

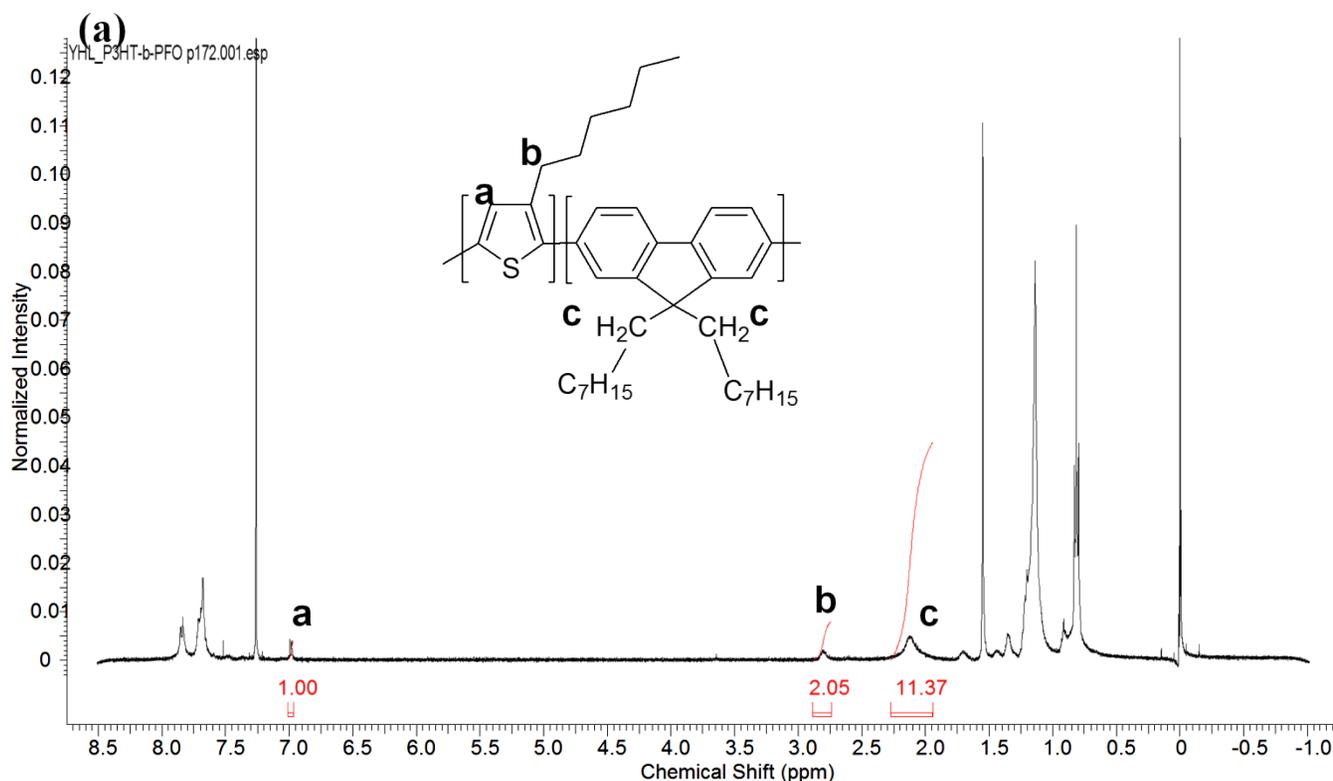
Lamellar and Liquid Crystal Ordering in Solvent-Annealed All-Conjugated Block Copolymers

