Influence of Amide-Containing Side Chains on the Mechanical Properties of Diketopyrrolopyrrole-based Polymers

Michael U. Ocheje,[a] Mariia Selivanova,[a] Song Zhang,[b] Thi Hai Van Nguyen,[a,] Brynn P. Charron,[a] Ching-Heng Chuang,[c] Yu-Hsuan Cheng,[c] Blandine Billet,[a] Suendues Noori,[a] Yu-Cheng Chiu,[c] Xiaodan Gu [b,*] and Simon Rondeau-Gagné [a,*]

[a] Department of Chemistry and Biochemistry, University of Windsor, Ontario, Canada, N9B 3P4

[b] School of Polymer Science and Engineering, University of Southern Mississippi, 118 College Drive, # 5050 Hattiesburg, Mississippi, United States, MS 39406

[c] Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

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Materials

Conjugated polymers **P1** to **P7**, incorporating various ratios of amide-containing alkyl chains or dodecyl alkyl chains, have been prepared following previously reported procedures.[1,2] Commercial reactants were used without further purification unless stated otherwise. All the solvents used in these reactions were distilled prior to use. Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ($Pd_2(dba)_3$•$CHCl_3$) was purchased from Sigma Aldrich and recrystallized following a reported procedure.[3] (*E*)-1,2-bis(5-(trimethylstannyl)thiophen-2-yl)ethene (TVT) and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione were synthesized according to literature.[4]

Materials Characterization

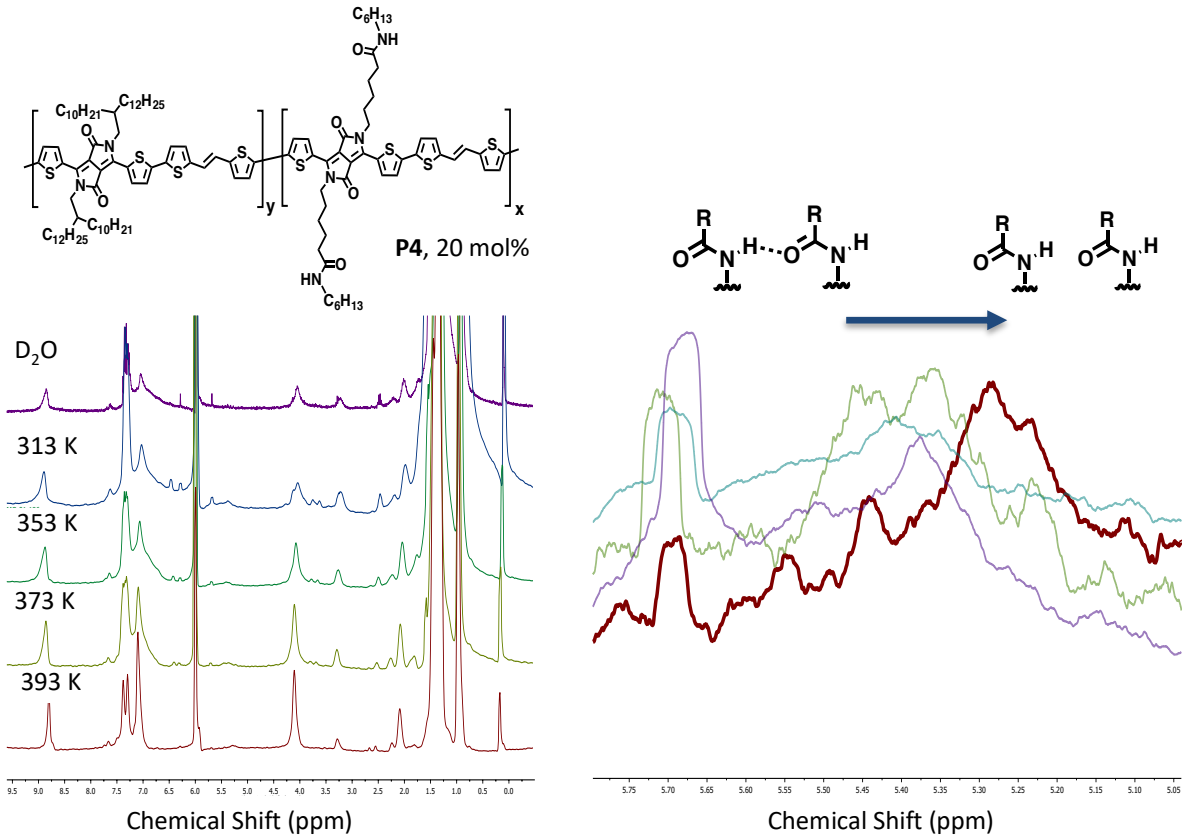

Figure S1. a) Variable Temperature (VT) NMR spectra of polymer **P4**, containing 20 mol% of amide-containing alkyl chains, in 1,1,2,2-tetrachloroethene-d_2; b) VT-NMR spectra of **P4** in 1,1,2,2-tetrachloroethene-d_2 zoomed on the amide region.

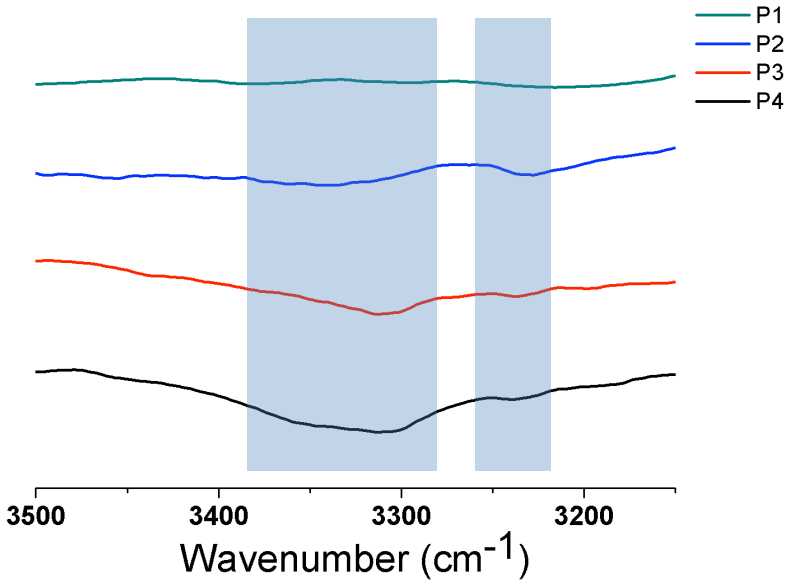

Figure S2. FTIR spectra of **P1** to **P4** in thin films, zoomed on the NH stretching region.

