Supporting Information for:

Surface Induced Orientation and Vertically Layered Morphology in Thin Films of Poly(3-hexyl thiophene) Crystallized From the Melt

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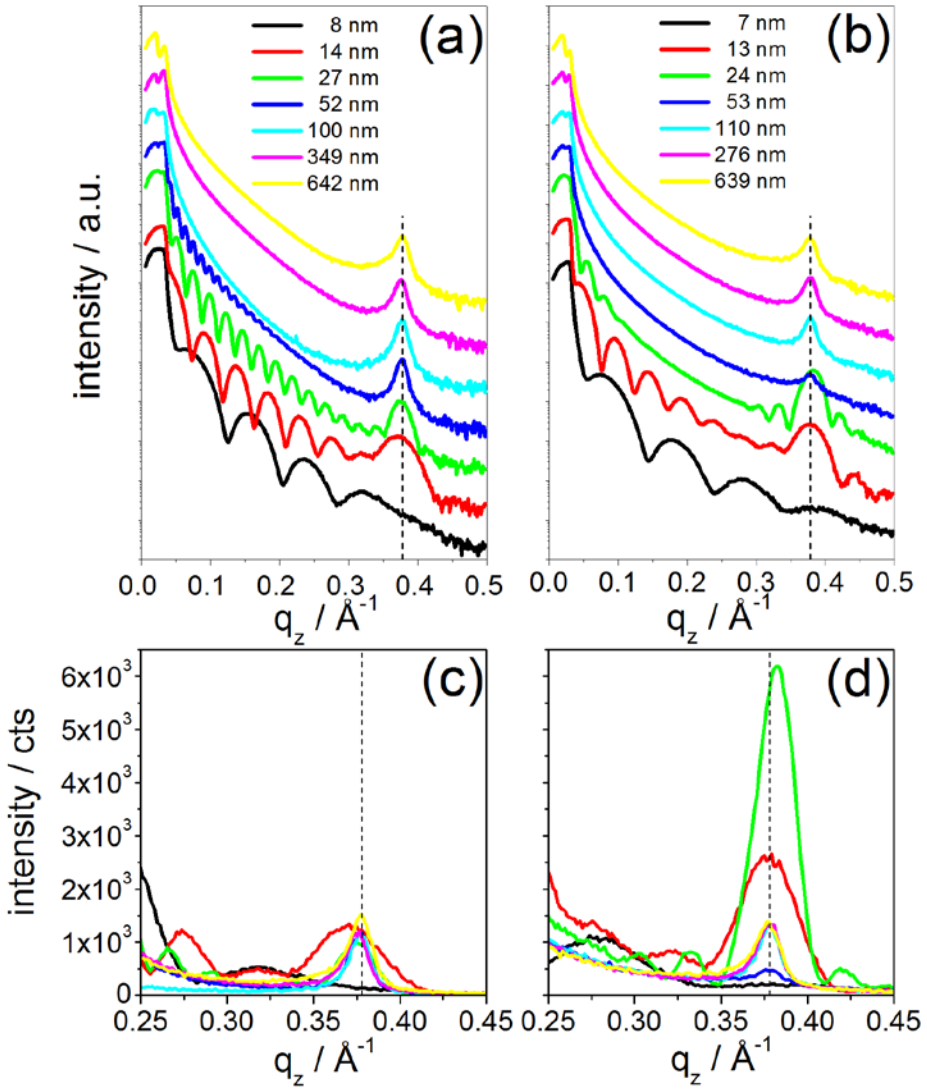

Figure S1: X-ray reflectivity curves of melt-crystallized SEP200 films on (a)/(c) silicon nitride (SiN) and (b)/(d) silicon (SiO_2/Si). For clarity the curves are vertically shifted in (a) and (b). In (c) and (d) the curves are shown on a linear scale (not shifted) in the range around the P3HT (100) Bragg reflection at $q_{100} \approx 0.38$ $Å^{-1}$(dashed vertical line).

