

Supporting Information

Aqueous processing of organic semiconductors enabled by stable nanoparticles with built-in surfactants

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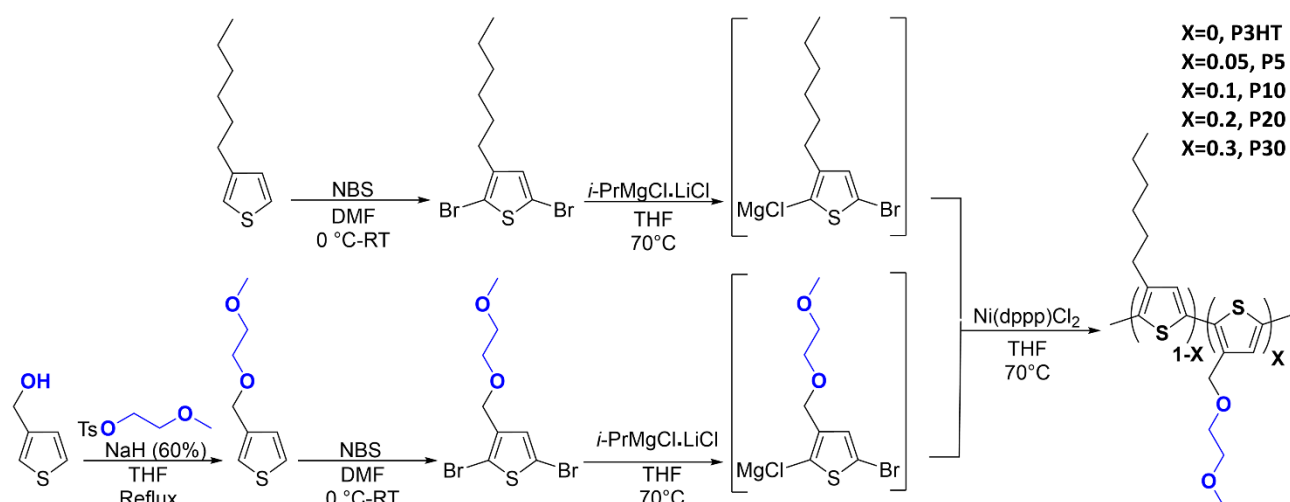
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Materials and Instrumentation

All chemicals and solvents that were used in the present study were purchased from known commercial suppliers like Sigma-Aldrich, Alfa Aesar, Fluorochem and Fisher without further purification. Aqueous dispersions were prepared with deionised (DI) water and “wet solvents” previously degassed by bubbling with nitrogen (N_2). Monomer synthesis and polymerisations were performed according to the literature procedures.

NMR spectra were recorded at 400 MHz on a Bruker Avance III spectrometer. Number-average (M_n) and weight-average (M_w) molecular weights were determined by gel permeation chromatography (GPC) using a Phenogel™ 5 μm 10E4A, LC Column 300 x 7.8 mm running in chlorobenzene (CB) at 80 °C and calibrated against narrow polydispersity polystyrene standards. Column chromatography was carried out using VWR silica gel (40-60 μm). Analytical thin layer chromatography was carried out on Merck Kieselgel 60 aluminium-backed silica plates, with visualization using short-wave ultraviolet light. UV-vis measurements were obtained from a Shimadzu UV-3600 Plus UV-Vis-NIR spectrophotometer. Cyclic voltammetry was carried out using a PalmSens EmStat3 potentiostat. Hydrodynamic diameter measurements were recorded by dynamic light scattering (DLS) at 25 °C using a Zetasizer Nano ZS operated with the software ZS Explorer. AFM images were captured in tapping mode using a Bruker Dimension Icon scanning probe microscope with a Bruker ScanAsyst-Air silicon tip on nitride lever. Thin films deposited via spray-coating utilised an airbrush gun Harder & Steenback (Evolution Silverline) fitted with a 0.15 mm nozzle and a 2 mL mounted cup. Polymer dispersions were prepared by ultrasonication using a Pulse 150 Ultrasonic Homogenizer, Benchmark Scientific fitted with a 6 mm probe. Transmission Electron Microscopy (TEM) samples were adsorbed on a glow discharged continuous carbon copper grid, 300 mesh (Agar Scientific) and analysed with a JEOL JEM1400Flash electron microscope at 120 kV. Images were taken with a Morada CCD camera and processed with iTEM software (EMSIS).

Polymer Synthesis and NMR Characterisation



Scheme S1: Schematic representation of the synthetic route to obtain the copolymers.¹

