

Electronic Supplementary Information (ESI) for:

Self-Assembly and Phase Transformations of π -Conjugated Block Copolymers that Bend and Twist: From Rigid-Rod Nanowires to Highly Curvaceous Gyroids

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Materials. All reactions were carried out under purified nitrogen. Ultrahigh purity nitrogen was purchased (purity of 99.99995%) and further purified by passing it through a column of molecular sieves and a BTS (Fluka) catalytic oxygen trap. THF and ether were freshly distilled after being refluxed with excess sodium metal and benzophenol used as the indicator for dryness. Magnesium, 3-bromothiophene, 1-bromohexane *N*-bromosuccinimide (NBS), [1,3-bis(diphenylphosphino) propane] dichloronickel (II) (Ni(dppp)Cl₂) and tert-butylmagnesium chloride were purchased from ACROS and used without further purification. Other reagents and solvents were used as received. *sec*-Butyllithium used as an initiator for the anionic polymerization was purchased from Aldrich. 2-Vinyl pyridine (2VP) monomers were purified by stirring the monomer in a flask with calcium hydride for several days followed by a drying treatment using a freeze-thaw technique with trioctyl aluminum (Aldrich, 25% solution in hexanes) as a drying agent before polymerization.

Synthesis of α -vinyl- ω -(bromo) end functional P3HT. 2,5-Dibromo-3-hexylthiophene (10g, 30mmol) was added into the dried THF (300mL) and the solution was stirred under dry nitrogen. After mixing, tert-butyilmagnesium chloride (2M, 16mL) was then added in the solution via a gas-tight syringe and the resulting mixture was refluxed at 70°C for 2 hrs. Upon cooling to room temperature, the solution was added with Ni(dppp)Cl₂ (0.332g, 0.6mmol). The mixture was stirred for 40mins before vinylmagnesium bromide (1M, 15mL) was added via a gas-tight syringe to the reaction flask for another 2 mins of stirring. Finally, the desired polymer was precipitated into methanol and washed sequentially with methanol, hexane and toluene by using Soxhlet extraction method. ¹H NMR (400 MHz, CDCl₃) for α -vinyl- ω -(bromo) end functional P3HT: δ 0.913 (t, 3H), δ 1.40 (m, 6H), δ 1.69 (t, 2H), δ 2.80 (t, 2H), δ 5.12 (d, 1H), δ 5.51 (d, 1H), δ 6.83 (m, 28H).

Synthesis of α -vinyl- ω -(phenyl) end functional P3HT. The above synthesized α -vinyl- ω -(bromo) end functional P3HT (Mn = 6800, 0.51 mmol, 3.0g) and Ni(dppp)Cl₂ (1.19 mmole, 0.65g) was added to a one-neck round bottom flask. Dried THF (300mL) was transferred into the flask and the solution was stirred under dry nitrogen until complete dissolution. An excess amount of phenylmagnesium bromide solution in THF (1M, 15mmol, 15mL) was added into the P3HT solution and the mixture was stirred overnight for the ω end-capping reaction. Finally, the desired polymer was precipitated into methanol (500mL) and further washed sequentially with methanol, hexane and toluene in a Soxhlet apparatus. The purified polymer was dried in vacuum overnight and afforded as a dark purple material. ¹H NMR (400 MHz, CDCl₃) for α -vinyl- ω -(phenyl) end functional P3HT: δ 0.913 (t, 3H), δ 1.40 (m, 6H), δ 1.69 (t, 2H), δ 2.80 (t, 2H), δ 5.12 (d, 1H), δ 5.51 (d, 1H), δ 6.83 (m, 28H), δ 7.43 ~ δ 7.47 (m, 5H).

Synthesis of P3HT-P2VP block copolymers. The synthesized α -vinyl- ω -(phenyl) end-functional P3HT (Mn = 6800, 0.10mmol, 0.7g) was dissolved in dry THF (300mL) and the solution was cooled down to -78°C. Then an excess amount of *sec*-butyllithium in hexane (1.3M, 0.6mmol, 0.43mL) (4-5 equal-mole of P3HT) was added in one portion via a gas-tight syringe. After 1 hr of lithiation reaction at

-78°C, the excess unreacted *sec*-butyllithium was removed by heating the solution to 40°C for 20mins. The solution was subsequently cooled back down to -78°C followed by adding different amount of 2-vinylpyridine monomer into the solution with the activated poly (3-hexyl thiophyllithium) for the anionic macroinitiation of 2-vinylpyridine. After 3 hours of polymerization, a degassed methanol (2mL) was added to terminate the reaction. The resulting solution was concentrated and precipitated into hexane. In order to obtain pure P3HT-P2VP block copolymer without P3HT homopolymer, the unreacted homopolymer P3HT was removed by using MeOH/water as an extraction solvent from the THF/hexane solution. Finally, the purified block copolymer P3HT-P2VP powder was obtained by removing MeOH aqueous solvent and dried in a vacuum oven.

Gel Permeation Chromatography (GPC). The molecular weight and molecular weight distribution of the synthesized block copolymers were measured 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 1mL/min and monodispersed polystyrene standards (Pressure Chemicals) were used for the system calibration.

¹H Nuclear Magnetic Resonance (¹H NMR). The synthesized block copolymers were dissolved in CDCl₃ and their ¹H-NMR spectra were recorded on a 400MHz Bruker Avance spectrometer at room temperature.