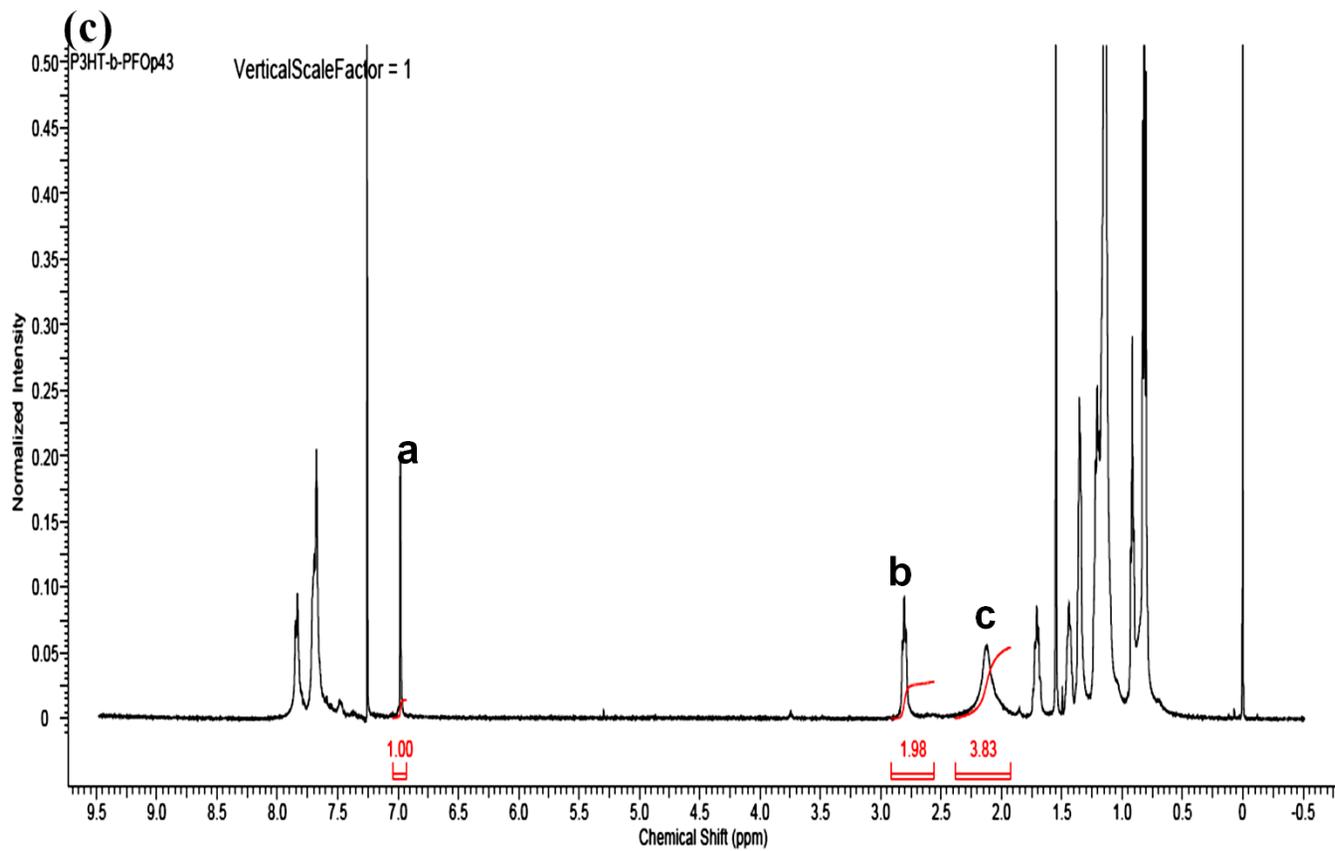
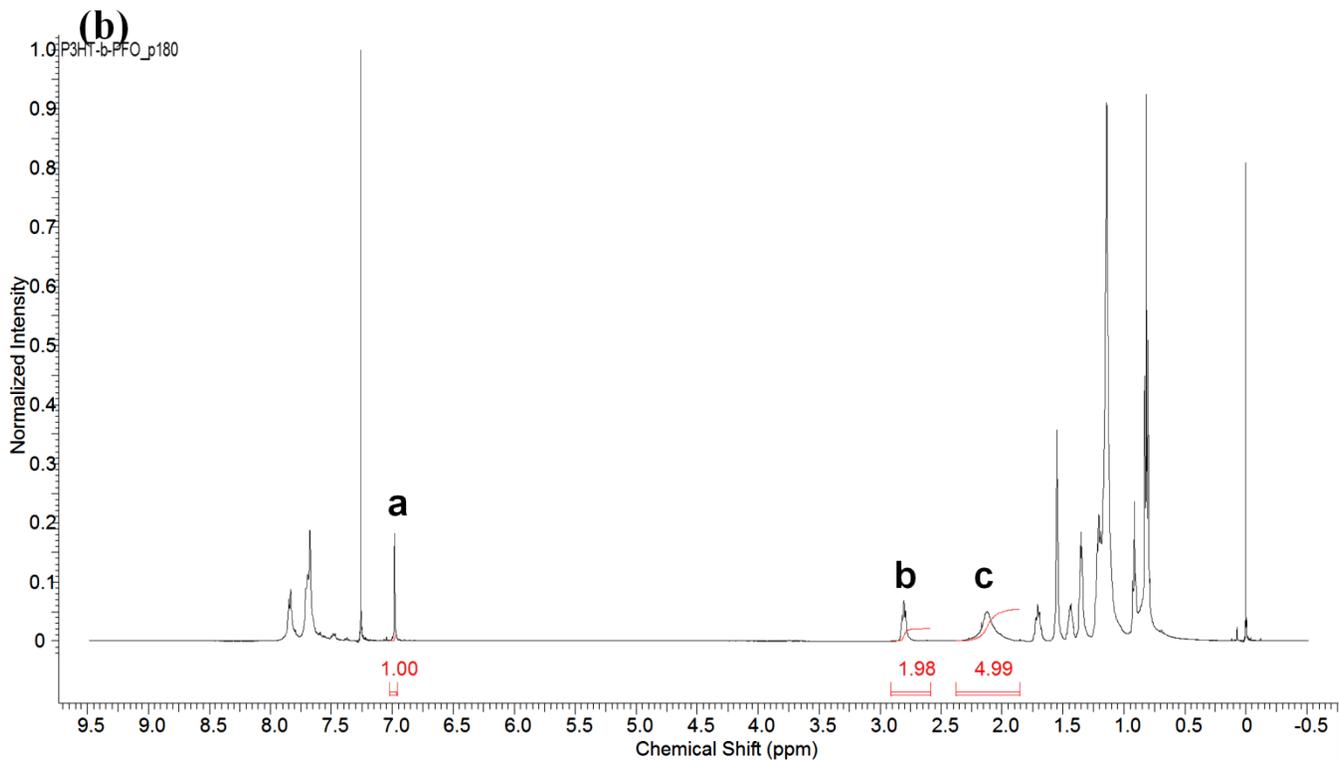
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Nuclear Magnetic Resonance Spectroscopy (NMR). ¹H NMR spectroscopy was performed on Varian 500 MHz. Samples were placed in 5 mm o.d. tubes with sample concentrations of about 5 mg/mL in d-chloroform (7.27 ppm) with 0.05% TMS as an internal standard. Spectra were processed using 1D NMR Processor in ACDLABS 12.0.