AFM of SEP200 Films on Silicon

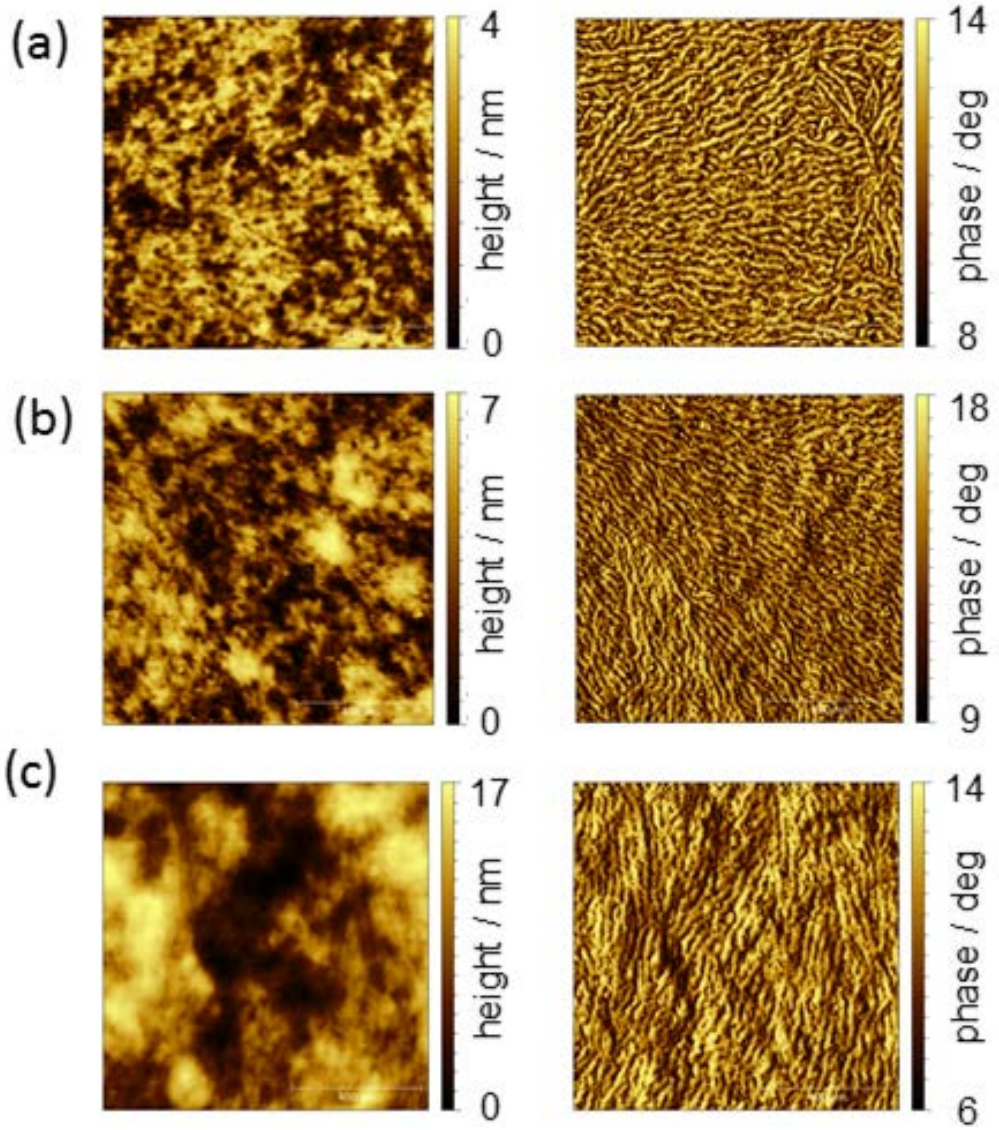

Figure S2: AFM height (left) and phase (right) images of melt-crystallized SEP200 films on SiO_2/Si with a film thickness of (a) 13 nm, (b) 53 nm and (c) 639 nm (image size: 1 µm x 1 µm).