Characterization of P3HT-P2VP Block Copolymers. The successful synthesis of the α -vinyl end-functionalized P3HT was confirmed by the presence of vinyl signals (δ 5.12 and δ 5.51) shown in the NMR spectrum (Figure S1(a)). The α -vinyl end functionalized P3HT was subsequently ω end-capped with a phenyl group using a Grignard reagent phenylmagnesium bromide. The ω end-capping reaction was performed to prevent lithium-halogen exchange between α -vinyl- ω -(bromo) end-functionalized P3HT and *s*-BuLi subsequently added for the anionic polymerization which would lead to different

lithiations at two ends of the P3HT. The success of the ω end-capping reaction was confirmed by the appearance of additional phenyl signals (δ 7.43 ~ δ 7.47) shown in Figure S1(b). The anionic macroinitiation reaction was subsequently carried out for the synthesis of P3HT-P2VP block copolymers. The disappearance of the vinyl signals in the ^1H NMR spectrum (Figure S1(c)) indicates the completion of the anionic macroinitiation reaction. The NMR signals for the end-phenyl group remain unchanged, indicating that the initiation occurs only from the vinylic chain end of **1**. Based on the comparison of the NMR (Figure S1(b)) peak-area between the end vinylic hydrogen, the end benzylic hydrogen and the thienyl hydrogen, both α -vinyl and ω end-capping reactions were found to gave high end-capping conversion efficiency (>90%). In addition, GPC was used to monitor the changes in the molecular weight and distribution of the synthesized polymers before and after the anionic macroinitiation. The α -vinyl- ω -(phenyl) end-functionalized P3HT and its precursor polymer α -vinyl- ω -bromo end functionalized P3HT both has a narrow molecular weight distribution with $\text{PDI} < 1.17$ (Figure S2). After the addition of 2-vinylpyridine monomers, there is a major shift in the GPC trace toward higher molecular weight, indicating the formation of P3HT-P2VP block copolymer. However, the GPC trace of the as-synthesized block copolymer shows a main peak with a minor shoulder of lower molecular weight shown as a dashed line in Figure S2. The main peak with a narrow molecular weight distribution in the GPC trace is clearly an evidence of a living chain growth mechanism involving the anionic polymerization of 2VP initiated by P3HT macroinitiator while the presence of low molecular weight shoulder is presumably a result of some P3HTs failed to be initiated during the anionic polymerization. This minor shoulder in GPC trace appeared in all copolymer synthesis accounts for less than 20% of initial P3HT. Thus, a solvent extraction procedure was performed to remove the uninitiated P3HT homopolymer in the product. The GPC trace of the purified P3HT-P2VP block copolymers exhibits a monomodal molecular weight distribution, indicating that almost all of the uninitiated or terminated P3HTs were removed after the extraction show as a dotted line in Figure S2. Subsequently, ^1H NMR was further used to evaluate the weight fraction of P3HT in each copolymer shown in Figure S1(c).

