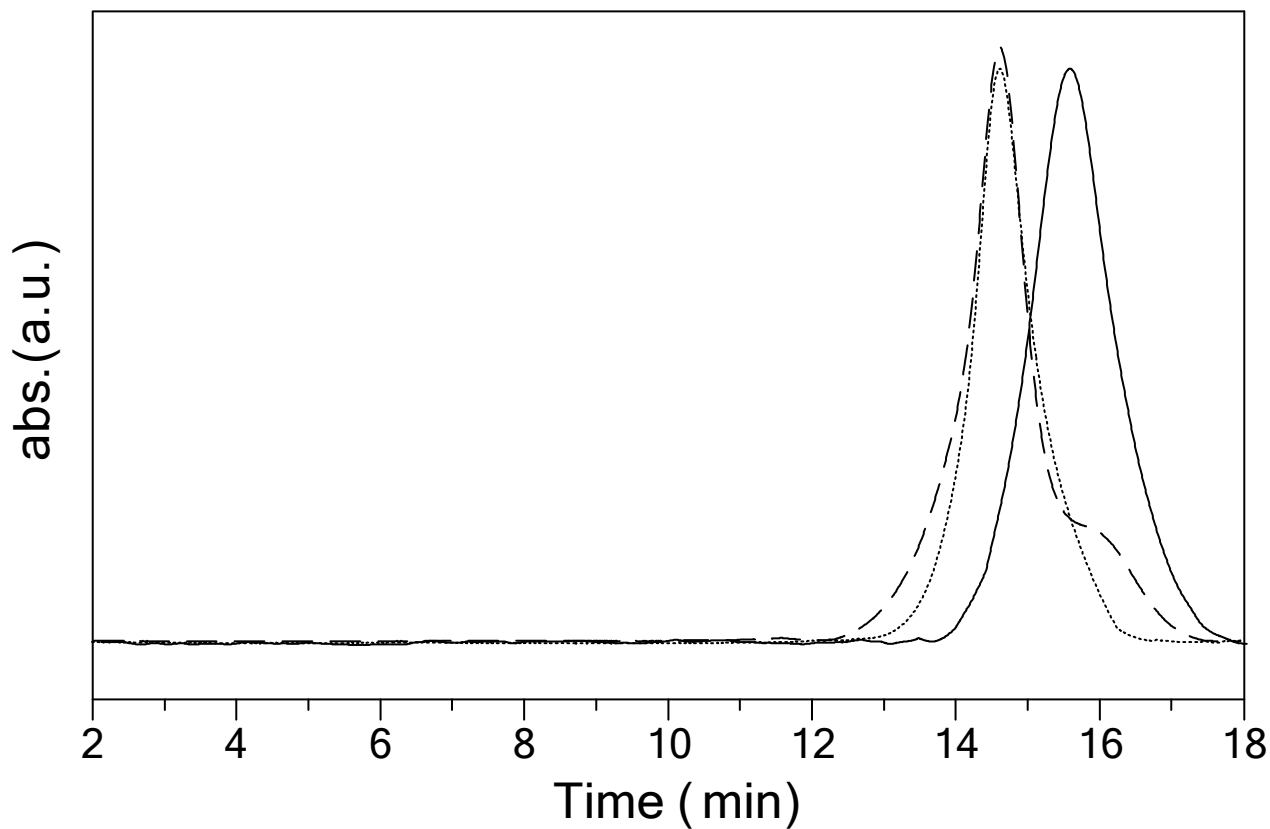


**Figure S3.** <sup>1</sup>H NMR spectra showing the structural assignments of α-vinyl-ω-(phenyl) end functional P3HT.

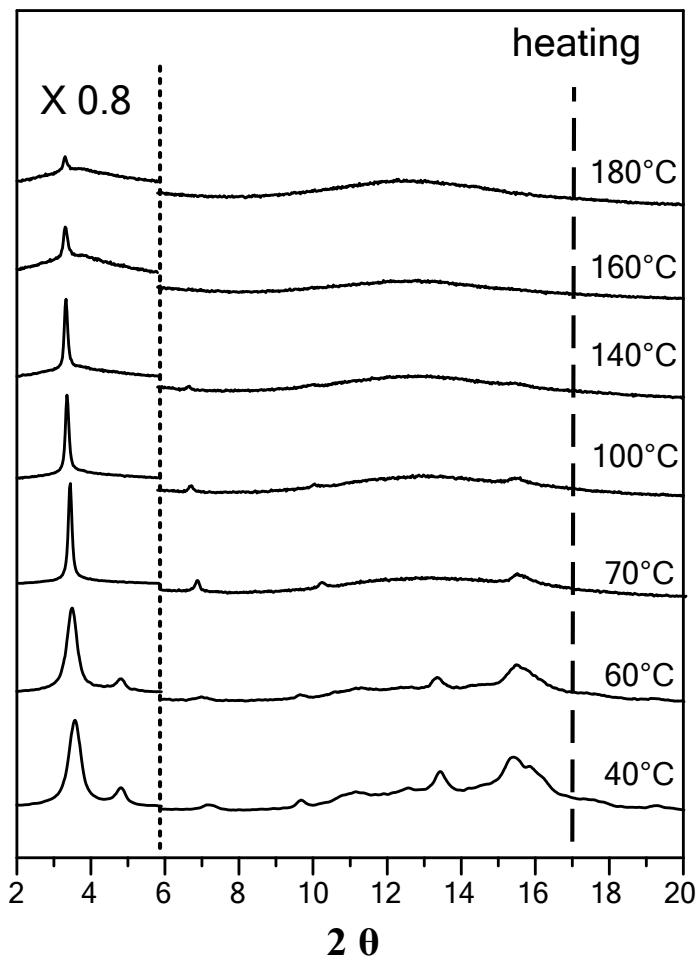


**Figure S4.** <sup>1</sup>H NMR spectra showing the structural assignments of P3HT-P2VP block copolymer. Based on the integrated area ratio between the  $\alpha$ -methylene-H ( $\delta = 2.4\text{--}2.9$  ppm) signal of the hexyl side-chain of P3HT and H-6 resonance signal ( $\delta = 8.0\text{--}8.4$  ppm) of P2VP, the weight fraction of P3HT in copolymer sample is found to be  $\sim 46\%$ .





**Figure S5.** GPC traces of poly (3-hexyl thiophene) homopolymer (—), as -synthesized P3HT-P2VP block copolymer (---), and purified P3HT-P2VP after extraction to remove uninitiated poly (3-hexyl thiophene) homopolymer (.....).



**Figure S6.** The temperature dependent WAXS spectra for the parent P3HT homopolymer precursor.