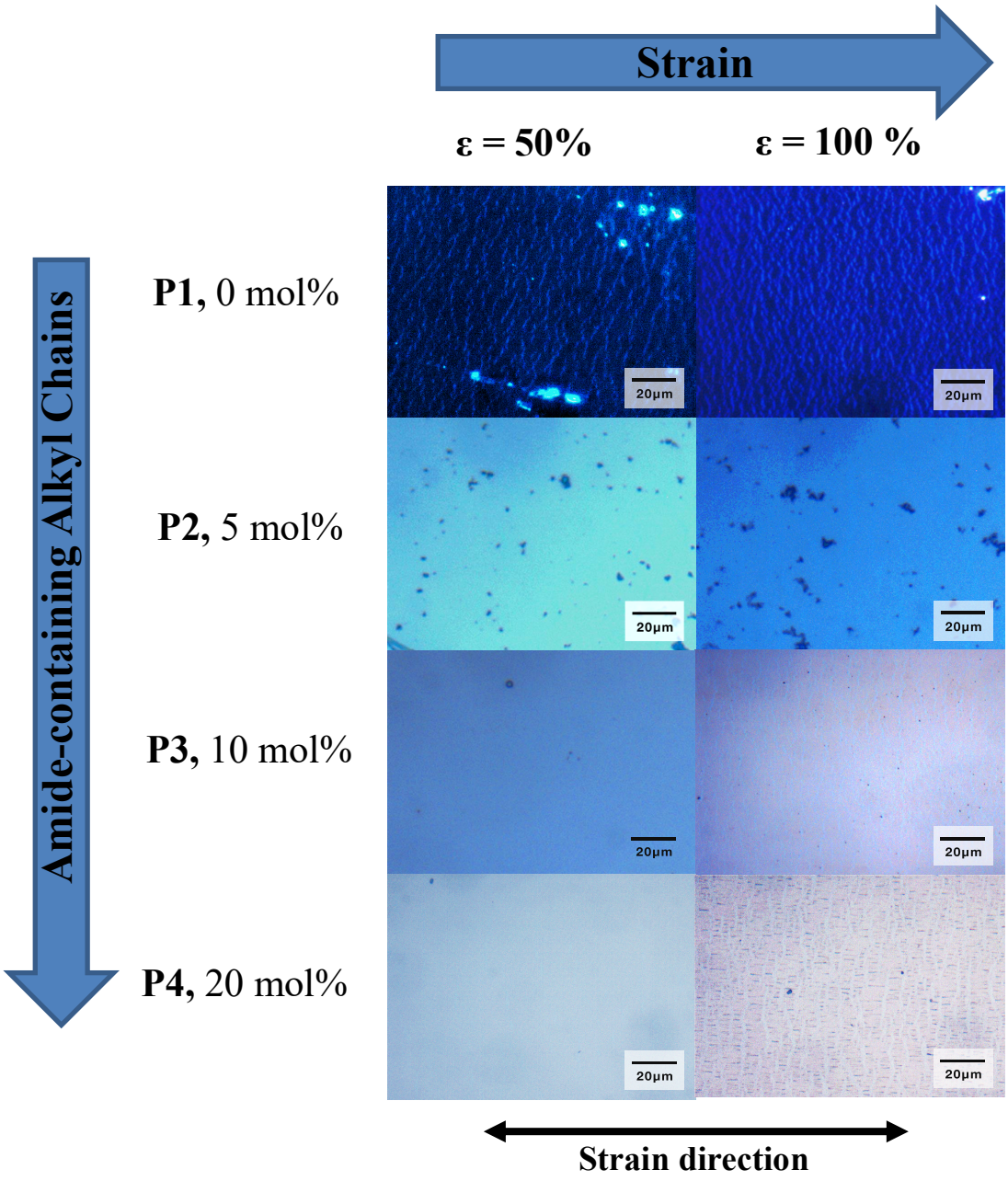

Figure S3. Optical microscopy images of **P1** to **P4** stretched at ε = 50 and 100%. Images of **P1** have been recorded on dark field for clarity. Scale bar is 20 µm

