Supporting Information

Circular Dichroism Imaging: Mapping the Local Supramolecular Order in Thin Films of Chiral Functional Polymers

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Film preparation

Films A-C were prepared by spin coating a CHCl₃ (100 μ L, 1.5 % w/w) solution of the polymer (30 sec @ 1000 rpm then 10 sec @ 4000 rpm) on a cover slip glass.

Film **D** was prepared by dropping CHCl₃ (60 μ L, 0.18 % w/w) on a cover slip glass and letting the solvent evaporate thoroughly in a chamber saturated with CHCl₃ vapours.

ECD measurements

ECD measurements were carried out with a Jasco-710 spectropolarimeter. For each film, several spectra were acquired after rotating the sample (by 90° and flipping). These spectra did not differ significantly, ensuring that no artifact due to linear dichroism and linear birefringence was present in the film.

Microscopy

Fluorescence microscopy images were acquired using a BX51M imaging binocular microscope equipped with a mercury lamp USH-1030OL and an Olympus XC30 digital color camera. Polarized light microscopy images were acquired using a ZEISS SteREO Discovery V8 microscope, equipped with linear polarizing filters and a Canon Power Shot A640 camera.

CDi Measurement and Processing

CD*i* experiments were performed using a nitrogen-flushed Module A end-station spectrophotometer at B23 Synchotron Radiation CD Beamline at the Diamond Light Source.^[S1] The beam light was positioned in the measurement chambers using the XY stage of B23^[S2]. Results obtained were processed using CDApps.^[S3]

SVD Analysis

Single value decomposition (SVD) was used as factor analysis. SVD were carried out using the Matheson algorithm in Olis Globalworks incorporated in CDApps.^[S4] SVD provides a rigorous, model-free analytical method for the characterization of 3D datasets. The results of an SVD analysis can be fitted to equilibrium models to obtain components, mechanistic and thermodynamic information.

Fluorescence microscopy images

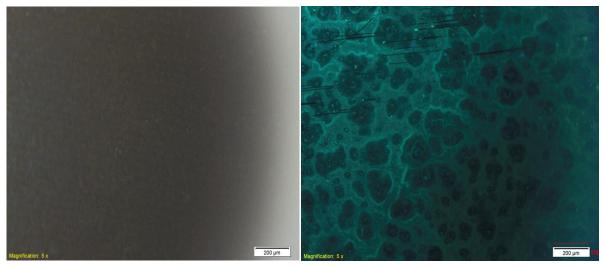


Figure S1. Microscopy image of film A under visible (left) and UV 365 nm light (right).

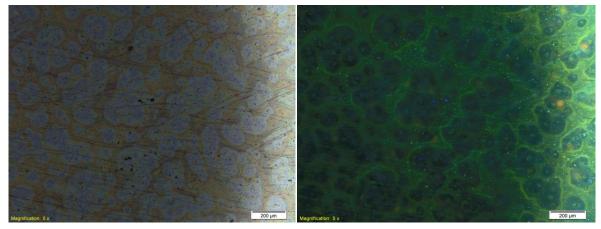


Figure S2. Microscopy image of film C under visible (left) and UV 365 nm light (right).

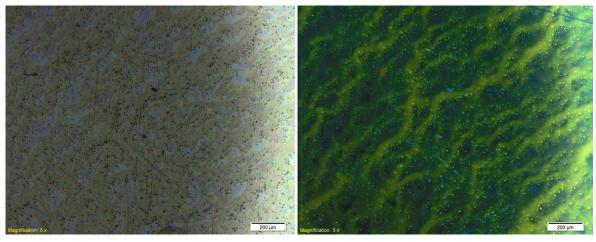


Figure S3. Microscopy image of film **D** under visible (left) and UV 365 nm light (right).

Polarized light microscopy images

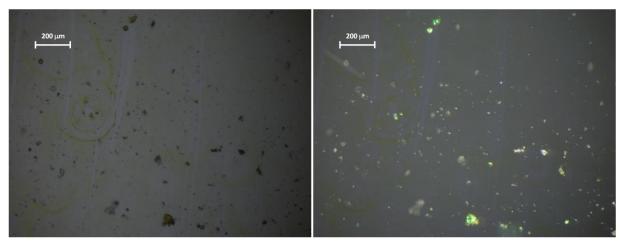


Figure S4. Microscopy image of film A with parallel (left) and crossed polarizing filters (right).

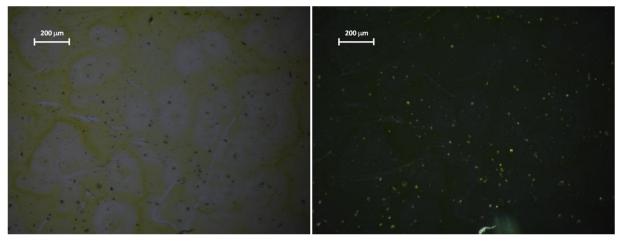


Figure S5. Microscopy image of film C with parallel (left) and crossed polarizing filters (right).

