Supplementary Materials for:

Connecting soft X-ray anisotropy with local order in conjugated polymers

*Joshua H. Litofsky[1], Enrique D. Gomez[1,2,3]**

[1]Department of Chemical Engineering, The Pennsylvania State University, University Park, 16802, USA

[2]Department of Materials Science and Engineering, The Pennsylvania State University, University Park, 16802, USA

[3]Materials Research Institute, The Pennsylvania State University, University Park, PA 16802

1. Polymer characterization

Molecular weights and dispersities were calculated through gel phase chromatography (GPC) using a standard polystyrene calibration. The percent regioregularity was calculated using ^{1}H NMR by comparing the RR and RRa peaks. Results are tabulated in **Table S1**.

Table S1. Molecular weight, dispersity, and regioregularity of polymers used in this study

Polymer	M_n (kg/mol)	*Đ*	Percent regioregularity
RR P3HT	19.5	1.8	95
RRa P3HT	37.1	2.2	58

2. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to determine the percent crystallinity of the RR/RRa P3HT blends using the previously described Snyder method (**Table S2**).[1] DSC traces are shown in **Figure S1** with the percent crystallinity plotted against percent RR P3HT shown in **Figure S2**.

Table S2. Melting temperature and melting enthalpy of P3HT blends used in this study

Percent RR (%)	T_m (°C)	Melting Enthalpy (J/g)	Crystallinity
100	238	22.6	58.0
95	237	21.2	54.2
90	231	19.7	50.5
85	228	17.9	45.9
80	230	16.7	42.7
75	228	15.7	40.3
50	225	7.5	19.3
10	218	1.6	4.2
0	N/A	0.0	0.0

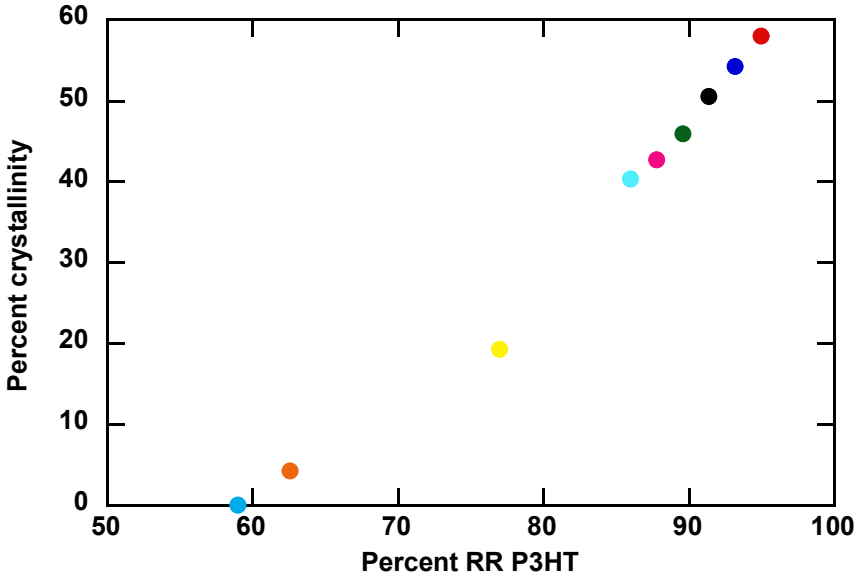

Figure S1. Percent crystallinity plotted against percent regioregular loading in RR/RRa P3HT blends.

2. Resonant soft X-ray scattering

RSoXS experiments were carried out at beamline 11.0.1.2 at the ALS in transmission geometry as previously described.[2] A q range of .002 $Å^{-1}$ to .07 A^{-1} was obtained by using a 50 mm detector distance. 2D images were corrected for solid angle geometry, dark counts and incident beam flux variation using the Nika software package (**Figure S2**).[3] Scattering profiles were obtained by azimuthally integrating 2D images (**Figure S3**). 2D data was also reduced as a function of polar angle to determine the P3HT chain tilt within domains (**Table S3**).