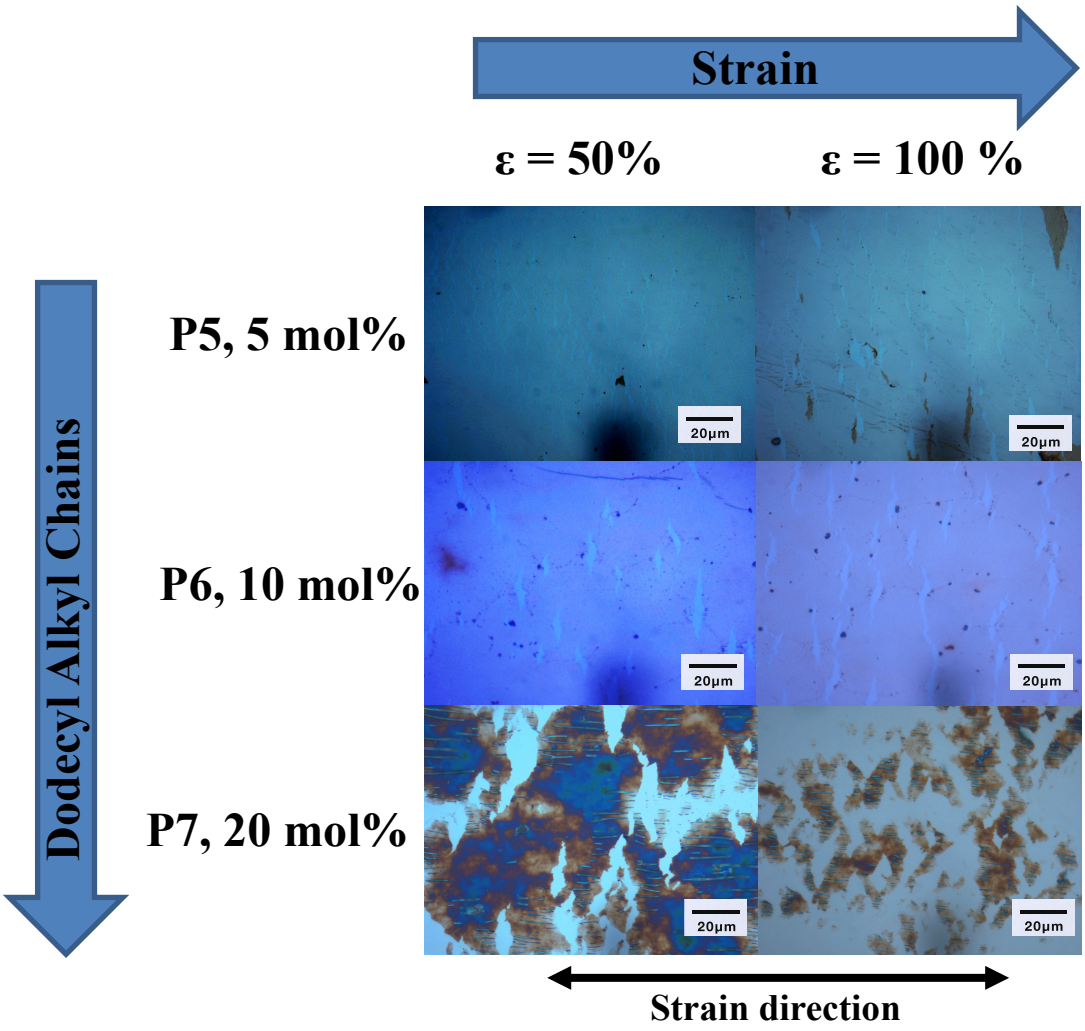

Figure S4. Optical microscopy images of **P5** to **P7** stretched at ε = 50 and 100%. Scale bar is 20 μm

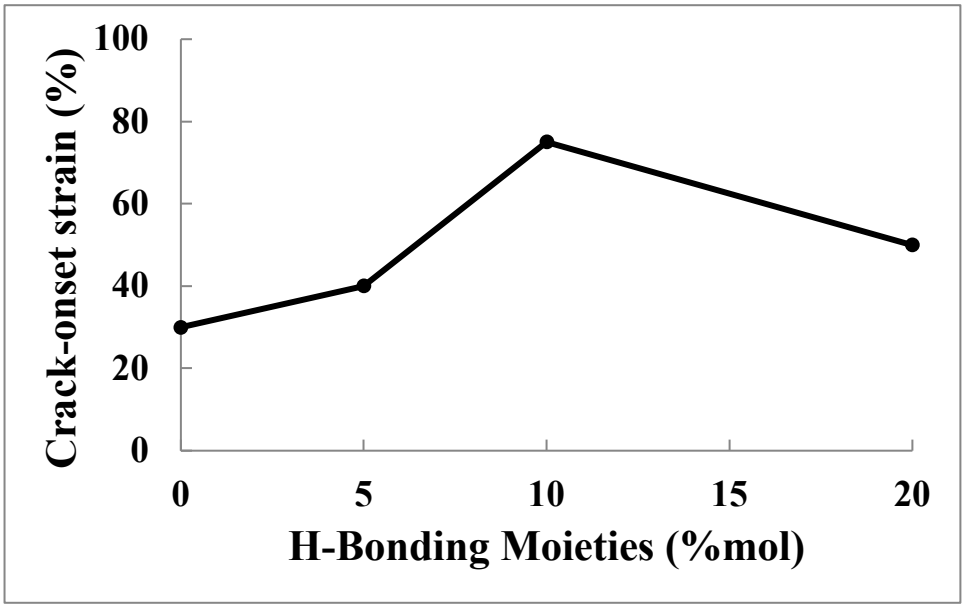

Figure S5. Crack-onset strain for polymer **P1** to **P4**, incorporating 0 to 20 mol% of amide-containing alkyl chains, as measured by soft-contact lamination on PDMS and SiO_2.

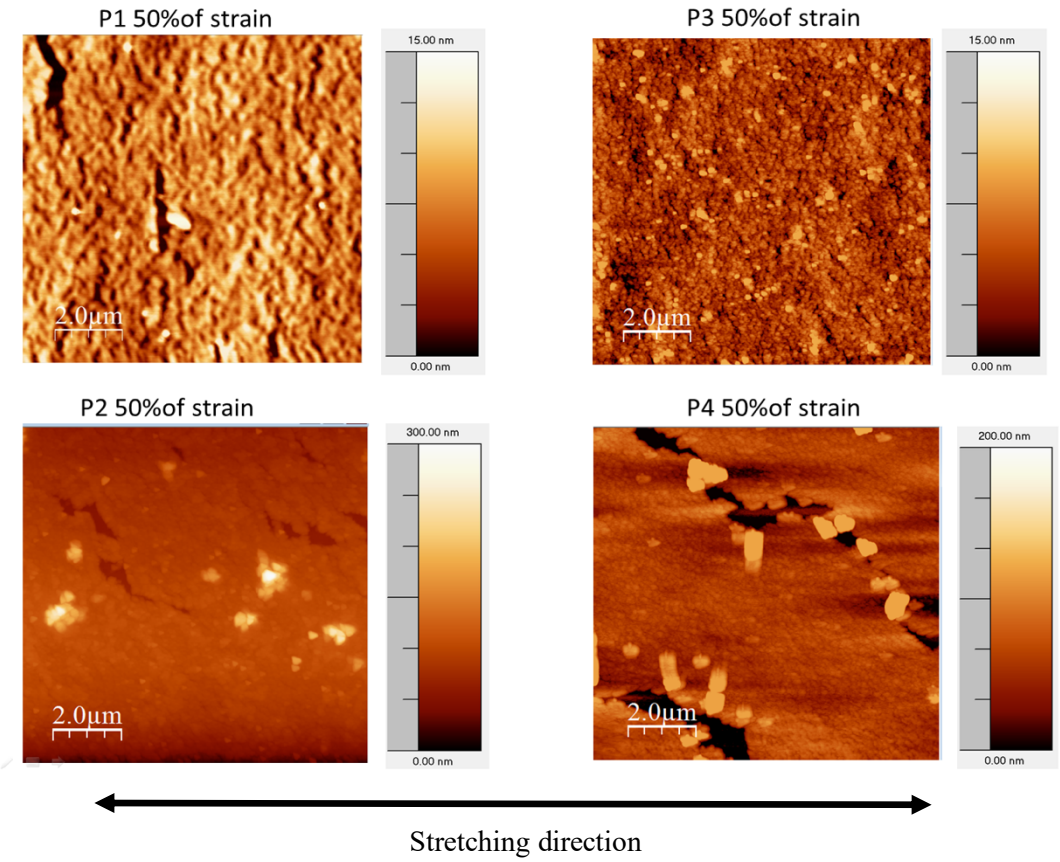

Figure S6. Atomic force microscopy (AFM) height profiles of **P1** to **P4** at 50% strain. Scale bar is 2 µm.