Crystal Structure of P3HT-3

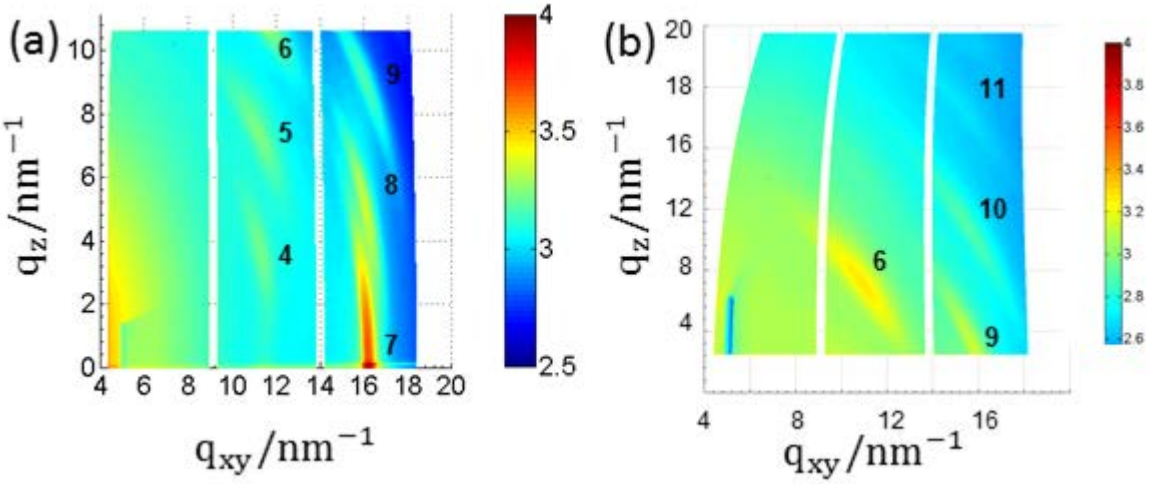

Figure S3: High resolution GID patterns of a melt-crystallized P3HT-3 film on SiO_2/Si with $D \approx 250$ nm ($\alpha_i = 0.17°$, $\lambda = 1.55$ Å^{-1}). The intensities are on a logarithmic scale. Measurements were done at beamline ID10B at the ESRF using an area detector PILATUS 300k (Dectris).

Table S1: Bragg reflections q_{obs} for P3HT-3 from the GIWAXS measurements ('film' geometry, Fig. 3b in the manuscript and Fig. S3) in comparison to a bulk sample ('bulk' transmission geometry, Fig. S4). Assuming a monoclinic unit cell with the lattice parameters a = 1.582 nm, , $b = c$ = 0.77 nm and γ = 95.5° the Miller indices (hkl) yield the positions q_{calc}.

Peak	(hkl)	film q_{obs}/nm^{-1}	bulk q_{obs}/nm^{-1}	q_{calc}/nm^{-1}
1	1 0 0	3.9	3.97	3.99
2	2 0 0	7.9	7.93	7.98
3	3 0 0	11.9	11.93	11.97
4	1 $\bar{1}$ 1	11.9	11.93	11.97
	1 $\bar{1}$ $\bar{1}$			11.97
5	2 $\bar{1}$ 1	13.5	13.59	13.60
	2 $\bar{1}$ $\bar{1}$			13.60
6	3 $\bar{1}$ 1	16.1		16.07
	3 $\bar{1}$ $\bar{1}$			16.07
7	0 2 0	16.2	16.42	16.38
	0 0 2			16.38
8	1 2 0	16.9	17.20	17.24
9	2 2 0	18.4	18.89	18.91
10	3 2 0	20.6	21.25	21.20
11	4 2 0		24.07	23.95