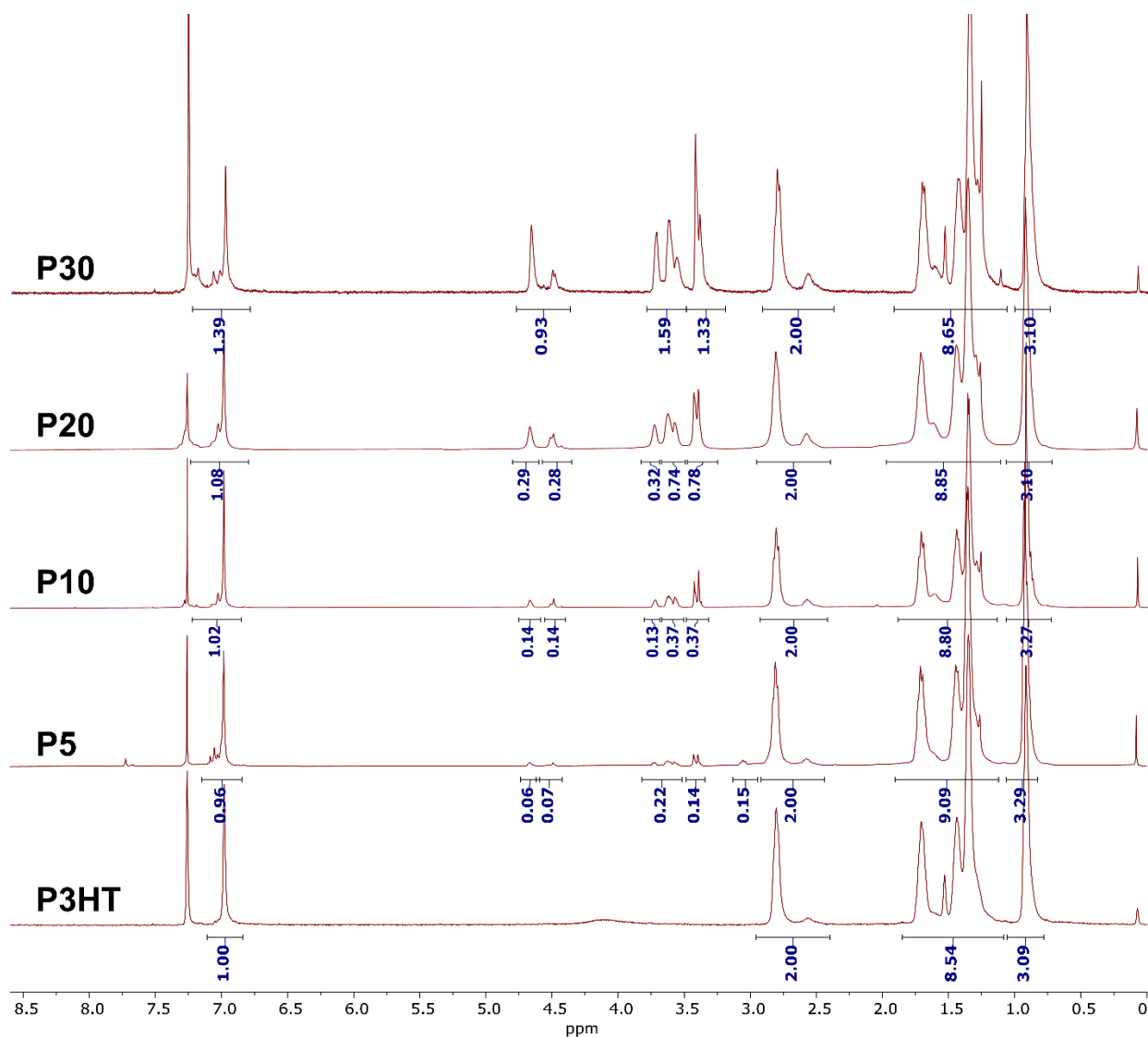


Figure S1: ¹H NMR spectra of the polymers in deuterated chloroform.

Polymer Dispersion Preparation

Polymer dispersions using surfactants

In a sealed vial, 10 mg of the corresponding polymer sample was dissolved in 1 mL of degassed THF. In a second vial, 75 mg of sodium dodecyl sulphate (SDS) were solubilised in 10 mL of DI water. The vial containing the aqueous phase was placed on ice bath, thereafter the organic polymeric solution was injected to the second vial. Once finished the addition of the organic phase the emulsification was performed by ultrasonication using a 6 mm probe at 50 watts of power with a programmed time lapse of 4 minutes with intervals of 4 seconds of sonication and pause (2 minutes of effective sonication). The obtained emulsion was stirred at 50 °C under a constant flux of N₂ to evaporate the organic solvent. The resulting dispersion was then filtered using 1 micron glass filter (or using a funnel fitted with glass wool).

Surfactant free polymer dispersions

The procedure to obtain surfactant free polymer dispersions was like the previously described emulsification. The procedure was reproduced avoiding the use of surfactant (SDS) in the aqueous phase. Ultrasonication parameters remaining the same for these samples.

Dynamic Light Scattering (DLS)