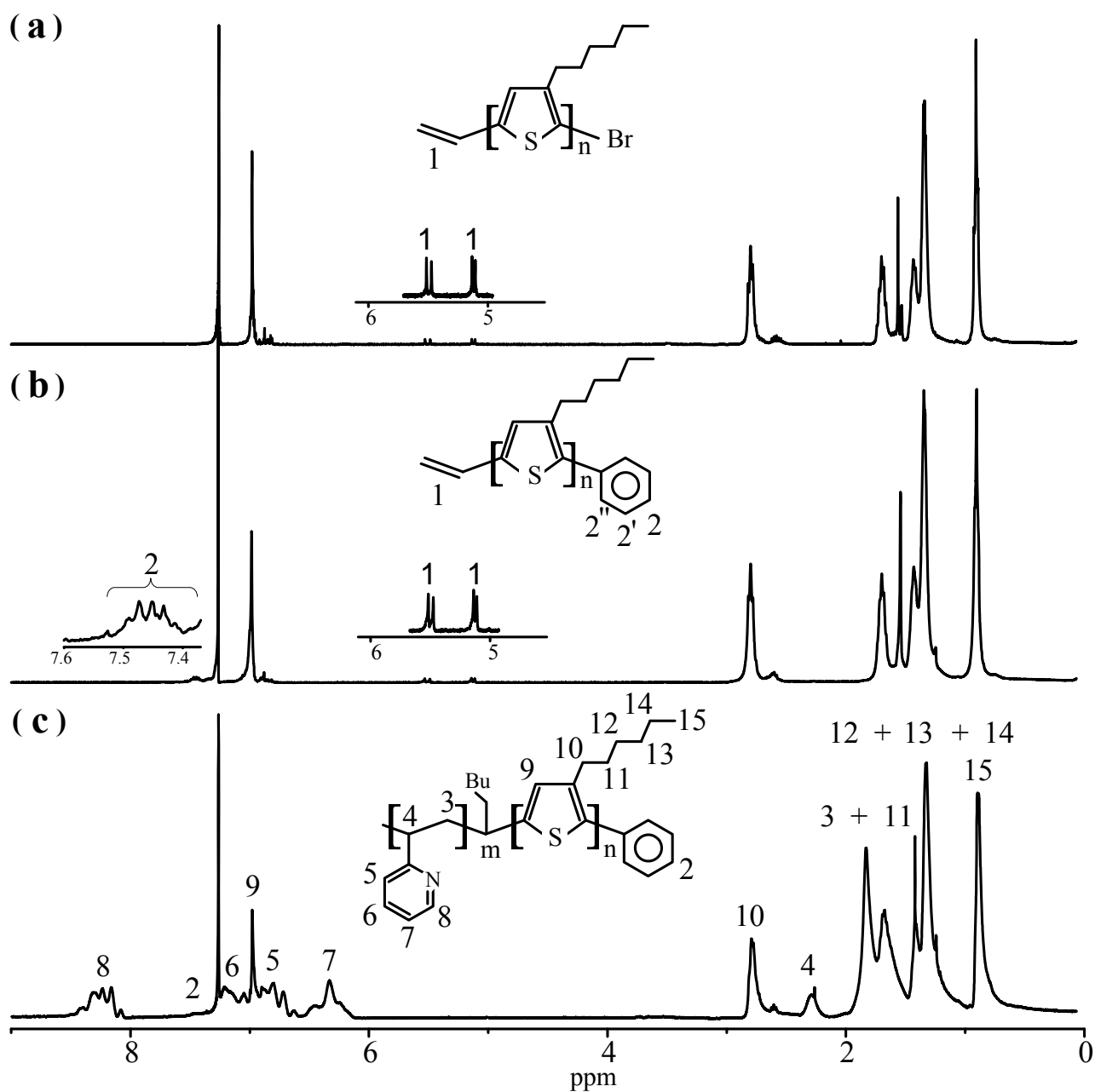


Figure S1. ^1H NMR spectra showing the structural assignments of (a) α -vinyl- ω -(bromo) end functional P3HT and (b) α -vinyl- ω -(phenyl) end functional P3HT and (c) P3HT-P2VP block copolymer.

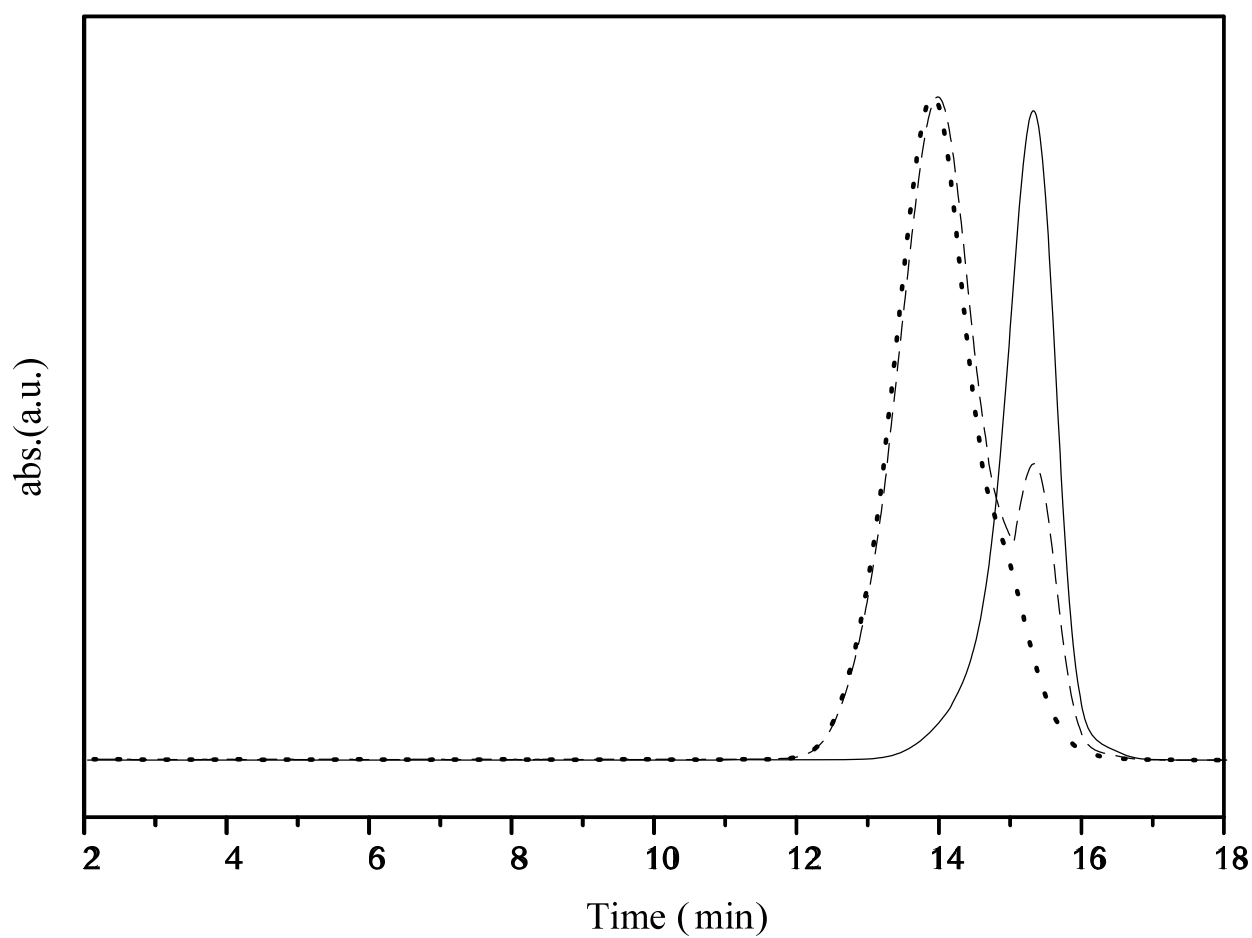


Figure S2. GPC traces of poly (3-hexyl thiophene) homopolymer (——), as -synthesized P3HT-P2VP block copolymer (———), and purified P3HT-P2VP after extraction to remove uninitiated poly (3-hexyl thiophene) homopolymer (.....).

sec-Butyl lithium was used to initiate the end-functionalized vinyl group of P3HT without affecting P3HT π -conjugated system. ^1H -NMR was used to verify that no peaks shifted nor peak area changed related to the thiophyl hydrogens after the addition of the initiator.