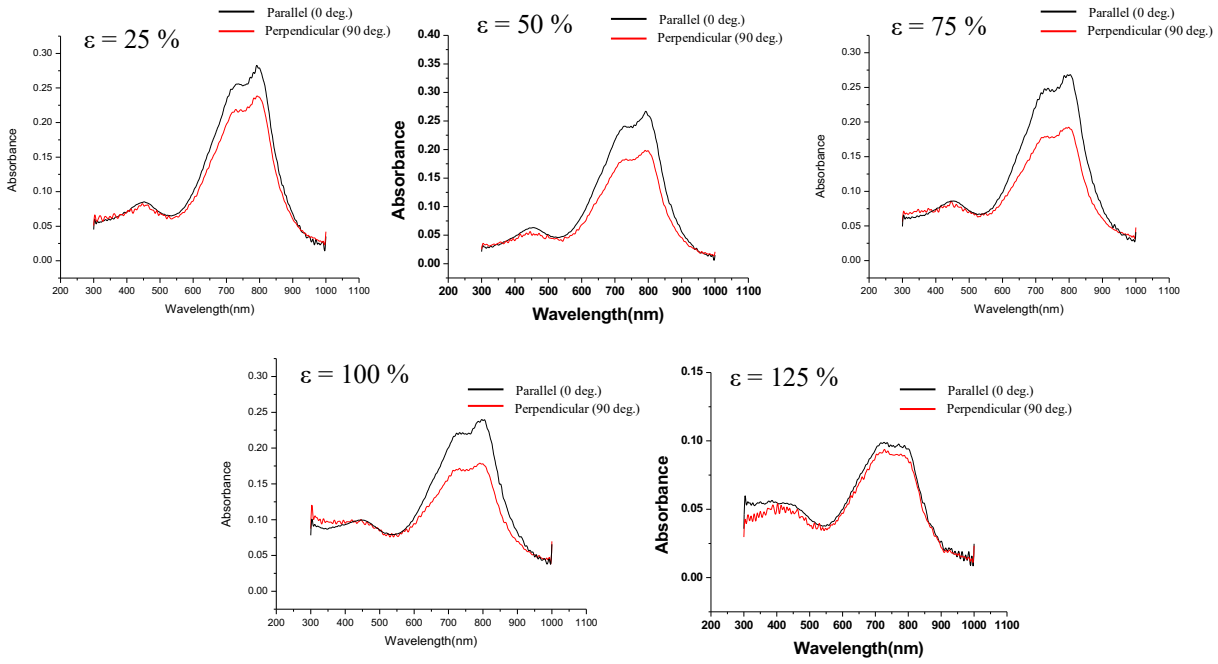

Figure S7. Polarized UV-vis spectra of **P1** stretched at different strains, with the polarization direction of light parallel (0°, black curve) and perpendicular (90°, red curve) to the stretching direction.

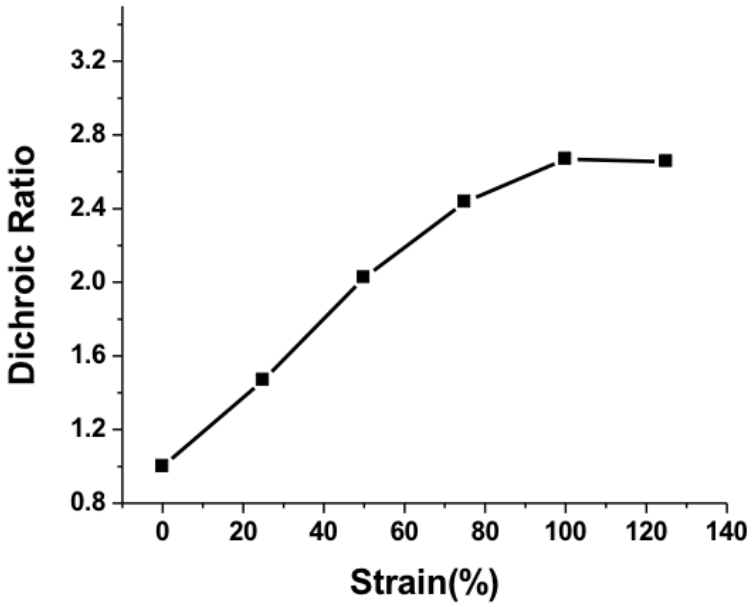

Figure S8. Dichroic ratios measured for **P1** at various strain. The dichroic ratio is defined as $\alpha_{//}$ / $\alpha_{\perp}$.