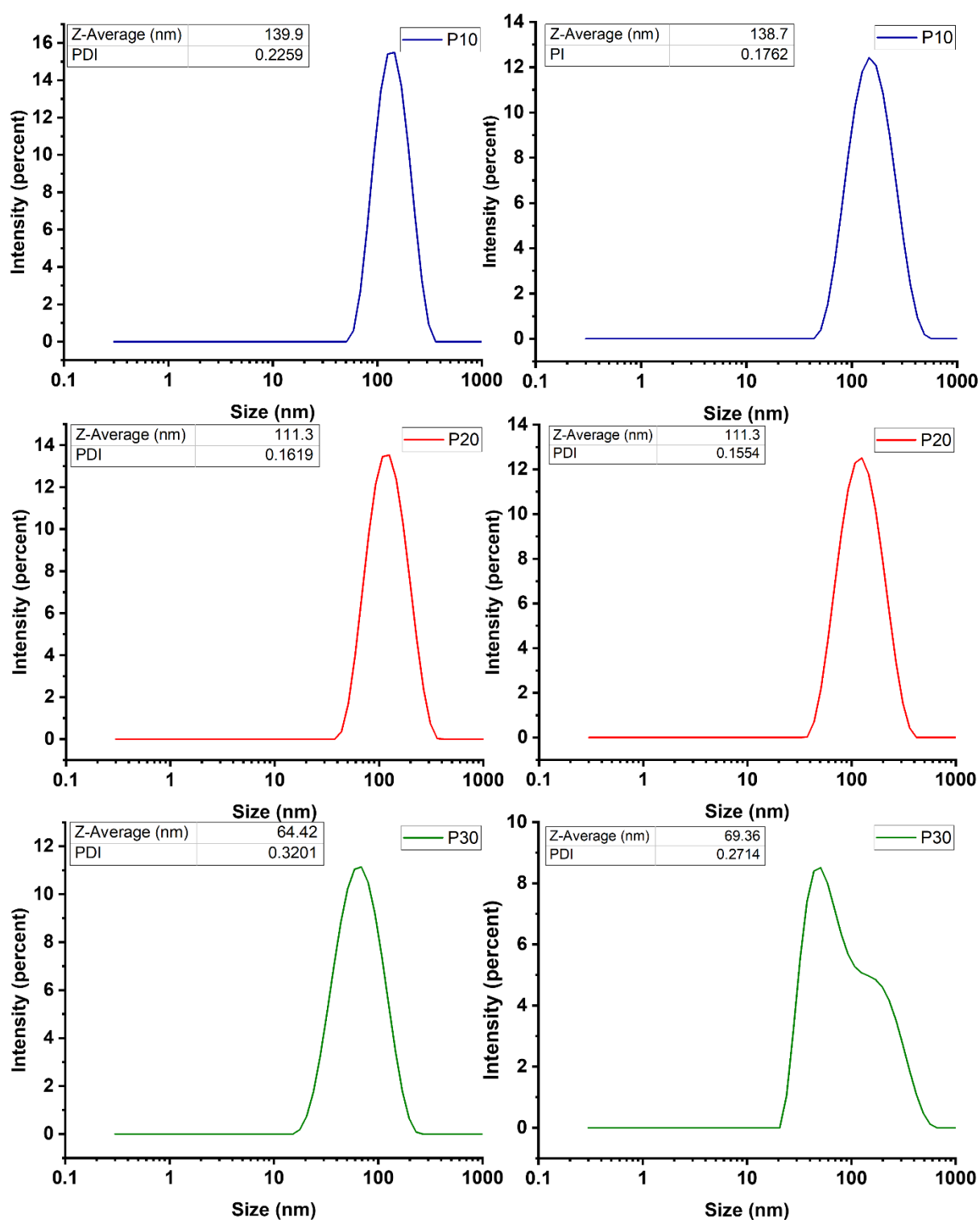


Figure S2: Representative DLS plots of the particle size measurements for the aqueous dispersions of **P10**, **P20** and **P30** on Day 1 (right) and Day 42 (left) of the stability measurements. Plots are the average result from 3 measurements from aliquots of 5 μ L of each dispersion diluted in 1 mL of DI water.

UV-Vis Spectroscopy

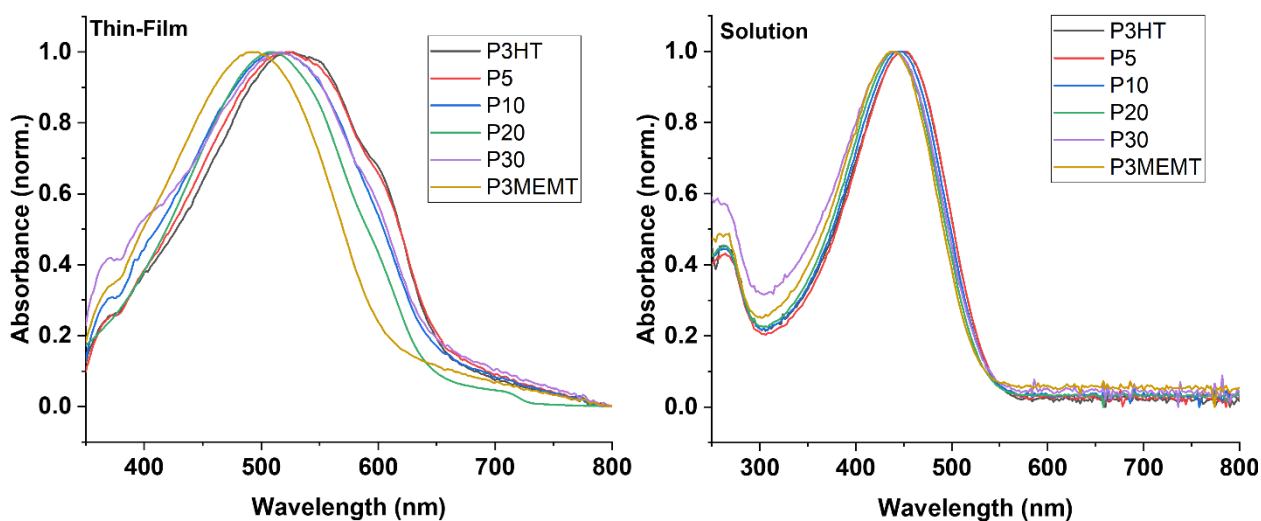


Figure S3: UV-vis spectra of the polymer series in chloroform solution (left) and solid state (right). Aliquots of 10 μL from stock solution of 1 mg/mL of polymer, were diluted in 3 mL of chloroform to run the corresponding UV-vis measurement. Thin films were spin-coated from chloroform solutions (5 mg/mL) of the corresponding polymer over glass substrates.

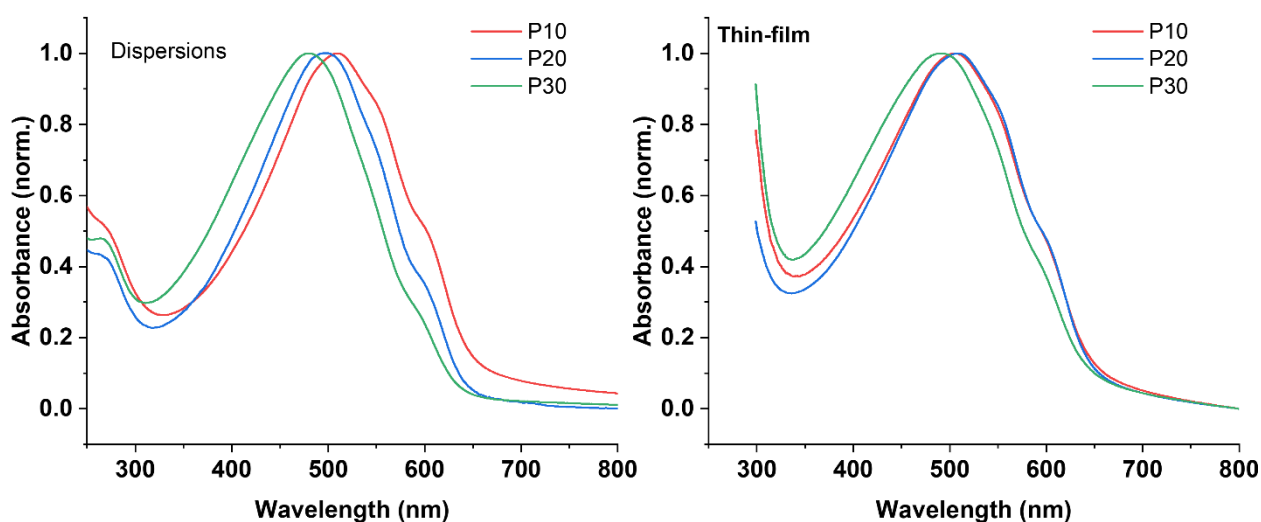


Figure S4: UV-vis spectra of the dispersions generated in water (left) and thin films deposited via spray-coating (right) at 90 $^{\circ}\text{C}$ with a distance of 15 cm from nozzle to substrate using the aqueous dispersions of P10, P20 and P30.