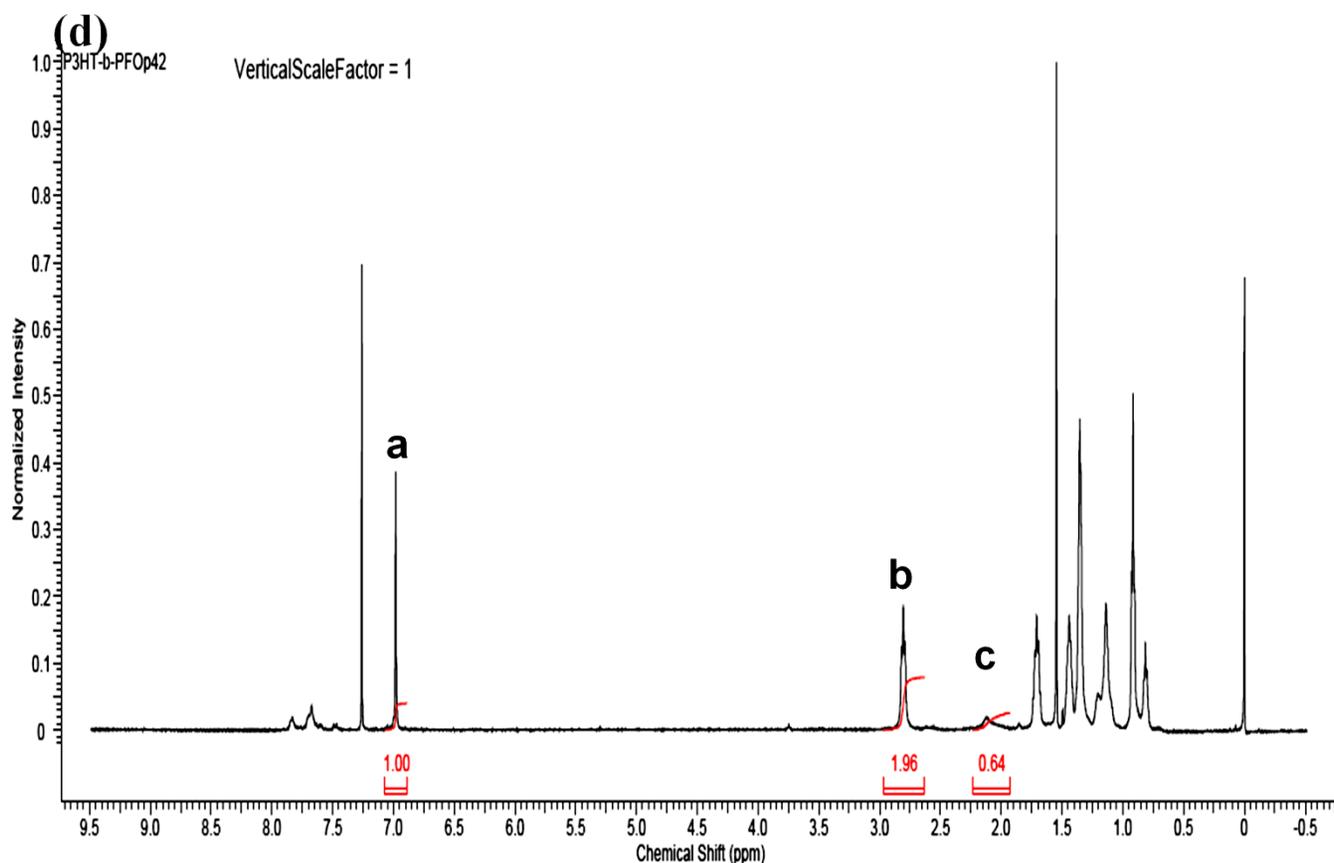


Fig. S1. ^1H NMR spectrum of (a) P3HT36-*b*-PF100, (b) P3HT81-*b*-PF105 (c) P3HT84-*b*-PF80 and (d) P3HT84-*b*-PF13.

GIXS measurement at Argonne National Laboratory. The measurements were carried out on Sector 8-ID-E at the Advanced Photon Source, Argonne National Laboratory.¹ Beamline 8-ID-E operates at an energy of 7.35 keV and images were collected from a Pilatus 1MF camera (Dectris), with two exposures for different vertical position of the detector. After flatfield correction for detector nonuniformity, the images are combined to fill in the gaps for rows at the borders between modules, leaving dark only the columns of inactive pixels at the center. Using the GIXSGUI package² for Matlab (Mathworks), data are corrected for X-ray polarization, detector sensitivity and geometrical solid-angle. The beam size is 200 μm (h) x 20 μm (v). Sample detector distance is 204 mm. Sample measurement and thermal annealing were carried out under vacuum which is in the range of $2\sim 3 \times 10^{-6}$ bar, with the sample stage interfaced with a Lakeshore 340 unit.