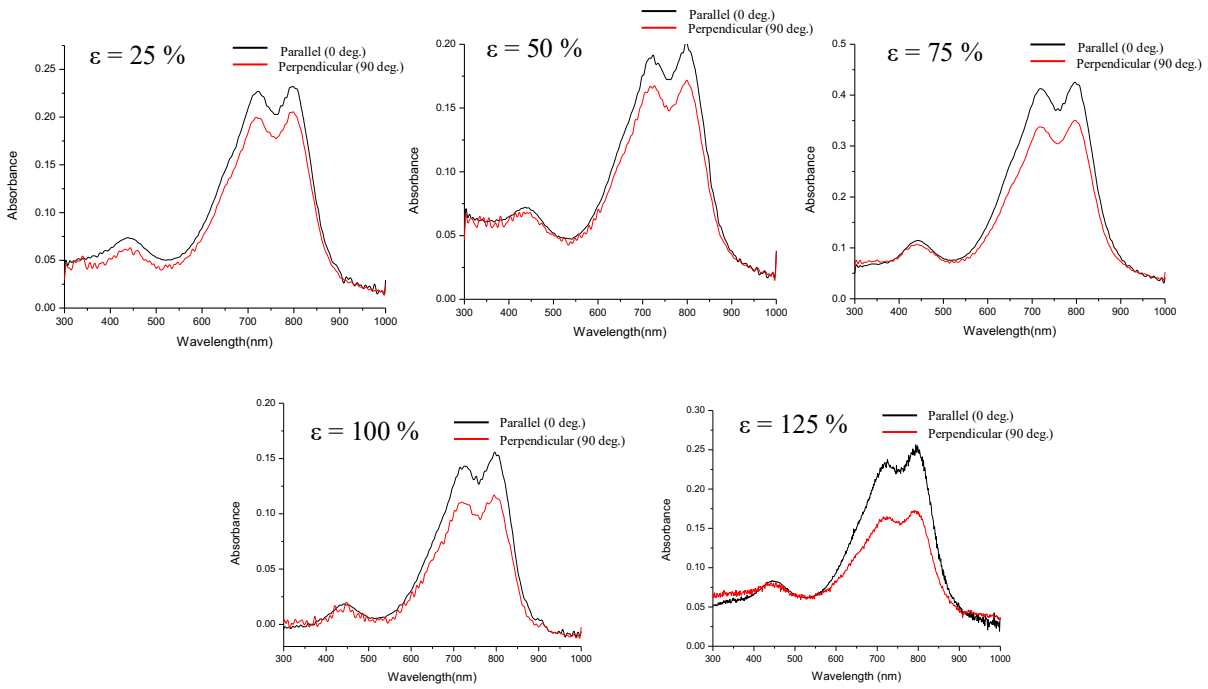

Figure S9. Polarized UV-vis spectra of **P3** stretched at different strains, with the polarization direction of light parallel (0°, black curve) and perpendicular (90°, red curve) to the stretching direction.

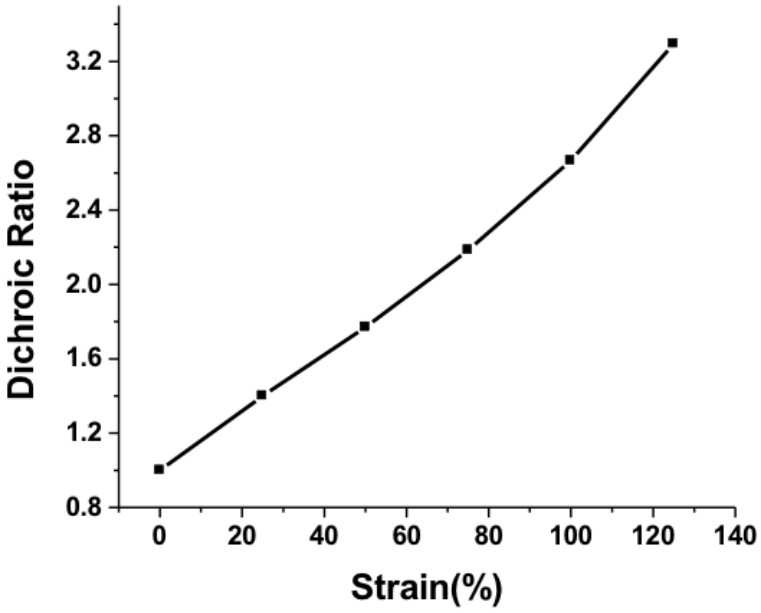

Figure S10. Dichroic ratios measured for **P3** at various strain. The dichroic ratio is defined as $\alpha_{//} / \alpha_{\perp}$.

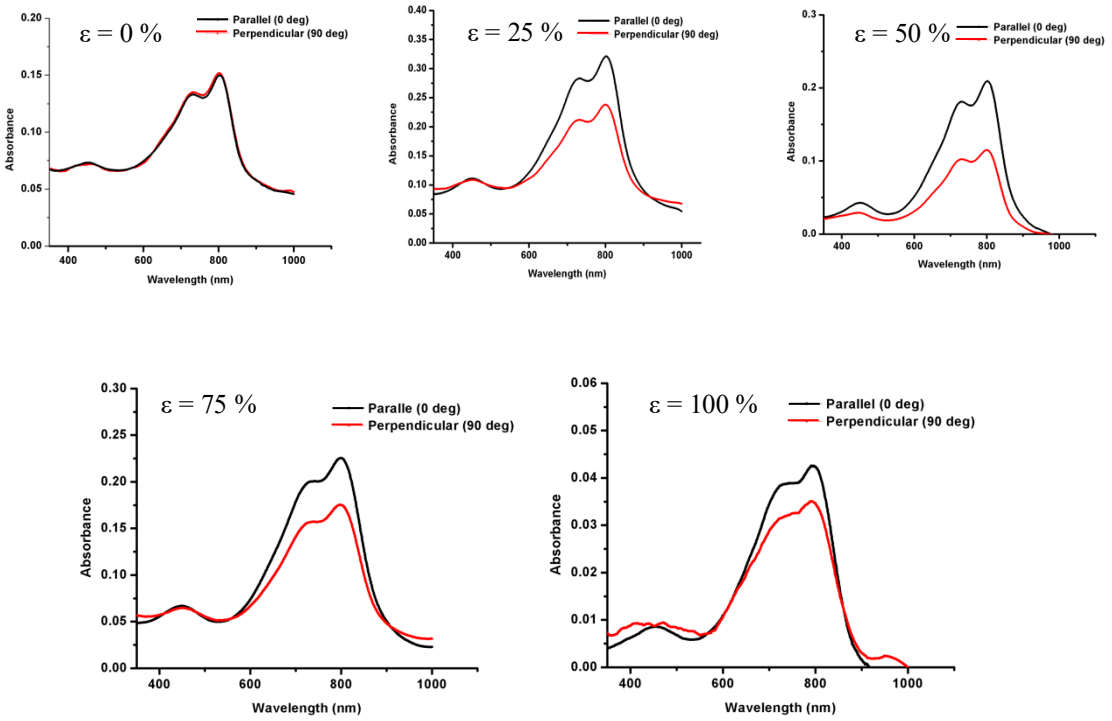

Figure S11. Polarized UV-vis spectra of **P6** stretched at different strains, with the polarization direction of light parallel (0°, black curve) and perpendicular (90°, red curve) to the stretching direction.