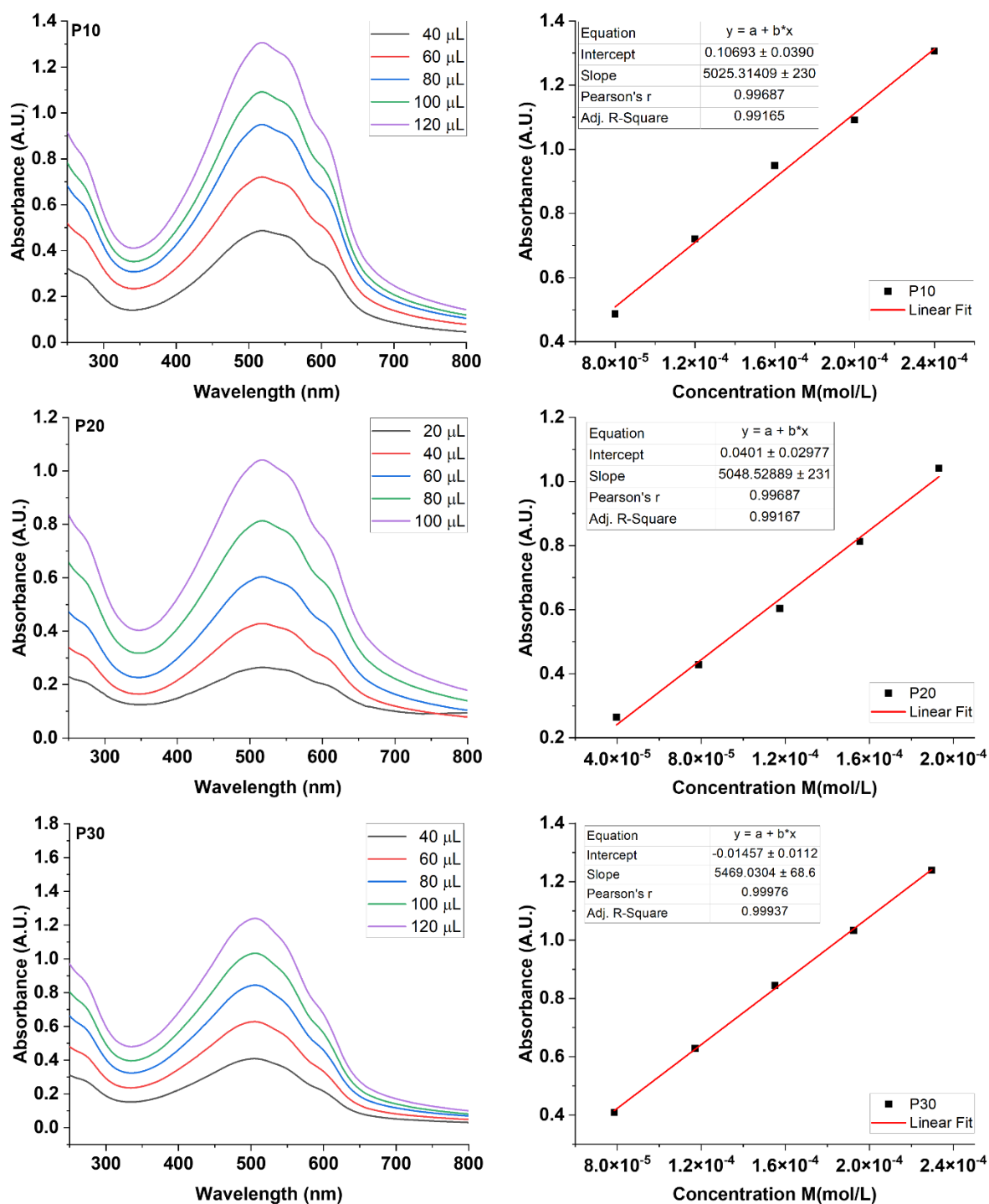


Figure S5: UV-vis calibration curves. Recorded UV-vis spectra (left) and linear fits obtained from the calibration curve of absorbance vs concentration (right) for **P10**, **P20** and **P30** dispersions. Reference dispersions were prepared from the emulsification of 1 mL of each polymer solution (10 mg/mL) in 10 mL of water containing 75 mg of SDS. Subsequently, the organic phase was evaporated under stirring at 40 °C with N₂ flux. Aliquots of 20 μL were added to a UV-vis cuvette with 3 mL of water and UV-vis spectra were recorded to generate the calibration curve.

Cyclic Voltammetry (CV)

CV was performed with a 0.1 M solution of tetrabutylammonium hexafluorophosphate in acetonitrile at a scan rate of 100 mV/s, plots correspond to the second scan of each measurement.

The reference, counter and working electrode were Ag/Ag⁺, platinum and ITO, respectively.