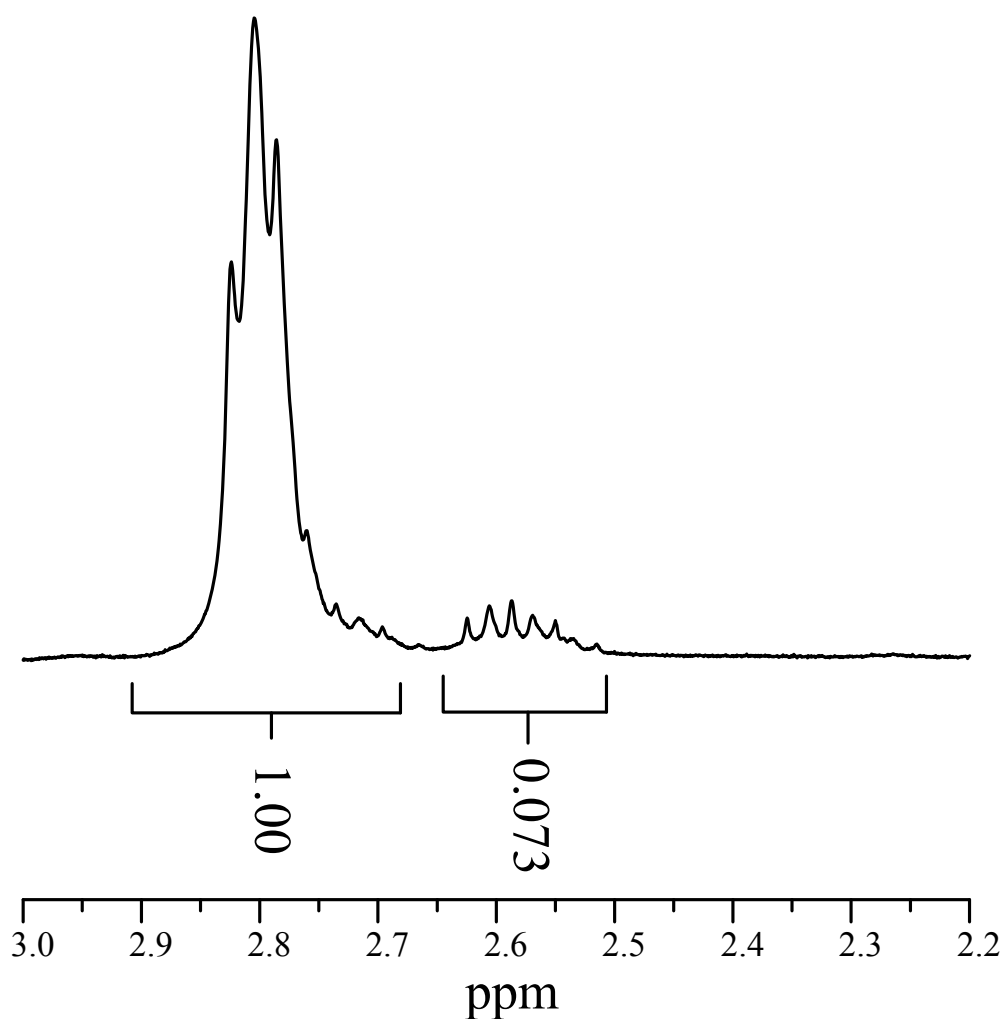


Figure S3. ^1H NMR spectra showing the α -methylene-H of the hexyl side-chain in the head-to-tail ($\delta = 2.8\text{ ppm}$) and in the head-to-head ($\delta = 2.58\text{ ppm}$) configurations.

Based on the integrated area ratio between the two signals, the regioregularity of P3HT for all the synthesized block copolymers is found to be ~93%.

TEM Investigation of P3HT-P2VPs

TEM images on P3HT-P2VPs were taken to show that the self-assembled structures are highly order over large area of 1 μm x 1 μm .