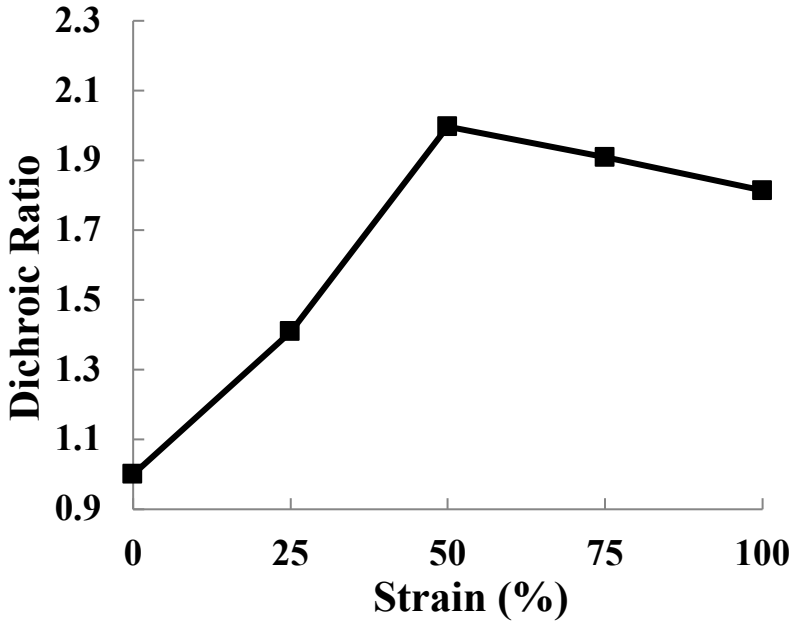

Figure S12. Dichroic ratios measured for **P6** at various strain. The dichroic ratio is defined as $\alpha_{//} / \alpha_{\perp}$.

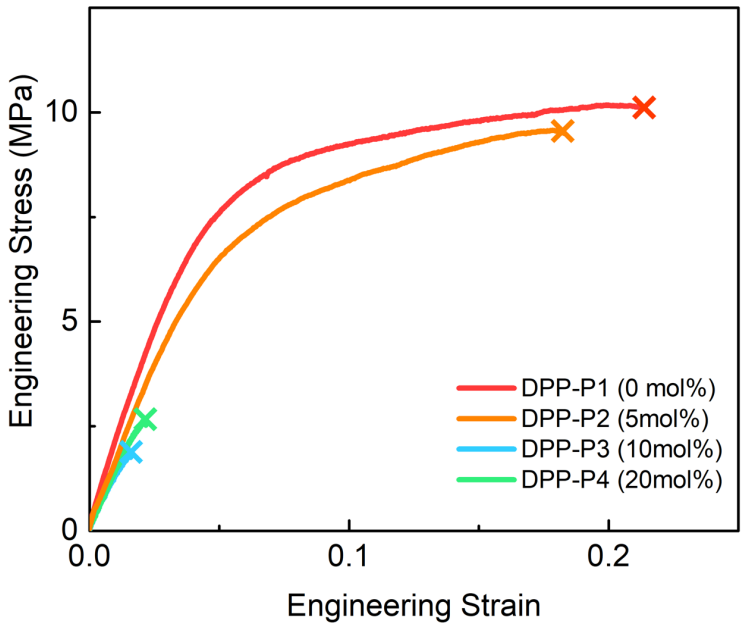

Figure S13. Stress vs strain curves for polymer **P1** to **P4**, as measured by Film-on-Water (FOW) Tensile Pull Test. Strain rate of 2 x 10^{-4}/s, averaged on 5 samples. Sample thickness of 50 nm.

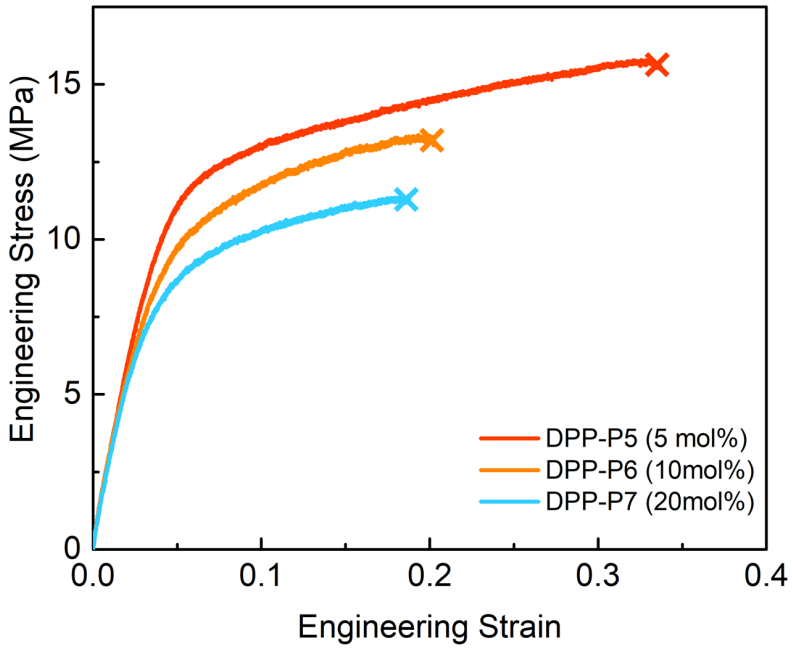

Figure S14. Stress vs strain curves for polymer **P5** to **P7**, incorporating 5 to 20 mol% of linear dodecyl side chains, as measured by Film-on-Water (FOW) Tensile Pull Test. Strain rate of 2 x 10^{-4}/s, averaged on 5 samples. Sample thickness of 50 nm.