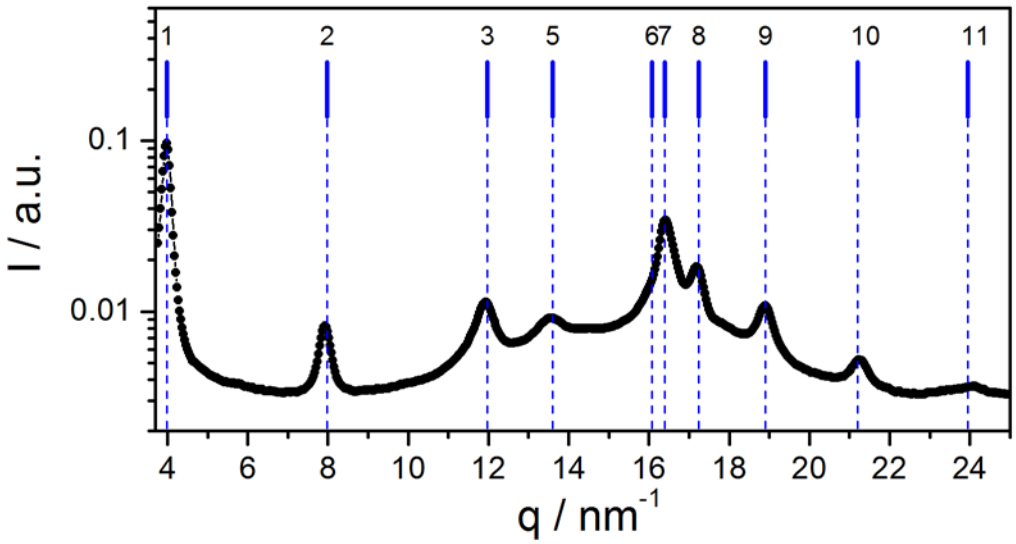

Figure S4: Diffractogram of a P3HT-3 bulk sample measured in transmission geometry after slowly cooling from the molten state (data from Ref. 1). The Bragg reflections were indexed according to a monoclinic unit cell with the parameters a = 1.582 nm, $b = c$ = 0.77 nm and γ = 95.5°.