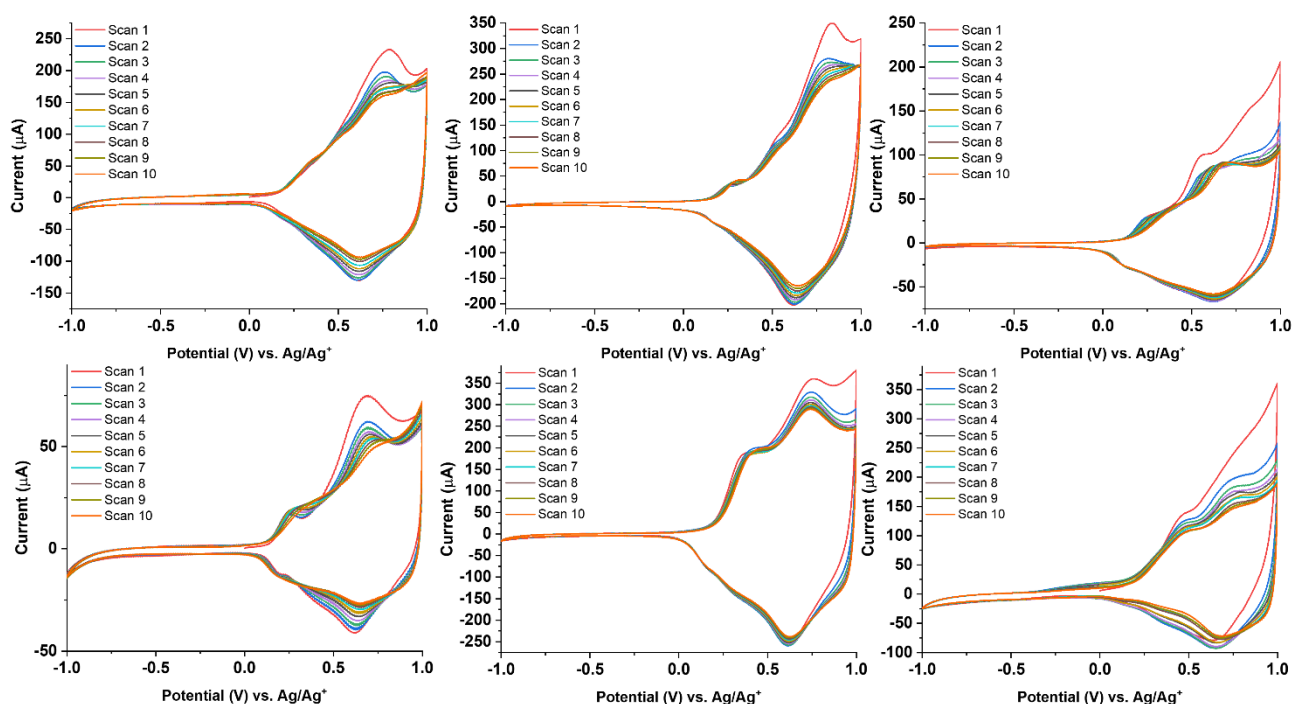


Figure S6: Cyclic voltammograms of (top) organic solution (5 mg/mL in chloroform) processed thin films and (bottom) aqueous dispersion (1 mg/mL) processed thin films of **P10** (left), **P20** (centre), and **P30** (right).

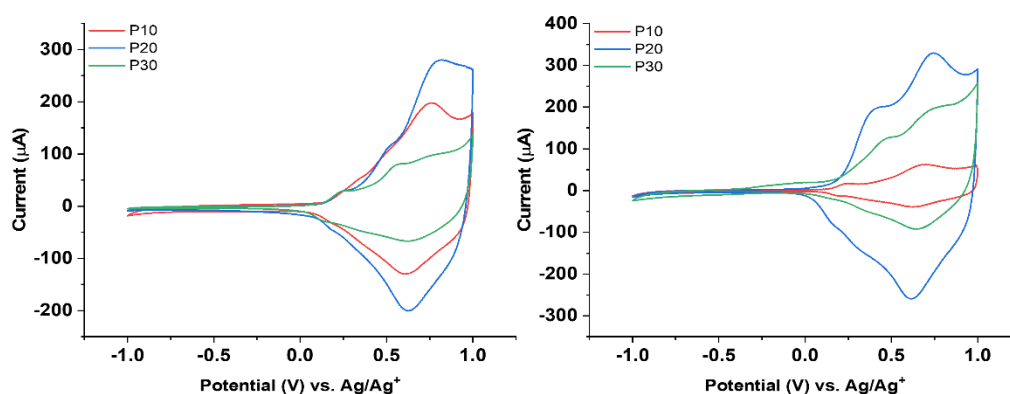


Figure S7: Cyclic voltammograms of the polymer thin films deposited via spin-coating (left) from chloroform solution (5 mg/mL) and spray-coated polymer dispersions (right) in water (1 mg/mL).

Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM)