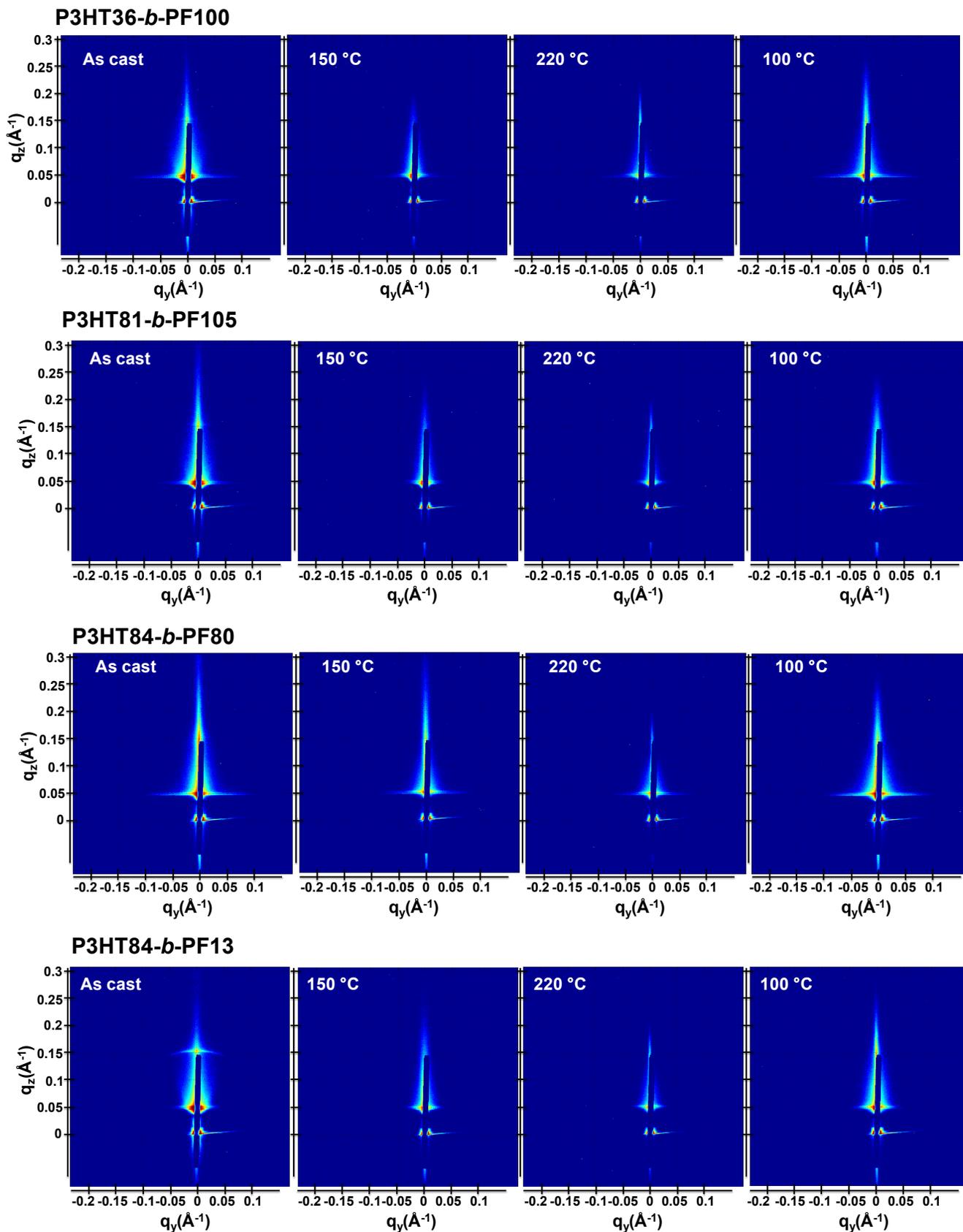


Fig. S2. GISAXS measurement for P3HT36-*b*-PF100, P3HT81-*b*-PF105, P3HT84-*b*-PF80, P3HT84-*b*-PF13. All samples were in-situ thermally annealed and measured at various temperatures. Samples were

measured at an incident angle of 0.25° and 5 seconds exposure time. All images plotted using the same color scale for the scattered intensity.