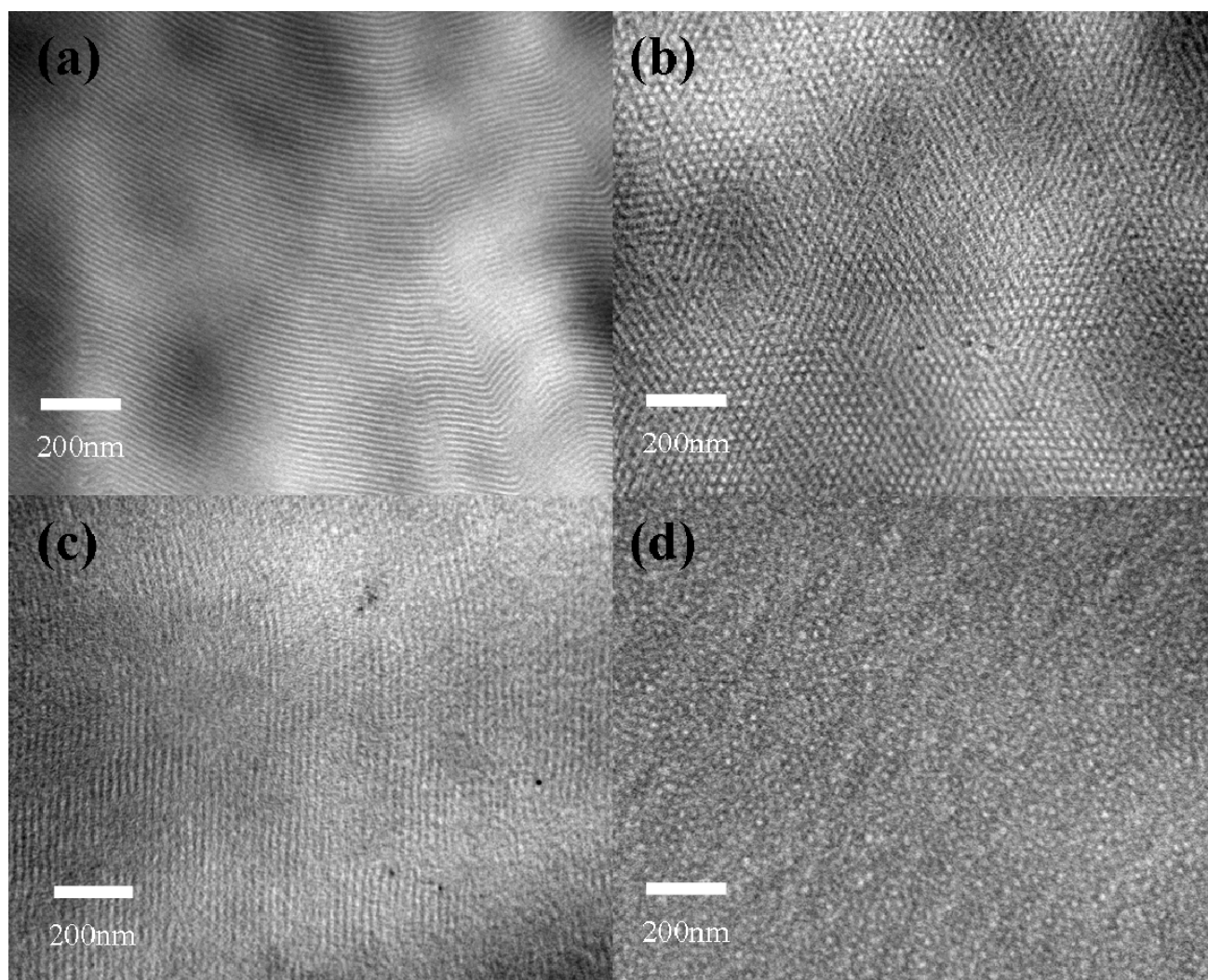


Figure S4. TEM micrographs of the P3HT-P2VP block copolymers at lower magnification. It reveals (a) the lamellar microstructure of HTVP46, (b) hexagonal close-packed cylinders (HCP) of HTVP68, (c) the side view of HCP of HTVP68 and (d) spherical microstructure of HTVP87.

Determination of ODT Temperature

The order-disorder transition temperatures for P3HT-P2VPs are determined by plotting the reciprocal SAXS intensity ($1/I_m$) and the reciprocal temperature as shown in Figure S5.