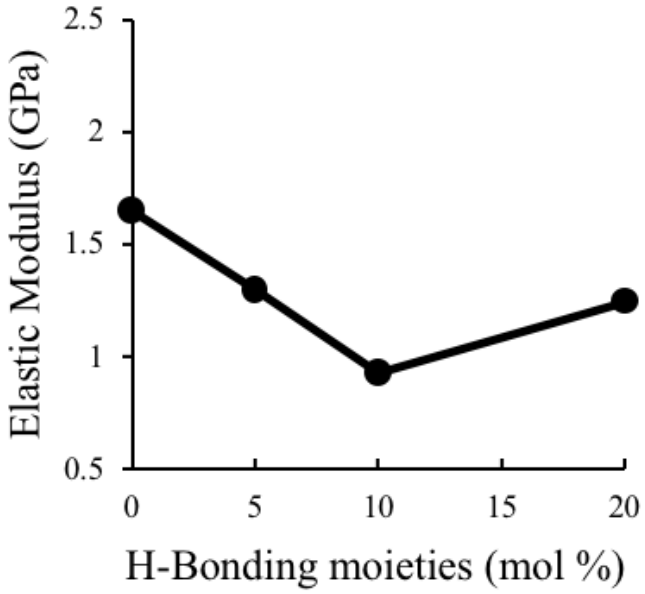

Figure S15. Elastic modulus of **P1** to **P4**, determined by nanoindentation with AFM. Film thicknesses ranged from 40-60 nm, as determined by AFM.

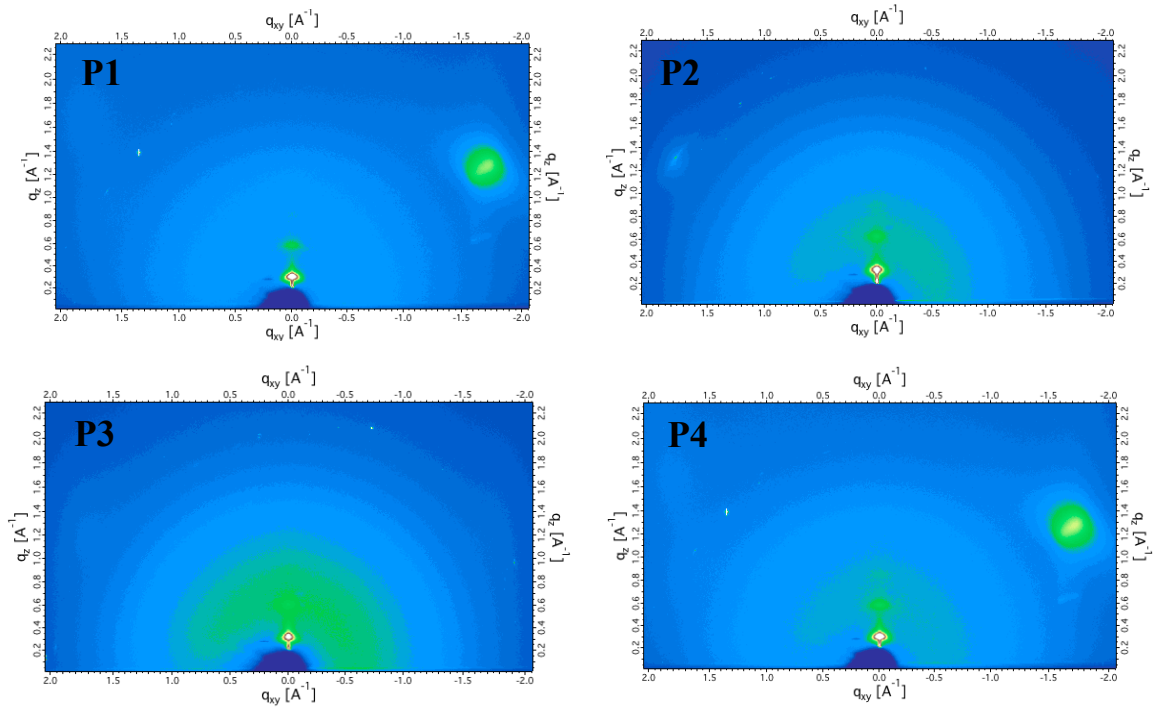

Figure S16. Grazing incidence XRD patterns of **P1** to **P4** spin-cast on OTS-treated SiO_2 substrate.

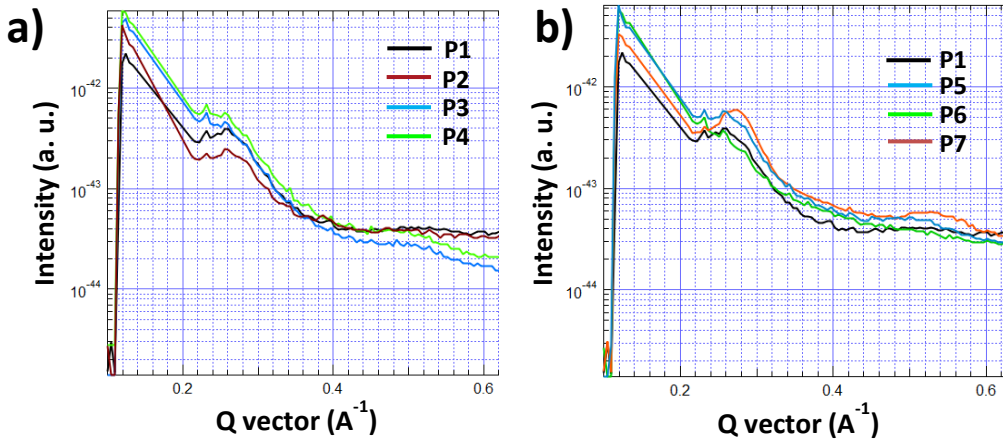

Figure S17. Grazing-incidence X-ray diffraction of a) **P1** to **P4**, and b) **P1** and **P5** to **P7.**