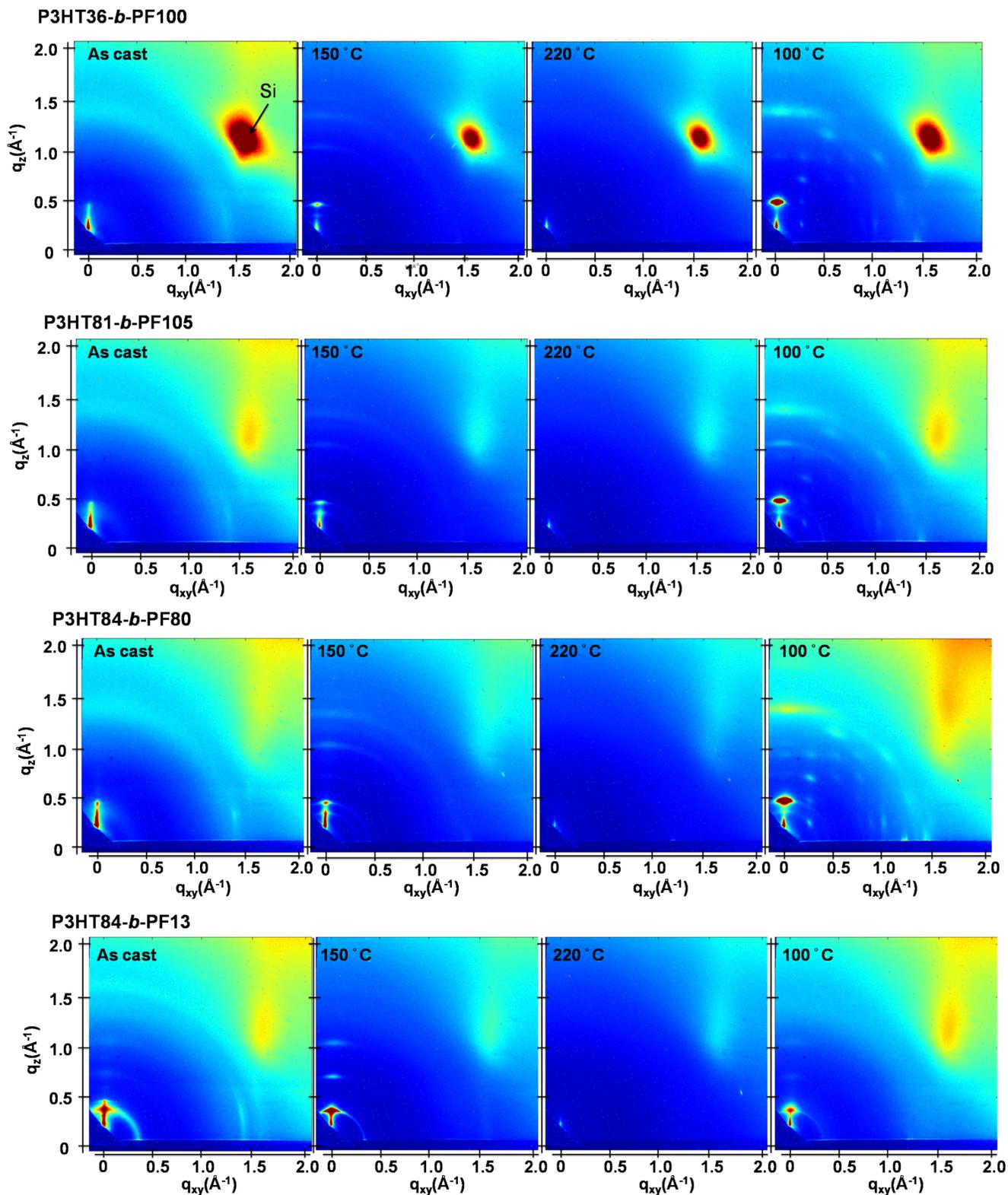


Fig. S3. GIWAXS measurement for P3HT36-*b*-PF100, P3HT81-*b*-PF105, P3HT84-*b*-PF80, P3HT84-*b*-PF13. All samples were in-situ thermally annealed and measured at various temperatures. Samples were

measured at an incident angle of 0.25° and 30 seconds exposure time. All images plotted using the same color scale for the scattered intensity.

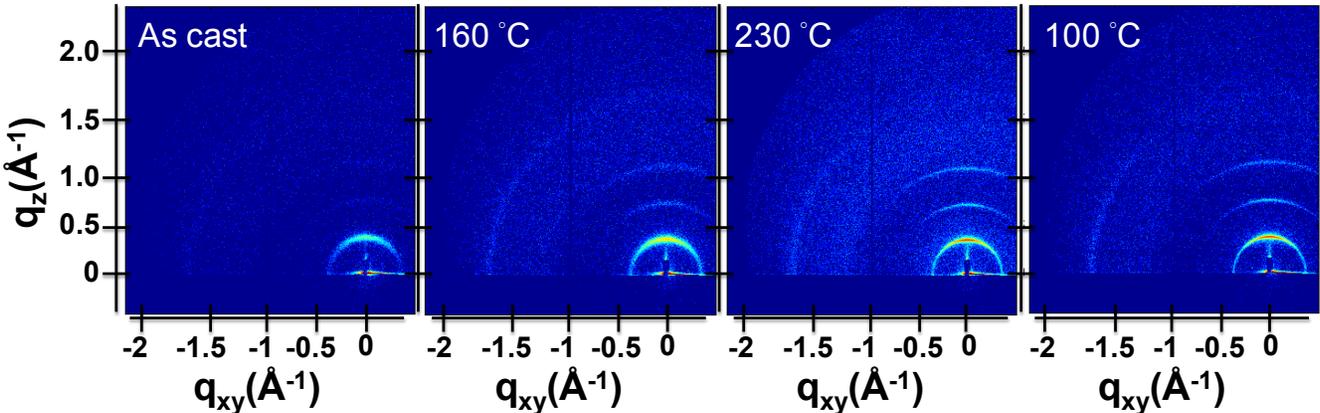


Fig. S4. GIWAXS patterns of a P3HT-Br thin films cast at room temperature and thermally annealed in-situ. All samples were measured at an incident angle of 0.25° and 20 seconds exposure time, and all images have the same color scale. The measurements were carried out at Argonne National Laboratory.