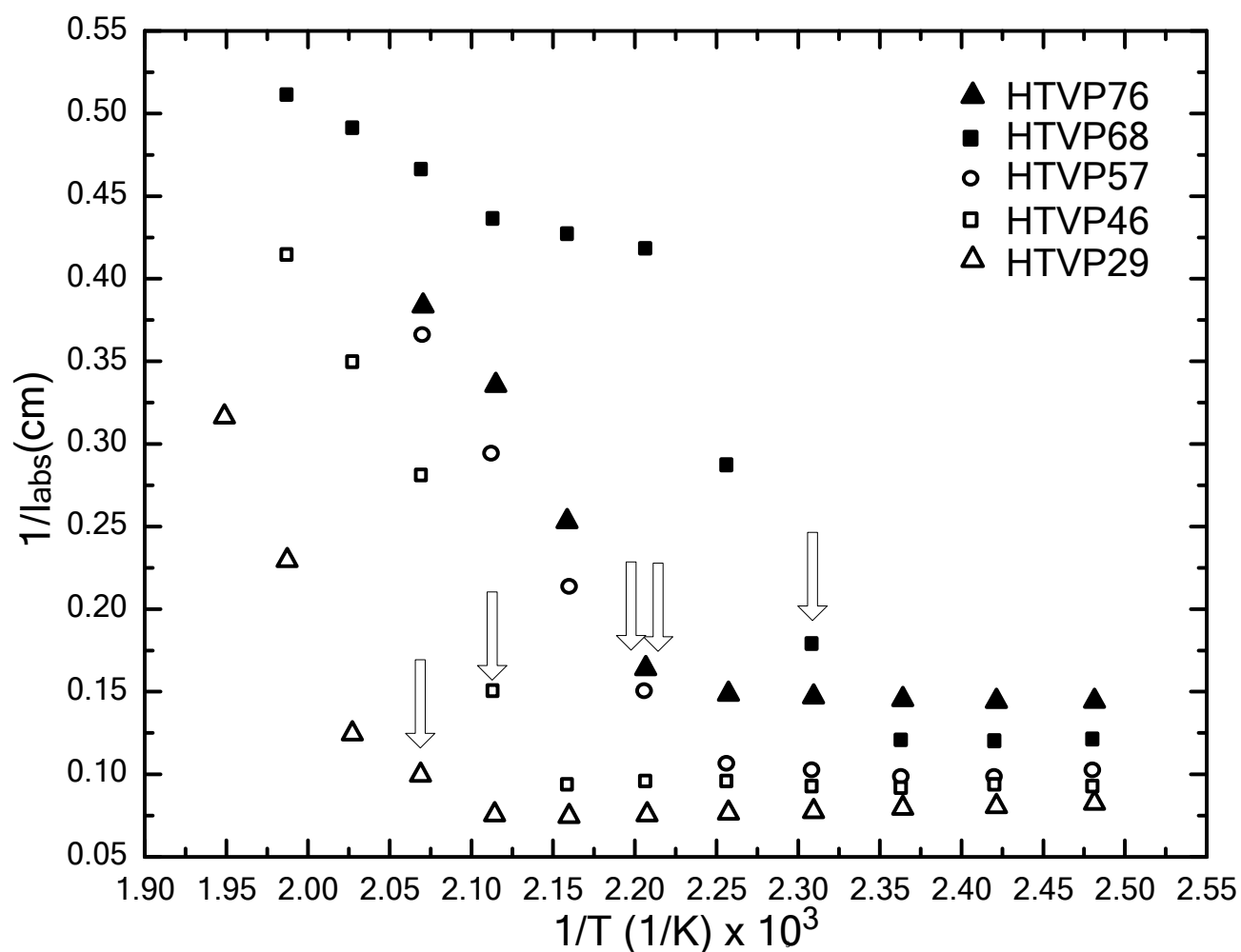


Figure S5. Relationships between the reciprocal SAXS intensity ($1/I_m$) and the reciprocal temperature ($1/T$) for HTVP76, HTVP68, HTVP57, HTVP46, and HTVP29. The arrows indicate the temperature at which high-order peaks disappear and show the order-disorder transition (ODT).

The WAXS spectra of HTVP29 and HTVP46 as a Function of Temperature

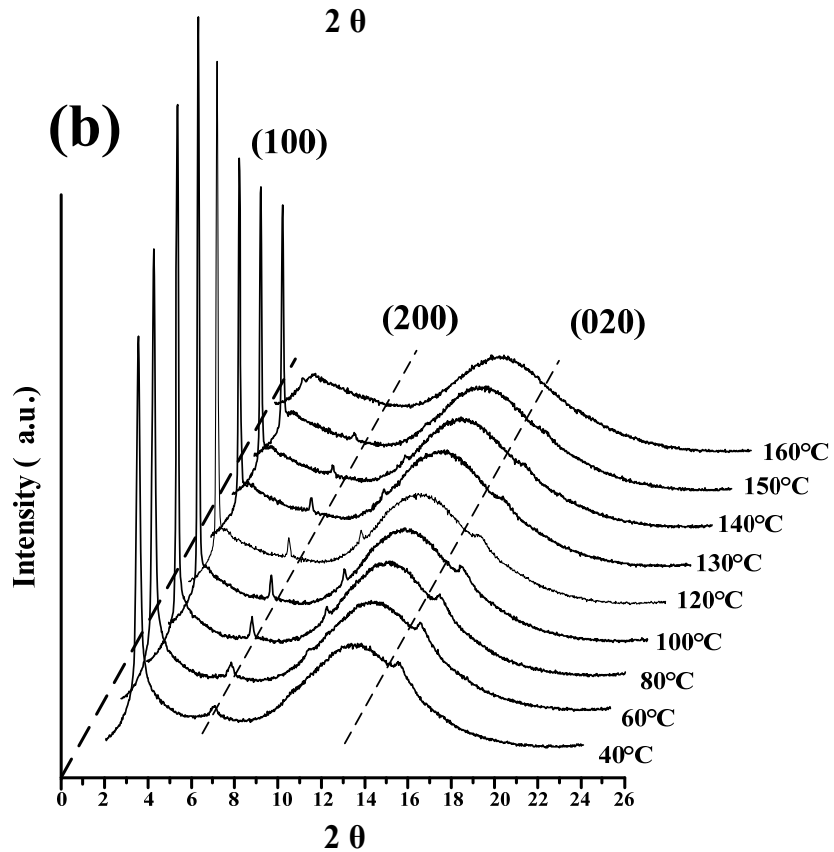
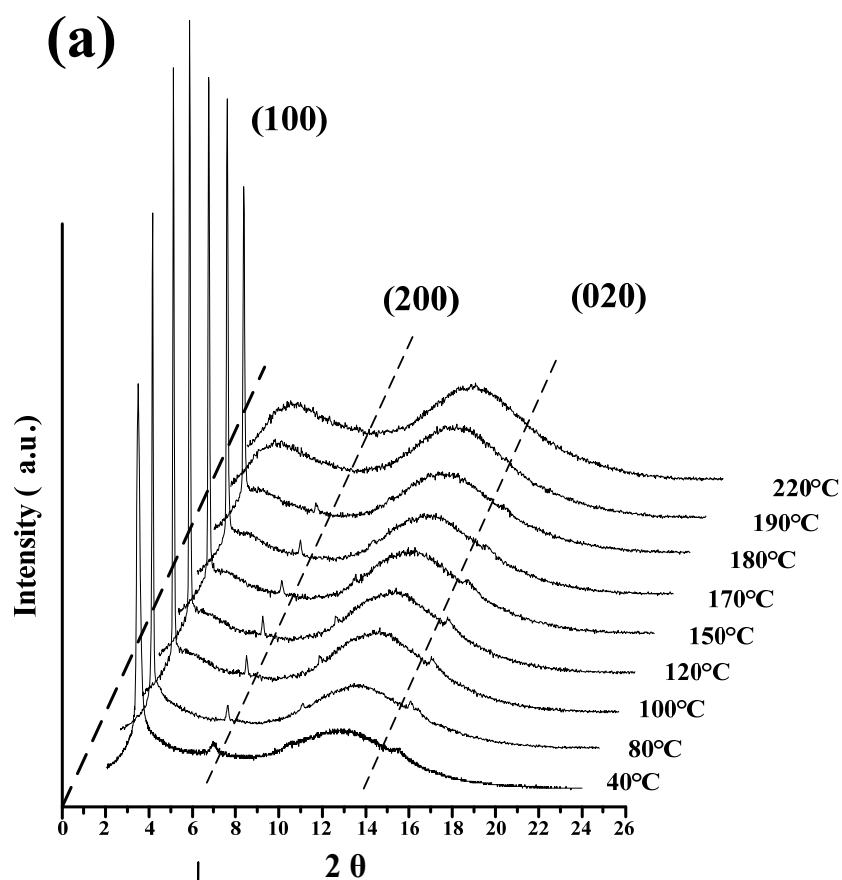