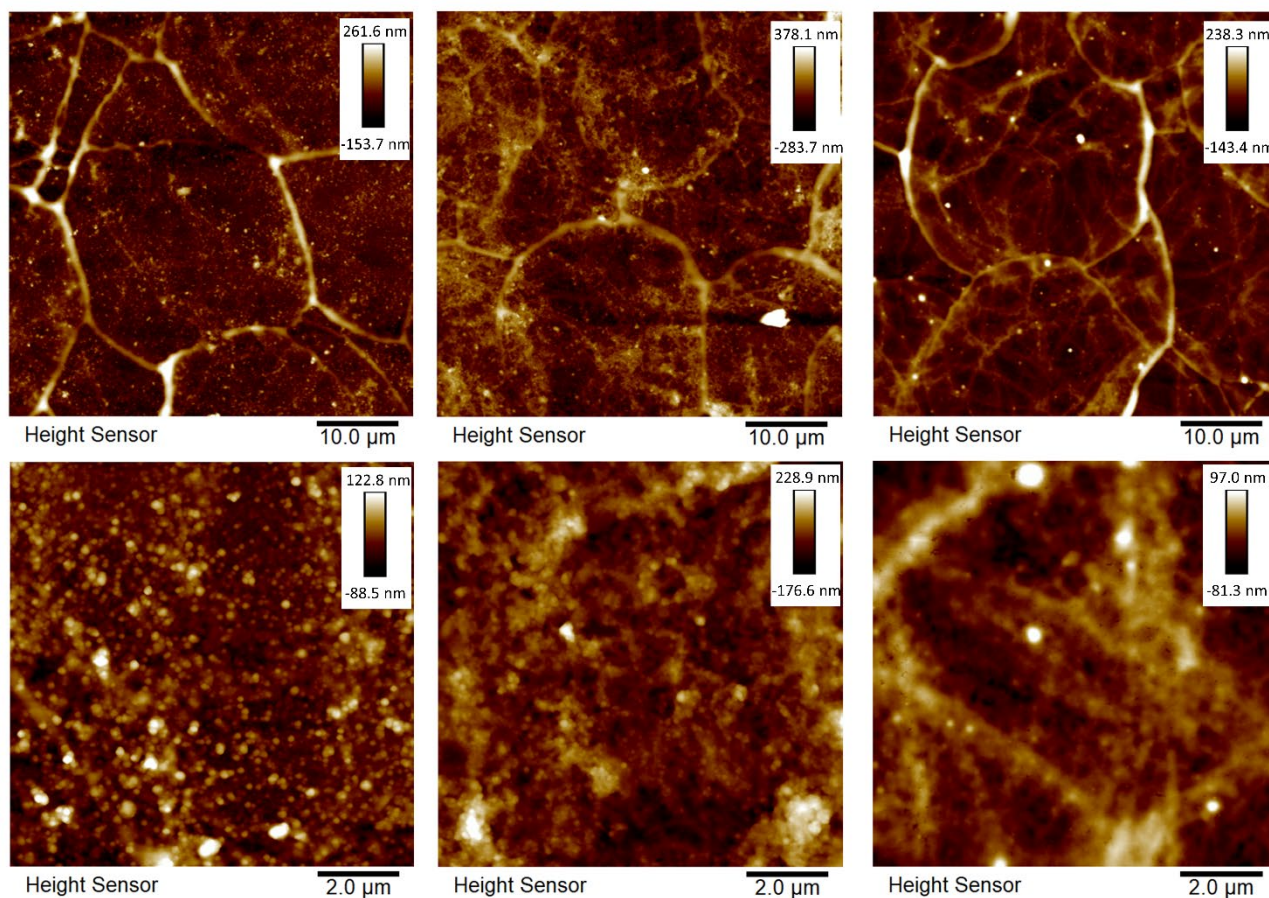


Figure S8: AFM micrographs for the polymer films deposited from dispersion by spray-coating at 90 °C. Micrographs of 50×50 μm (top) and 10×10 μm (below) areas of the same substrate for **P10** (left), **P20** (centre), and **P30** (right) films.

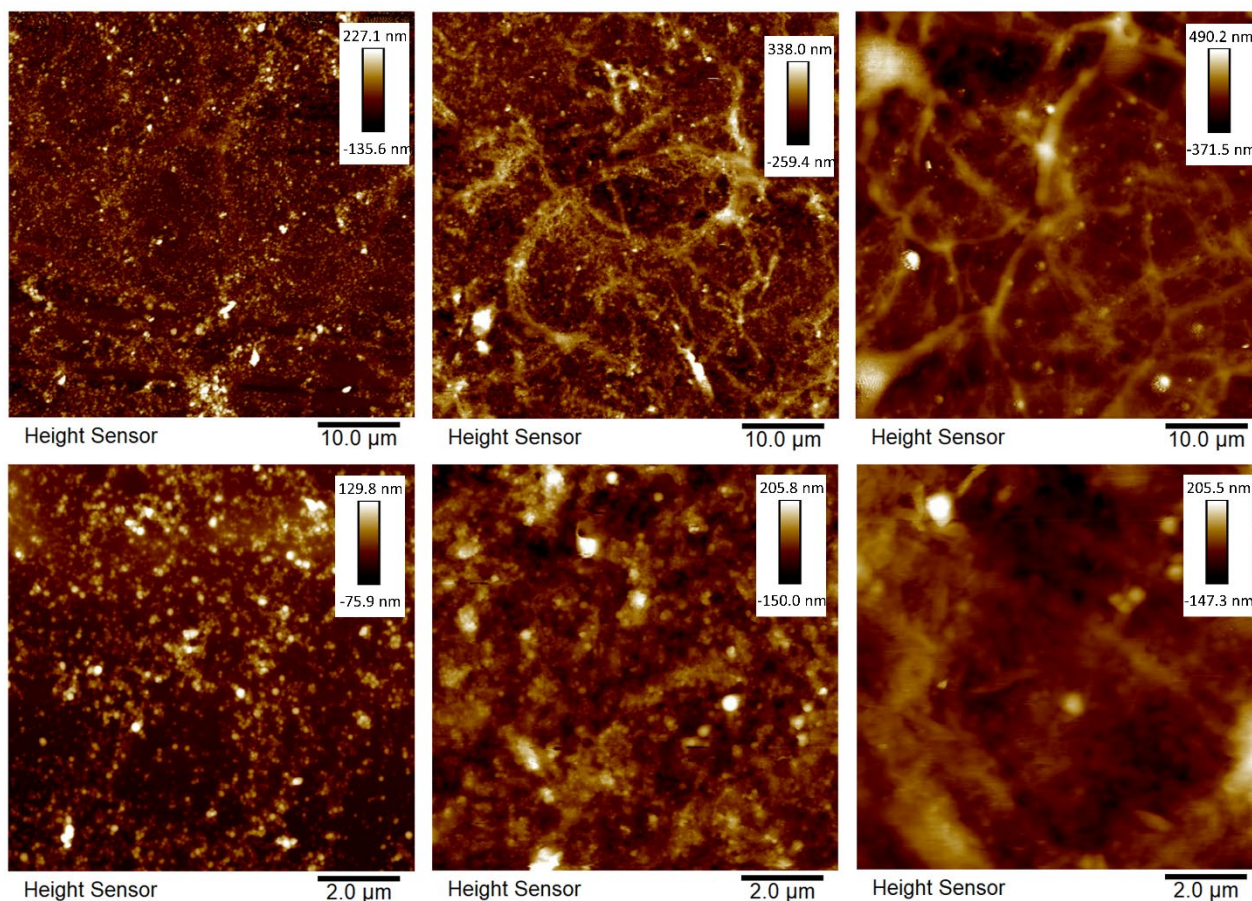


Figure S9: AFM micrographs for the polymer films deposited from dispersion by spray-coating at 65 °C. Micrographs of 50×50 μm (top) and 10×10 μm (below) areas of the same substrate for **P10** (left), **P20** (centre), and **P30** (right) films.