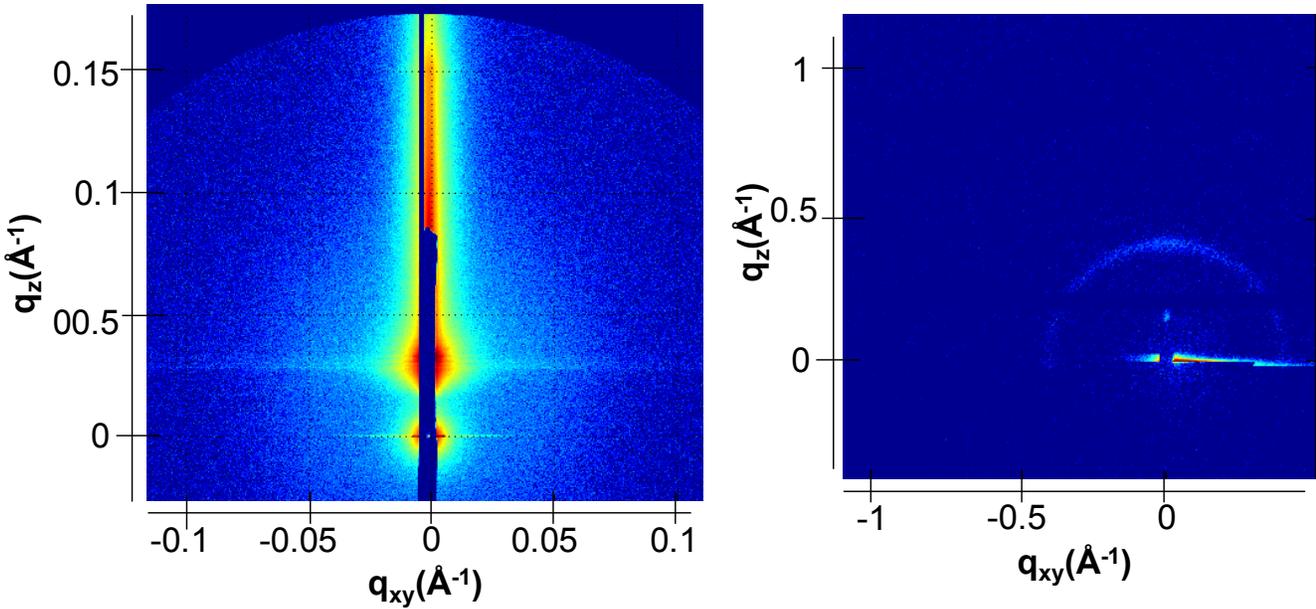


Fig. S5. GISAXS and GIWAXS measurement for P3HT homopolymer. Samples were annealed at room temperature with CHCl_3 vapors for 5 days. The measurements were carried out at Argonne National Laboratory.

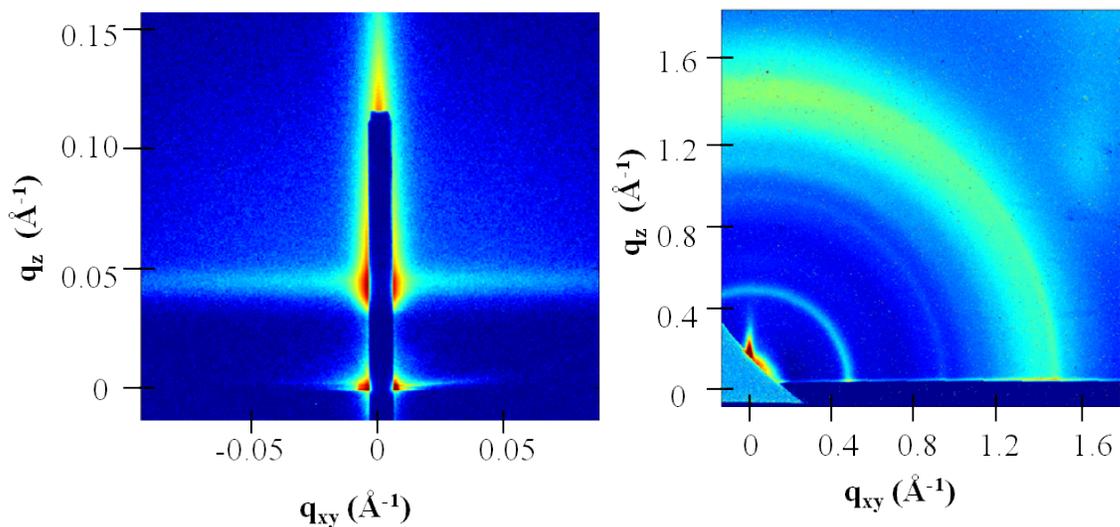


Fig. S6. GISAXS and GIWAXS measurement for β mesophase PF homopolymer. Samples were annealed at room temperature with CHCl_3 vapors for 5 days.