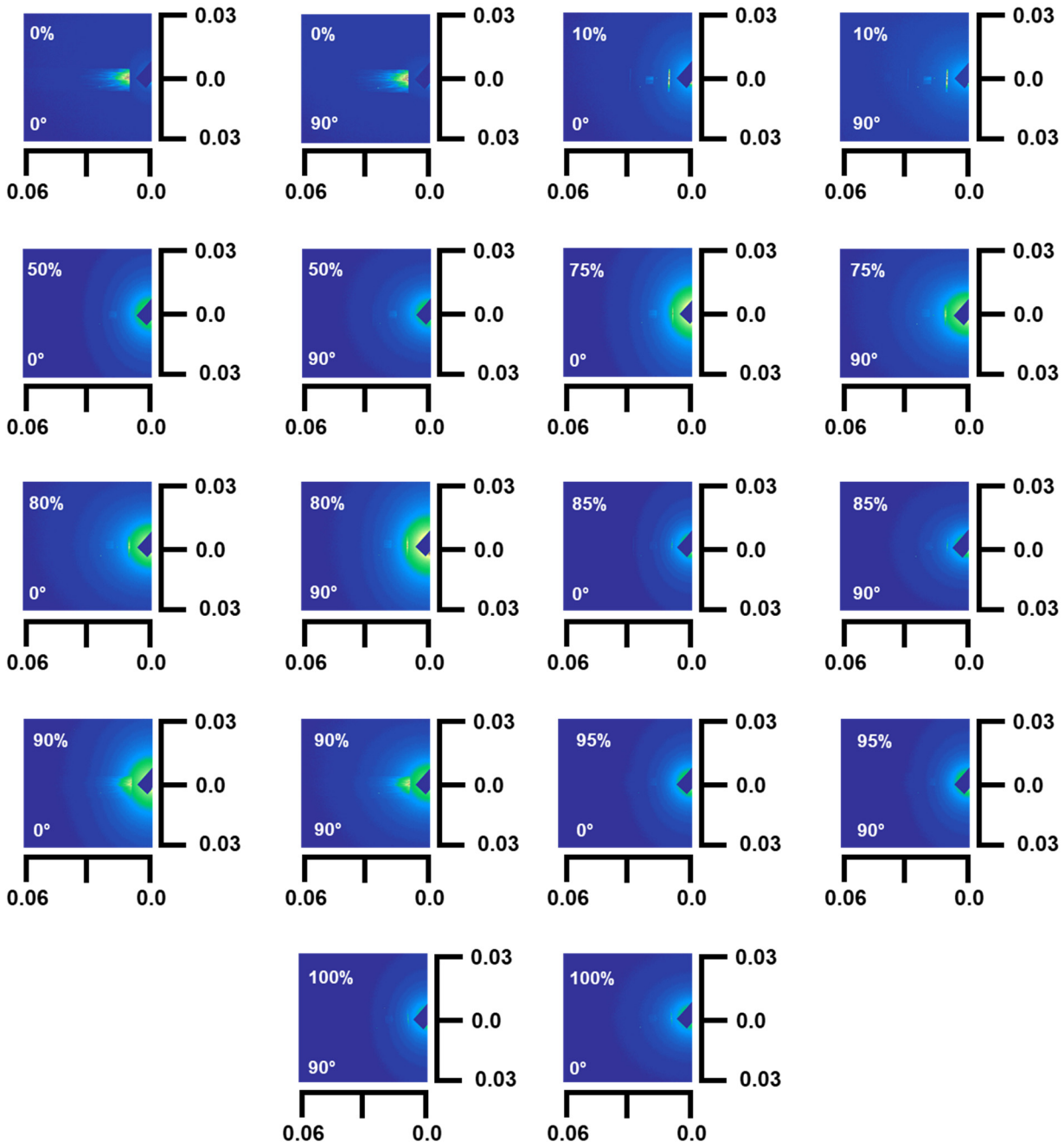

Figure S2. 2D scattering data from all samples at both the 0° and 90° polarizations. Percent RR P3HT is shown on the figures.