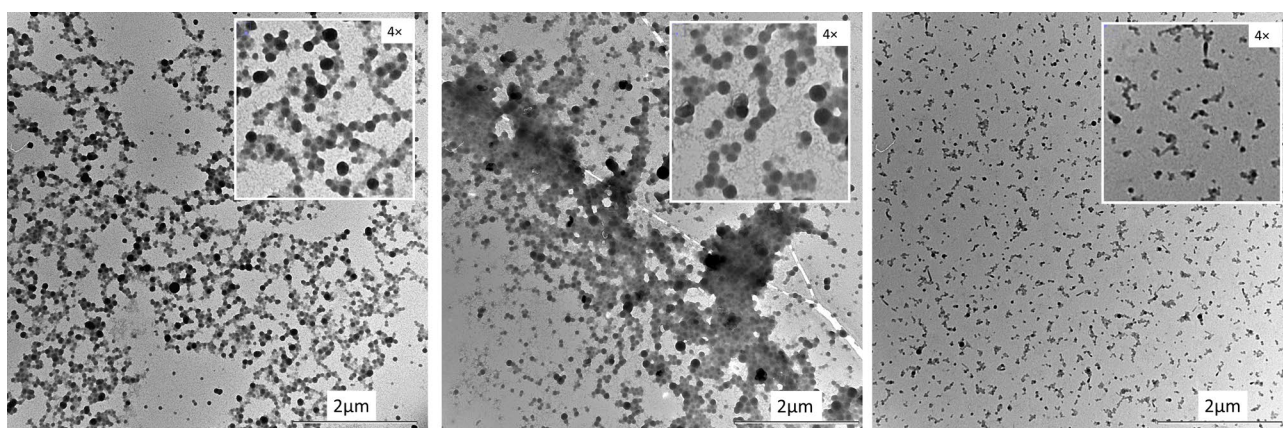


Figure S10: TEM images obtained by drop-casting the supernatant of the polymer dispersions after a centrifuge treatment (15060 rpm × 7 min) over a TEM grid. Images correspond to **P10** (left), **P20** (centre), and **P30** (right) samples analysed 8 months after their preparation.

Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS)

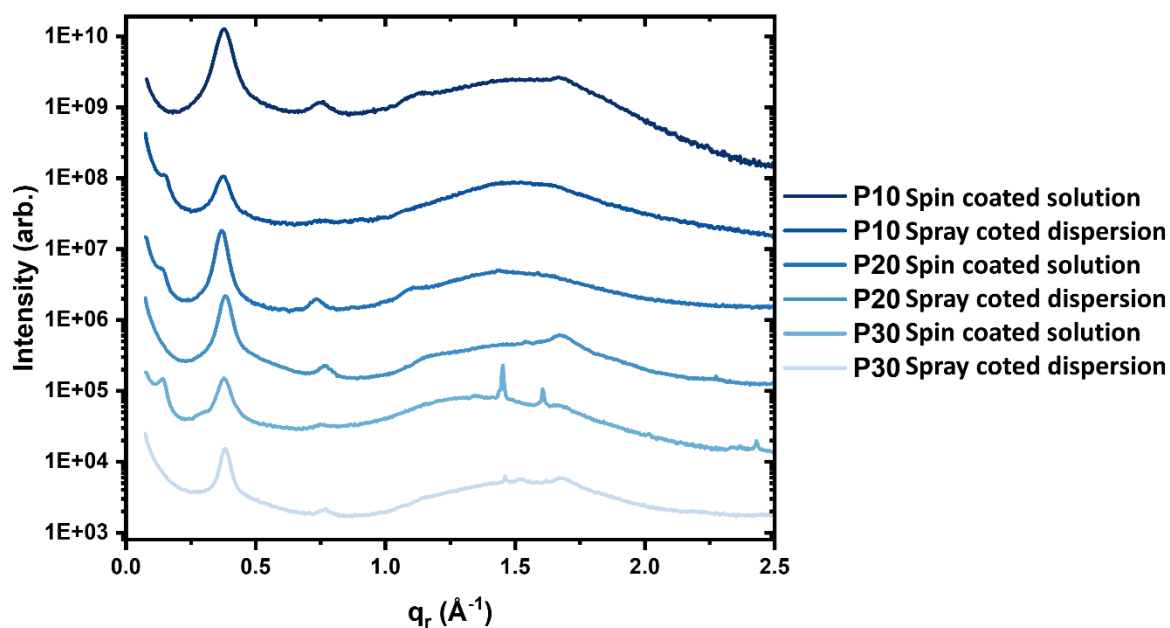


Figure S11: In-plane line cuts obtained for films deposited from organic polymer solutions in chloroform by spin-coating and films deposited via spray-coating using the aqueous polymer dispersions.