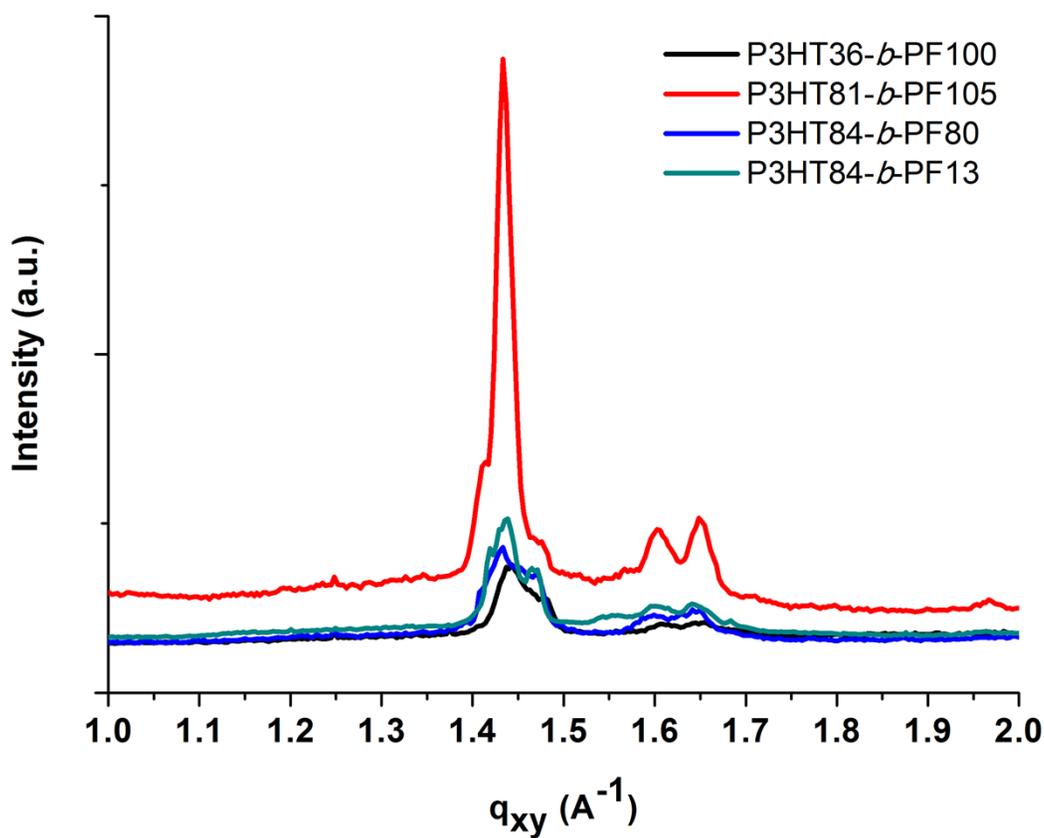


Fig. S7 Linecuts of GIWAXS measurements along $q_z \sim 0 \text{ \AA}^{-1}$ for solvent annealed samples.

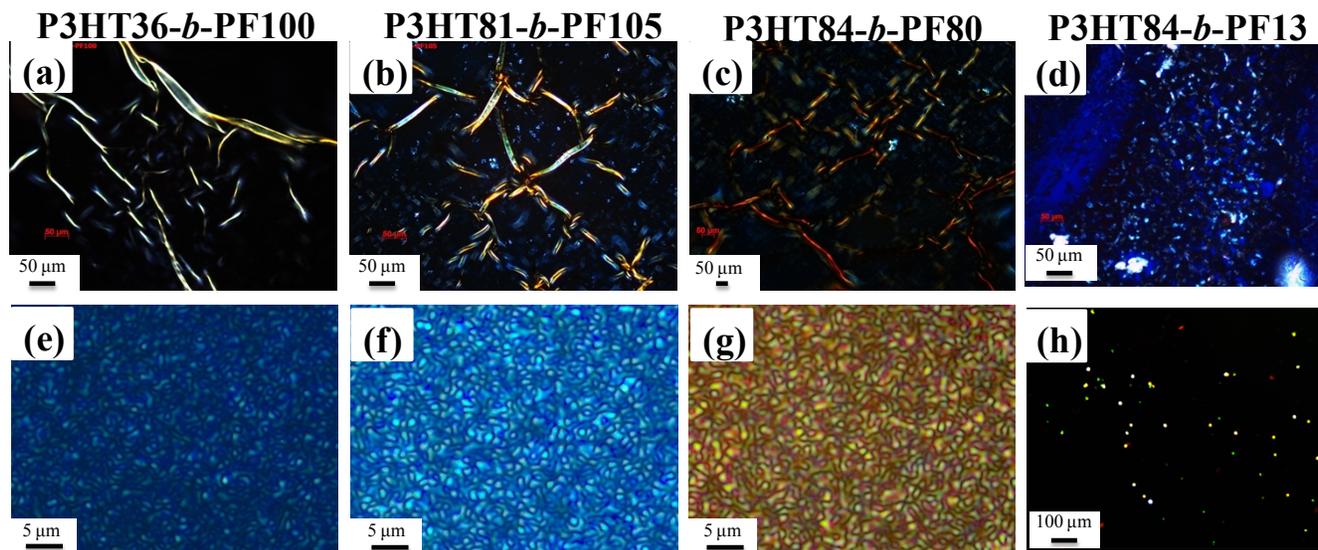


Fig. S8. Polarized optical microscopy images: (a)-(d) chloroform vapor induced smectic phases. (e)-(g) Additional thermal induced nematic phases. All measurements were carried out at room temperature.