Pole Figures Under Specular Condition

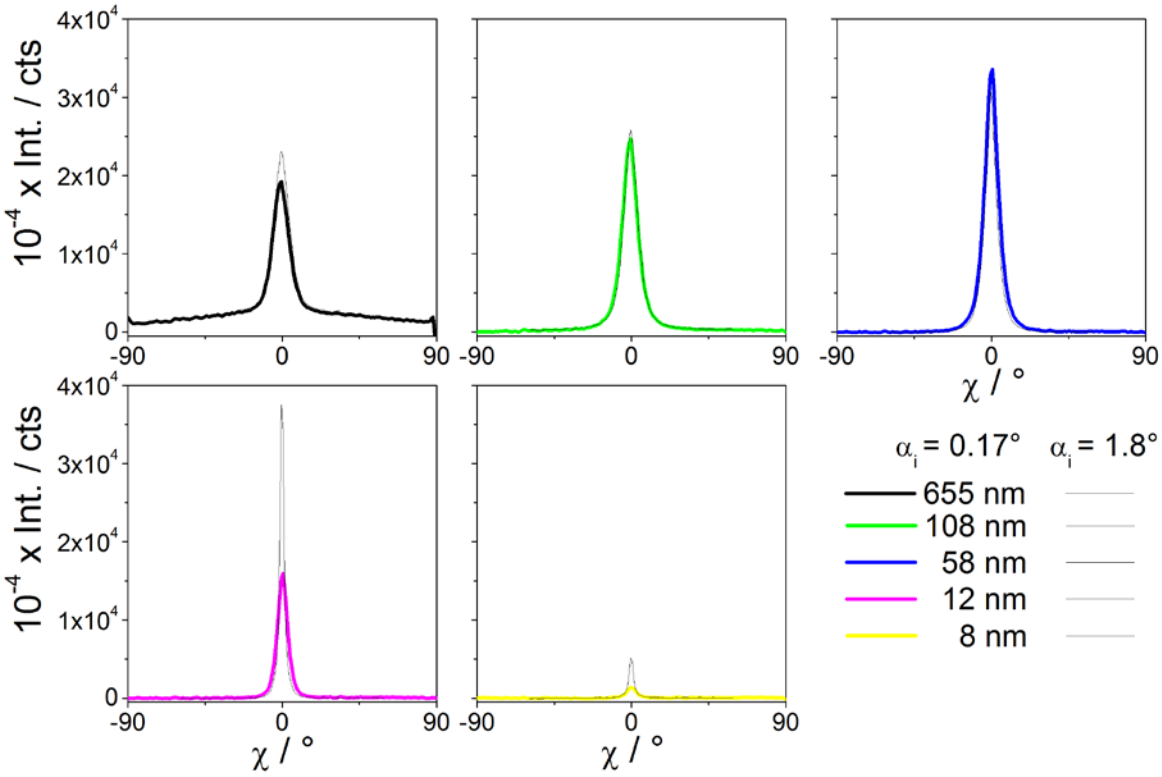

Figure S5: (100) pole figures of melt crystallized SEP200 films on SiN for film thicknesses ranging from 8 $\leq D \leq$ 655 nm for grazing indcidence conditions (α_i = 0.17° thick lines) and under the specular condition ($\alpha_i = \alpha_{100}$ = 1.8°, thin lines).

Analysis of the Incident Angle Dependent GID Measurements

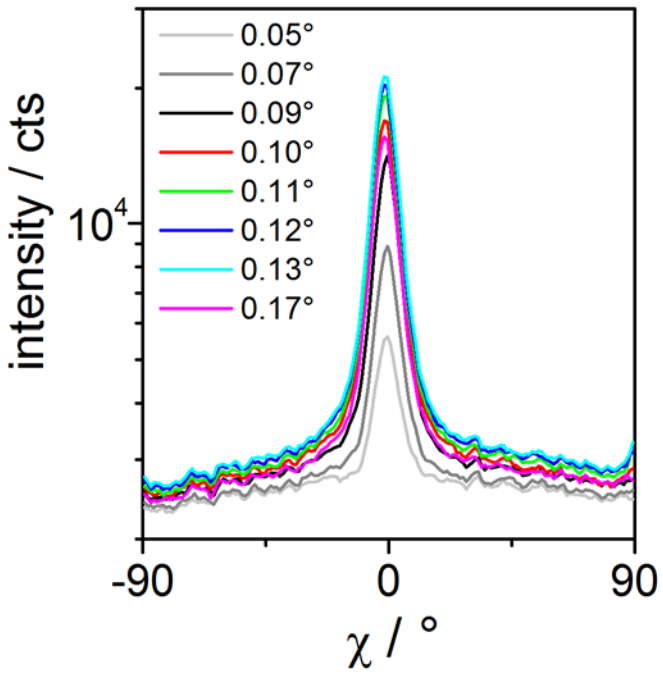

Figure S6: (100) pole figures of a melt crystallized SEP200 film on SiO_2/Si with D = 125 nm for different incidence angles α_i.

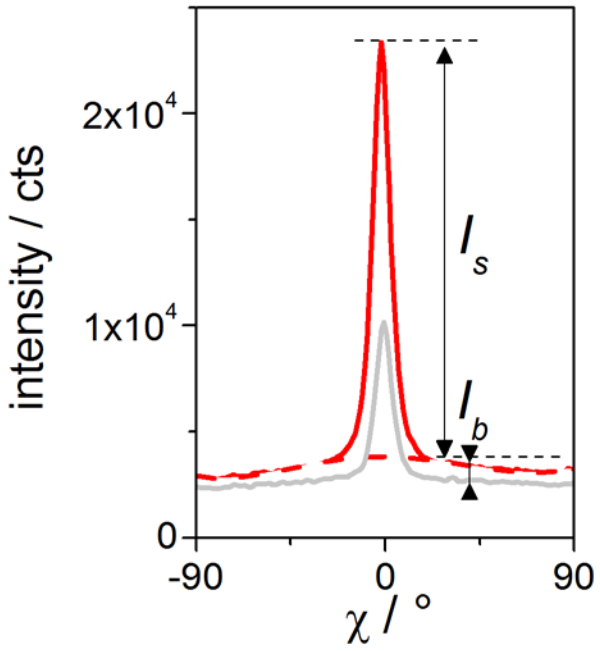

Figure S7: (100) pole figures of the 108 nm thick SEP200 film on SiN for α_i = 0.17° (red) and α_i = 0.10° (grey). The intensity $I_s(\chi)$ scattered from the highly oriented crystalline layer at the film surface can be represented by the indicated value I_s at the maximum of the pole figure at χ = 0°. The intensity $I_b(\chi)$ scattered from nearly isotropically oriented crystals in the bulk of the film was represented by its amplitude in the indicated angular range. For α_i = 0.10° the intensity in the range $|\chi|$ > 15° is solely due to scattering from air and substrate.