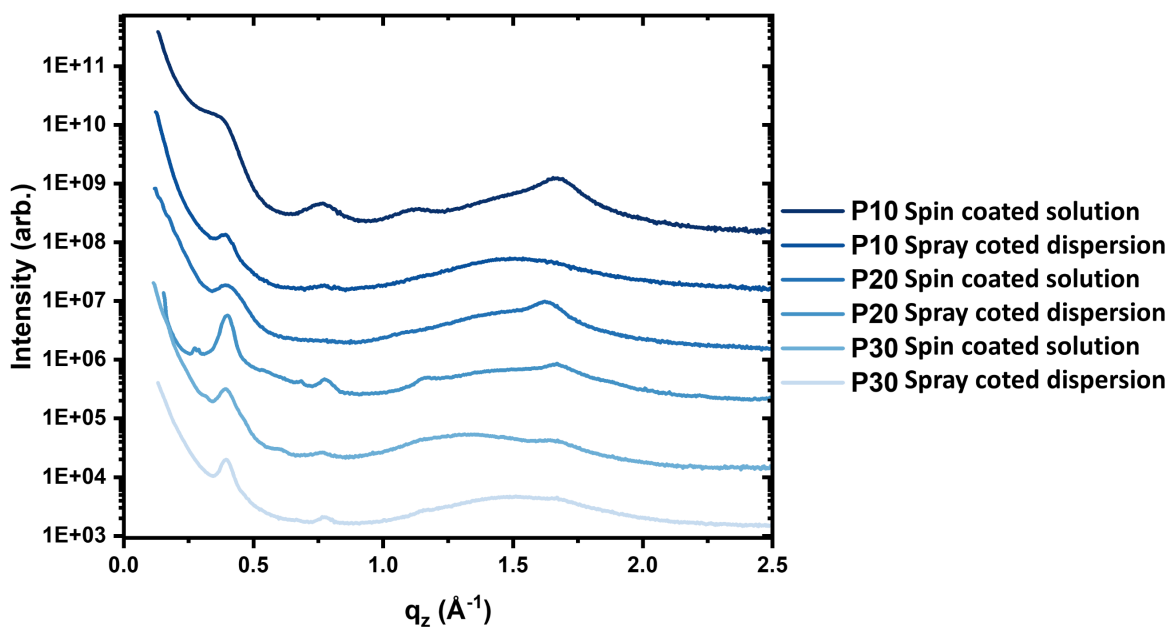


Figure S12: Out-of-plane line cuts obtained for films deposited from organic polymer solutions in chloroform by spin-coating and films deposited via spray-coating using the aqueous polymer dispersions.

Table S1: GIWAXS peak fits obtained for polymer films deposited from organic solutions and aqueous dispersions.

Material	In-plane				Out-of-plane		
	d_{100} (Å)	$L_{c,100}$ (Å)	d_{200} (Å)	d_{010} (Å)	d_{100} (Å)	d_{200} (Å)	d_{010} (Å)
P10							
Solution*	16.6	107	16.8	3.76		16.3	3.78
Aqueous dispersion**	16.8	101			16.1	16.2	
P20							
Solution*	17.0	144	17.1		15.1		3.87
Aqueous dispersion**	16.4	133	16.4	3.74	15.8	16.2	3.75
P30							
Solution*	16.6	114			15.8	16.6	
Aqueous dispersion**	16.4	159	16.4		15.9	16.3	

*Films spin-cast from chloroform solution (10 mg/ml).

** Films spray-coated from aqueous dispersions at 90 °C.

Organic Field-Effect Transistor Characterisation

Gold electrodes were patterned according to the literature² over silicon wafer. Gate dependence transfer characteristics of the devices was carried out by measuring I_{DS} vs. V_{GS} curves in the range -40 to 40 V at fixed V_{DS} of 5 V, using Keithley 4200-SCS Parameter Analyzer.

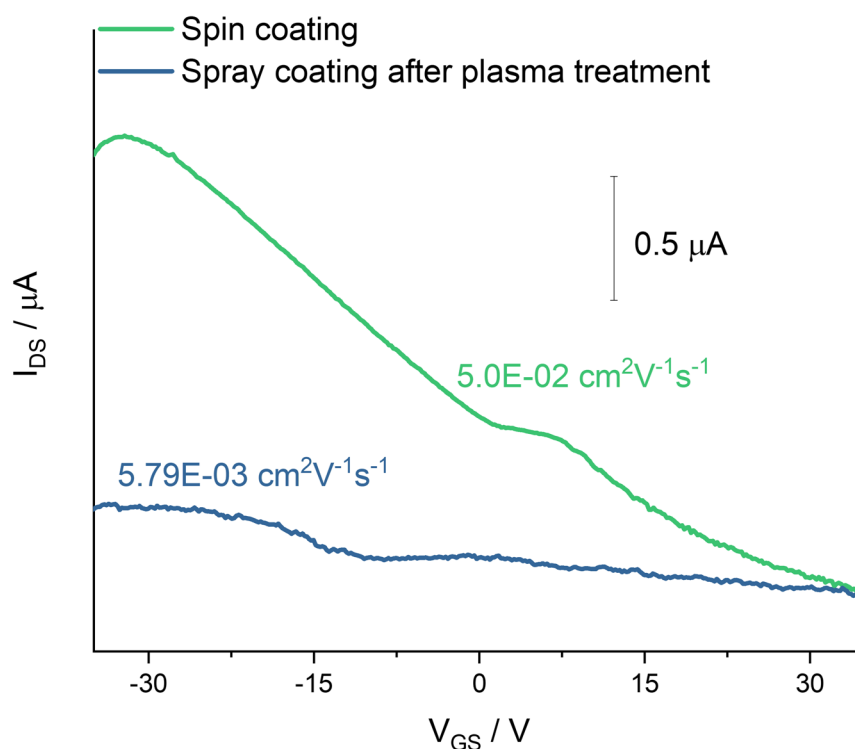


Figure S13: Transfer curve with mobilities obtained for devices fabricated using spin coating as processing method for a **P10** solution (5 mg/mL) and a device fabricated using spray coating to deposit the semiconductor layer from an aqueous polymer dispersion of **P10**.

References

1. P. A. Finn, I. E. Jacobs, J. Armitage, R. Wu, B. D. Paulsen, M. Freeley, M. Palma, J. Rivnay, H. Sirringhaus and C. B. Nielsen, *Journal of Materials Chemistry C*, 2020, **8**, 16216-16223.
2. X. Xu, P. Clément, J. Eklöf-Österberg, N. Kelley-Loughnane, K. Moth-Poulsen, J. L. Chávez and M. Palma, *Nano Letters*, 2018, **18**, 4130-4135.