Figure S6. The WAXS spectra for (a) HTVP29 heated from 40°C to 220°C and (b) for HTVP46 heated from 40°C to 160°C. Note that there is no crystal structure for HTVP29 and HTVP46 at a temperature $\geq 220^\circ\text{C}$.

The Effect of Annealing time at 220°C on Self-Assembled Structures (SAXS) and Crystallinity (WAXS) of P3HT-P2VPs

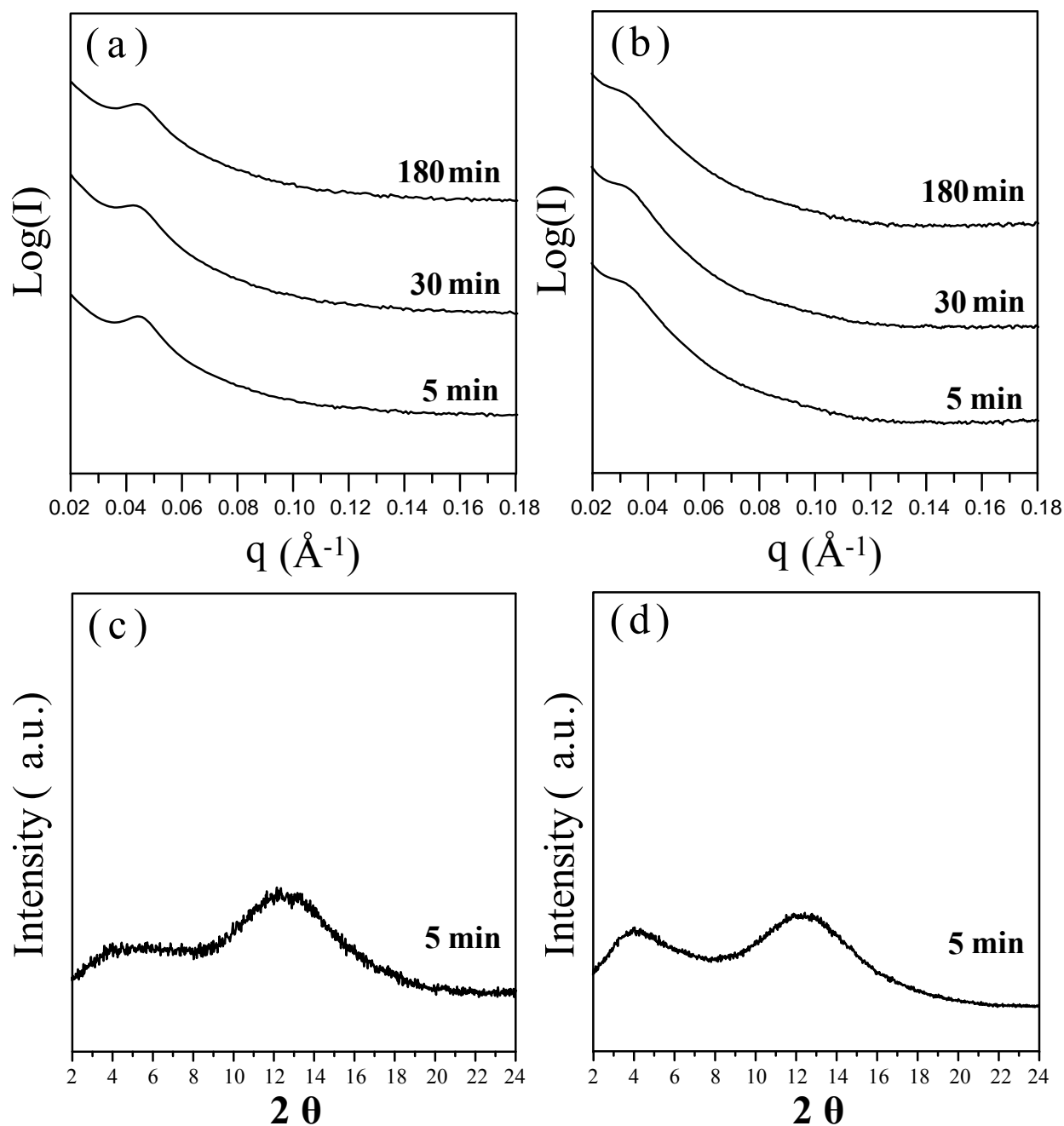


Figure S7. The SAXS spectra for (a) HTVP68 and (b) HTVP46 annealed at 220°C for different times. The WAXS spectra for (c) HTVP68 and (d) HTVP46 annealed at 220°C for only 5mins.