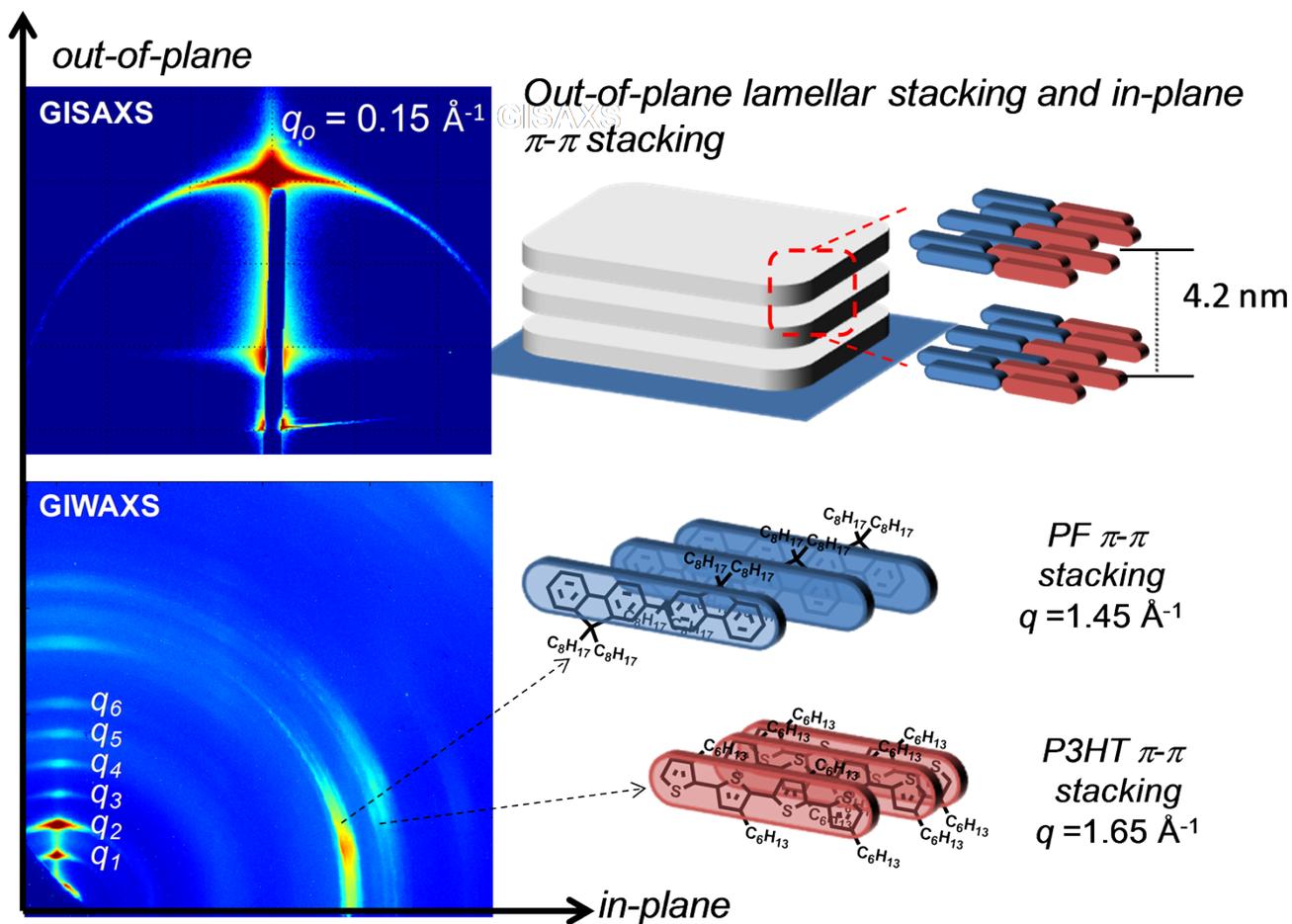


Fig. S9. Alternative schematic for lamellar ordering in solvent-annealed all-conjugated block copolymer films. The lamellar domain size in this schematic is determined by stacking through the alkyl side-chains of P3HT and PF polymers.

References

(1) Jiang, Z.; Li, X. F.; Strzalka, J.; Sprung, M.; Sun, T.; Sandy, A. R.; Narayanan, S.; Lee, D. R.; Wang, J., *J. Synchrot. Radiat.* **2012**, *19*, 627-636.

(2) Jiang, Z., *GIXSGUI is available for download:*

<http://www.aps.anl.gov/Sectors/Sector8/Operations/GIXSGUI.html>.