Morphology of P3HT-3 Films

The (100) pole figures for melt-crystallized P3HT-3 films on SiN are shown in Fig. S8. They are dominated by $I_s(\chi)$ up to much larger thicknesses, only the thickest film with D = 487 nm might show a certain contribution I_b from isotropically oriented crystals. This result

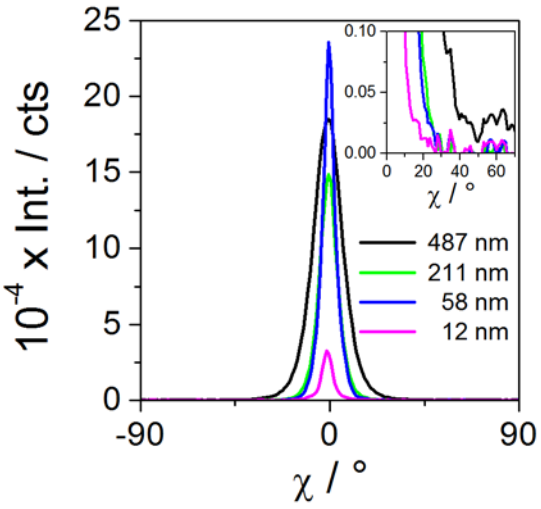

Figure S8: (100) pole figures of melt-crystallized P3HT-3 films on SiN for film thicknesses ranging from 12 $\leq D \leq$ 487 nm (α_i = 0.17°). The intensity background due to scattering from the air and the substrate was subtracted beforehand.

is consistent with the Scherrer analysis summarized in Tab. S2. For the thick films the width of the (100) Bragg reflection is more narrow than for SEP200 and already in the range of the instrumental resolution (cf. Fig. S9). The values for the thickest film are therefore to be taken with caution.

Table S2: Scherrer analysis of the (100) Bragg reflection for the P3HT-3 films on SiN using Eqn. 7. Assuming that $L_{100} \approx d_s$ the thickness of the layer with unoriented crystals, d_b, was estimated with Eqn. 8.

Sample	D/nm	θ_{100}/°	β^{100}/mrad	β_S^{100}/mrad	L_{100}/nm	d_b/nm
P3HT-3	12	2.81	9.01	8.20	18	-
	73	2.81	1.92	1.12	130	-
	211	2.80	1.46	0.66	220	-
	487	2.80	1.76	0.96	(152)	(27)

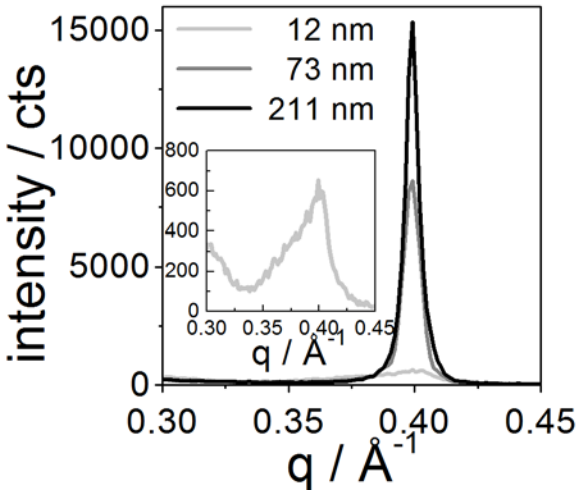

Figure S9: Selected θ-2θ scans in the range of the (100) Bragg reflection of melt-crystallized P3HT-3 films on SiN.

Reference

1. Balko, J.; Lohwasser, R. H.; Sommer, M.; Thelakkat, M.; Thurn-Albrecht, T., Determination of the Crystallinity of Semicrystalline Poly(3-hexylthiophene) by Means of Wide-Angle X-ray Scattering. *Macromolecules* **2013,** *46* (24), 9642-9651.