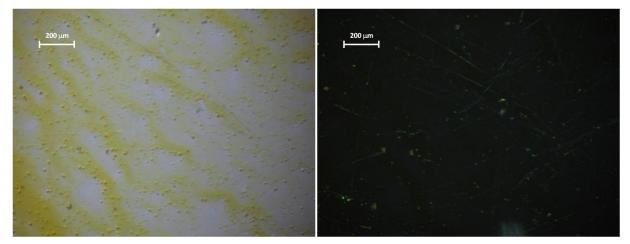


Figure S6. Microscopy image of film **D** with parallel (left) and crossed polarizing filters (right).

Experimental set-up for CDi



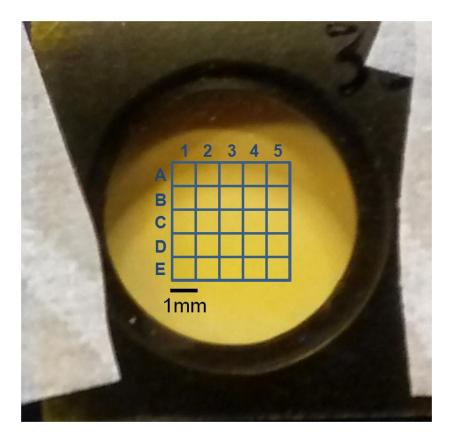


Figure S7. Experimental setup used in CDi measurements. Top: sample holder. The film is deposited on a cover slip glass with dimensions of 1.8x1.8 cm. Bottom: position of the irradiated 5x5 sampling grid with dimensions of 5x5 mm.

Additional maps

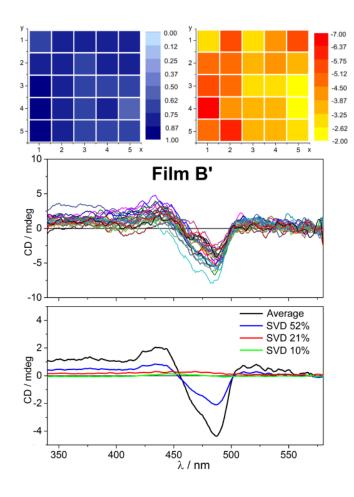


Figure S8. 2D maps: ECD intensity for film **B'** (490 nm) vs x-y (red/yellow); each square represents the spot mapped. Below the map: CDi spectra for the 25 spots mapped and the principal SVD (single value decomposition) spectral component extracted for each film.

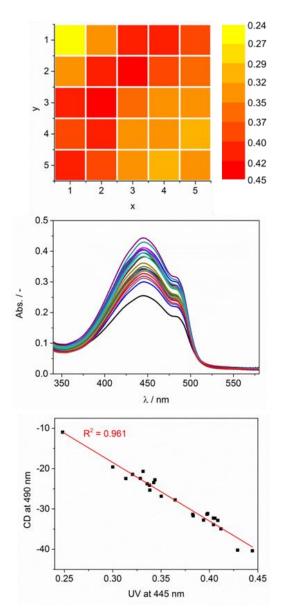


Figure S9. 2D map: space resolved absorbance for film C (445 nm) vs *x-y* (red/yellow); each square represents the spot mapped. Below the maps: space resolved absorption spectra for the 25 spots mapped. Bottom: correlation between CD*i* intensity of each spot at 490 nm and absorbance at 445 nm.

Comment: As discussed in the text, the CD*i* spectra of film C differ only for a scale factor. Taking advance of synchrotron radiation, on the 25 spots of the film of Figure S4, we measured absorption spectra, which are primarily sensitive to film thickness. The good correlation between space resolvedAbsorption and CD*i* intensity reveals that about 96 % of the variation of the ECD intensity can be explained by the variation of the absorption.

References

[S1] R. Hussain, T. Jávorfi, G. Siligardi, J. Synchrotron Radiat. 2012, 19, 132; T. Jávorfi, R. Hussain, D. Myatt, G. Siligardi, Chirality 2010, 22, E149.

[S2] G. Siligardi, R. Hussain, Structural Proteomics: High-Throughput Methods 2015, 255.

[S3] R. Hussain, K. Benning, D. Myatt, T. Javorfi, E. Longo, T. R. Rudd, B. Pulford, G. Siligardi, *J. Synchrotron Radiat*. 2015, 22, 862.

[S4] R. J. DeSa, I. B. C. Matheson. Method. Enzymol. 2004, 384, 1.