For HTVP68 annealed at 220°C for 5mins, 30mins or 180mins, we observe that the corresponding SAXS spectra related to different annealing times are almost the same. The SAXS spectra in Figure 7S(a) show a residual primary peak indicating a disordered phase. In addition, there is no crystalline peak left for HTVP68 annealed at 220°C for only 5mins as shown in Figure S7(c), indicating a melt state. A similar result on SAXS measurements was also obtained for HTVP46 annealed at 220°C for different times (Figure 7S(b)). In addition, there is no crystalline peak left for HTVP46 annealed at 220°C for only 5mins as shown in Figure S7(d), indicating also a melt state. As a result, it can be concluded that upon annealing at 220°C for 5 minutes, P3HT-P2VP samples are in a disordered melt state. Therefore, the annealing process (220°C for 5mins) used in the current study is sufficient to remove any thermal history incurred during the solvent casting process.

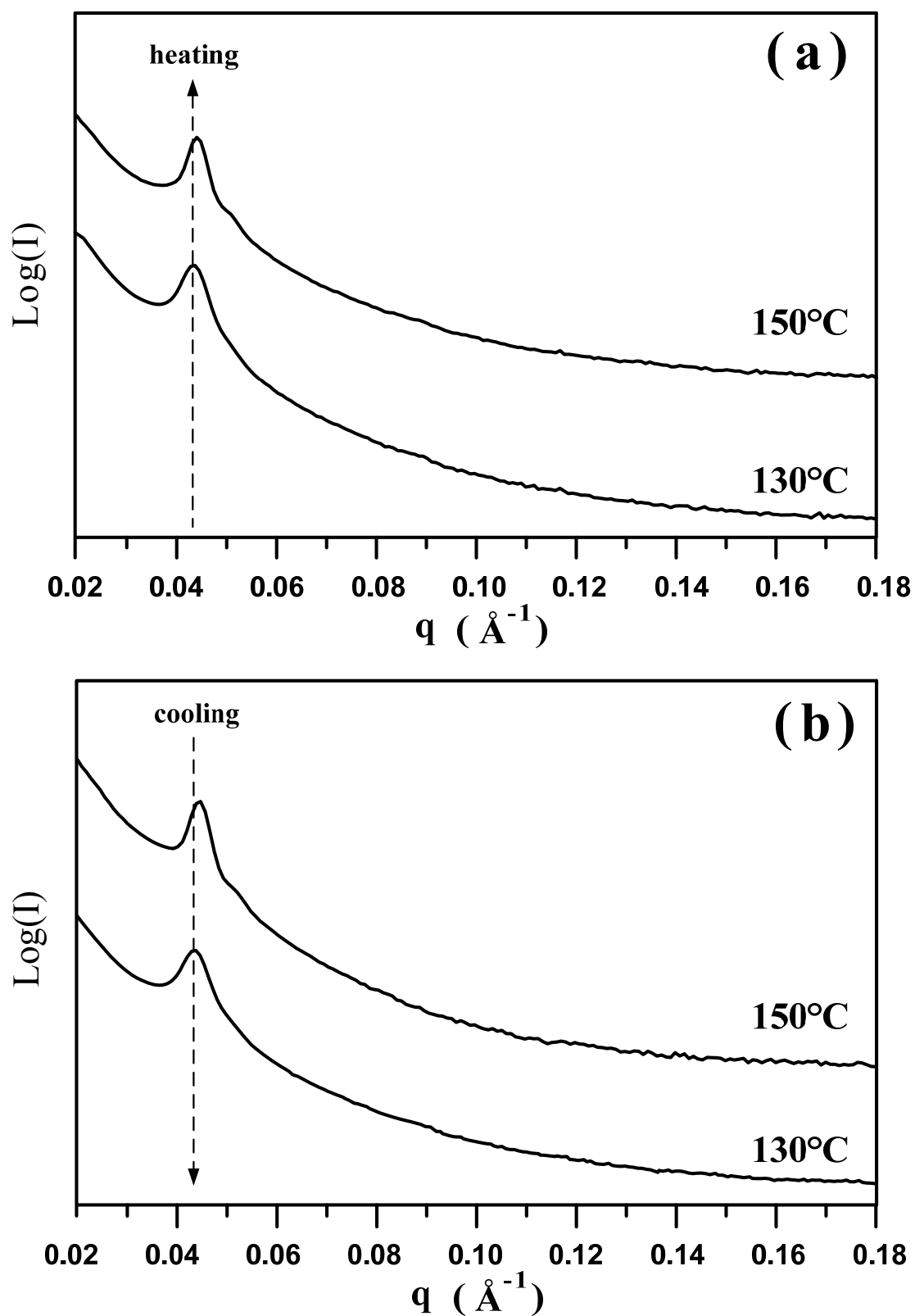


Figure S8: The SAXS spectra for HTVP68 as a function of two temperatures during a (a) heating and (b) cooling experiments. A vertical dashed line is added and passed through the very tip of the 1 order

peak. There is a shift in the q value for the 1st order peak between 130°C and 150°C, indicating a new set of scattering pattern (order-to-order transition) has emerged.