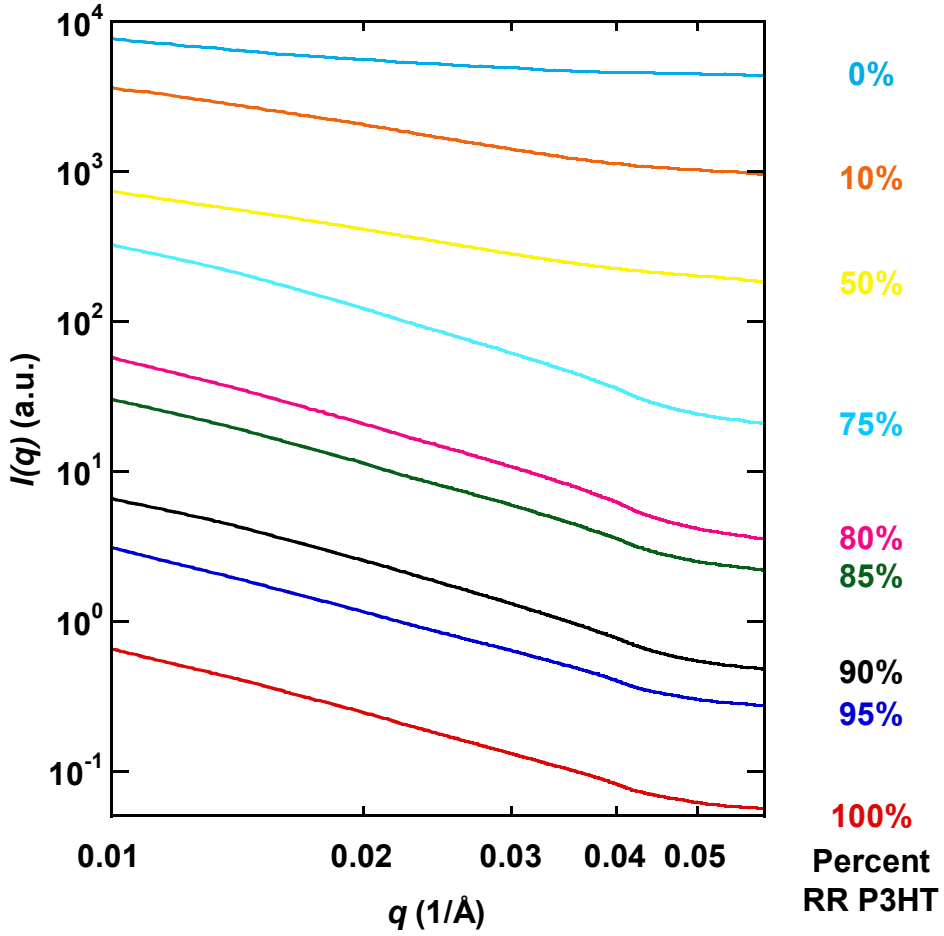

Figure S3. RSoXS scattering intensity as a function of q for RR/RRa P3HT blends. No distinct peaks are seen in any curve.

Table S3. Chain tilt (γ) of P3HT at various RR:RRa compositions

Percent RR P3HT	Chain tilt (γ)
100%	7°
95%	7°
90%	6°
85%	5°
80%	4°
75%	4°
50%	5°
10%	5°
0%	5°

5. RSoXS of P3HT films cast from 1,2,4-trichlorobenzene

For this study, P3HT was dissolved at a concentration of 10 mg/mL in chlorobenzene and stirred at 45° C overnight in a sealed container prior to casting. Stronger scattering anisotropy can be obtained from P3HT by changing the solvent to 1,2,4-trichlorobenzene, as shown in **Figure S4**.

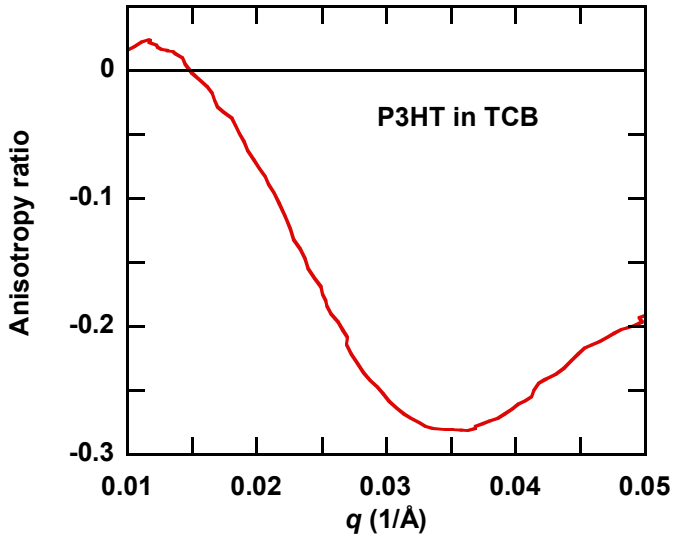

Figure S4. Anisotropy ratio as a function of q for RR P3HT in trichlorobenzene.

5. References

1. C.R. Snyder, R.C. Nieuwendaal, D.M. DeLongchamp, C.K. Luscombe, P. Sista and S.D. Boyd: Quantifying crystallinity in high molar mass poly (3-hexylthiophene). *Macromolecules* **47**, 3942 (2014).
2. E. Gann, A. Young, B. Collins, H. Yan, J. Nasiatka, H. Padmore, H. Ade, A. Hexemer and C. Wang: Soft x-ray scattering facility at the Advanced Light Source with real-time data processing and analysis. *Review of Scientific Instruments* **83**, 045110 (2012).
3. J. Ilavsky: Nika: software for two-dimensional data reduction. *Journal of Applied Crystallography* **45**, 324 (2012).