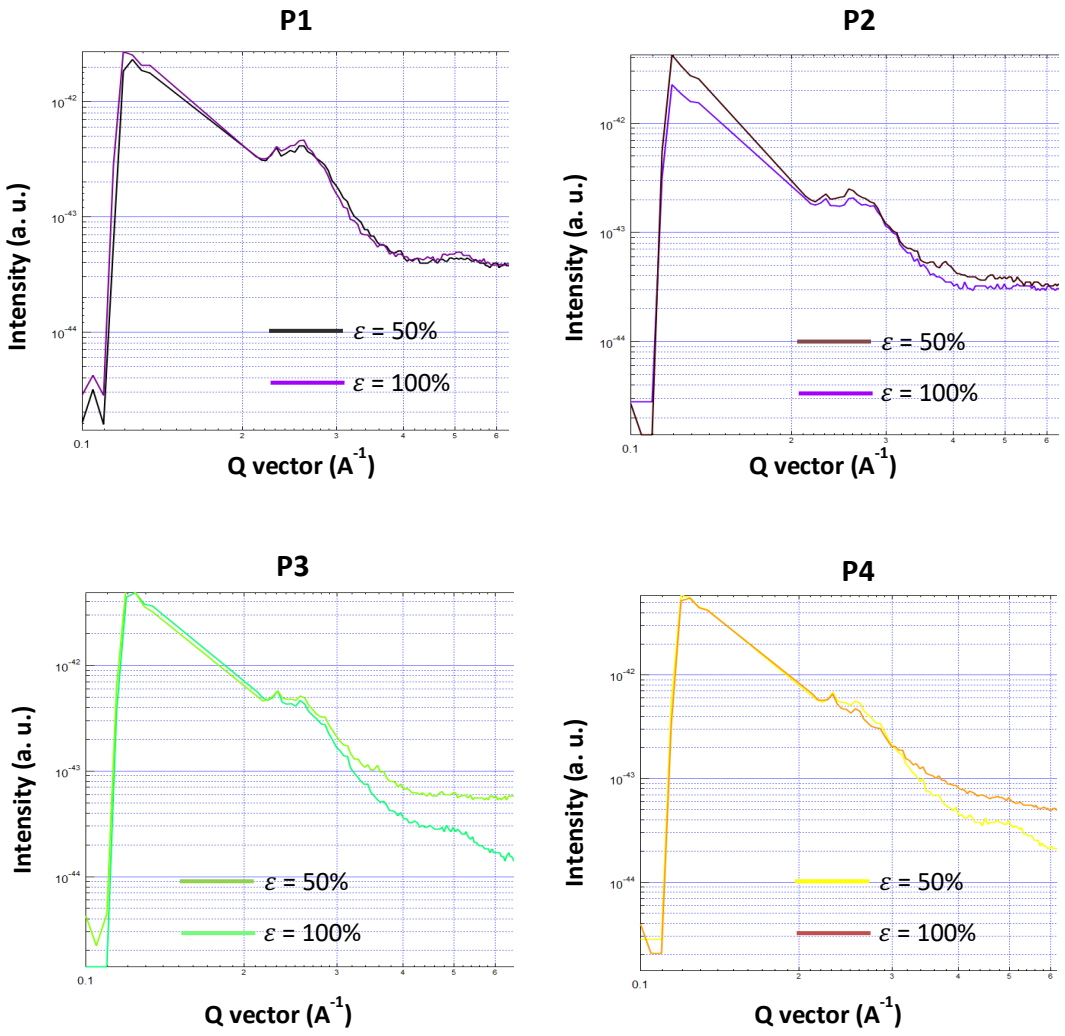

Figure S18. Grazing-incidence X-ray diffraction of stretched films of **P1** to **P4** at 50% and 100% strain elongation.

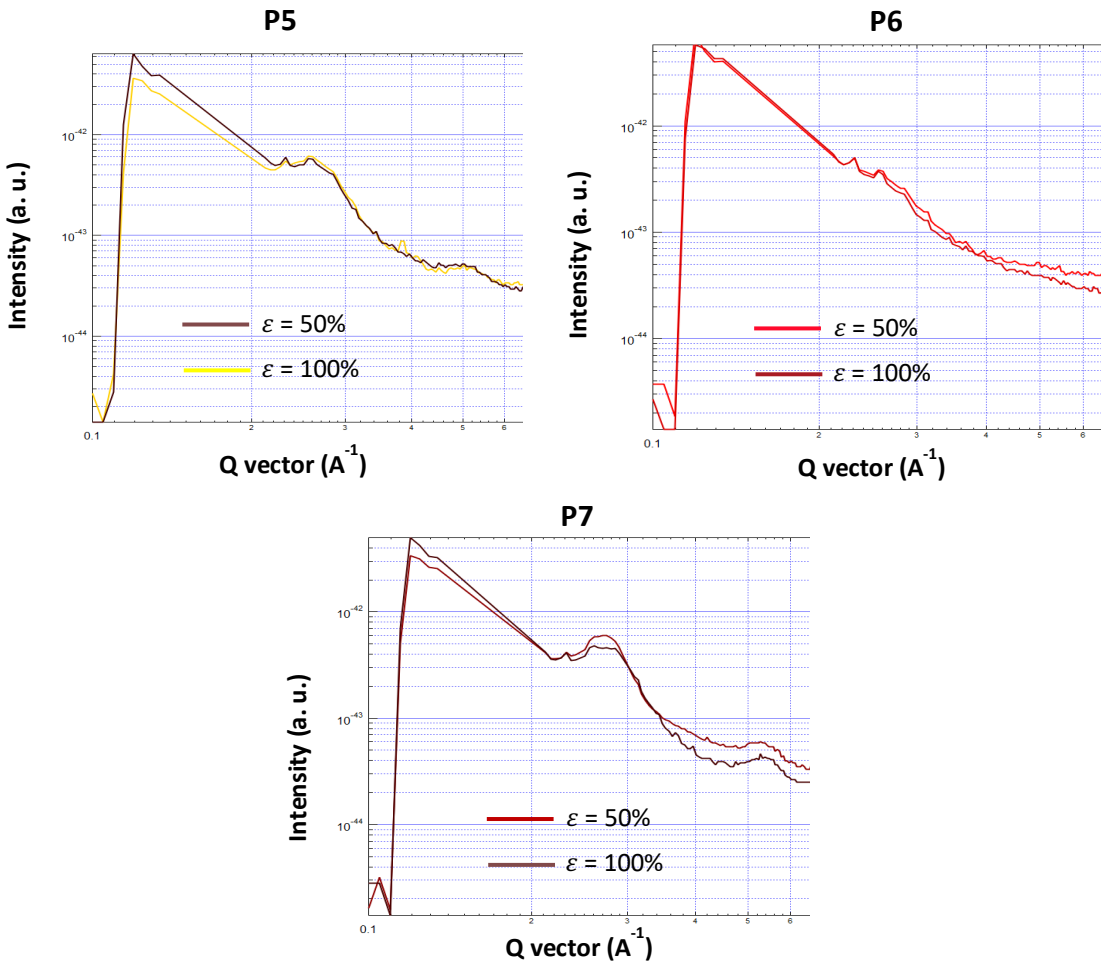

Figure S19. Grazing-incidence X-ray diffraction of stretched films of **P1** and **P5** to **P7** at 50% and 100% strain elongation.

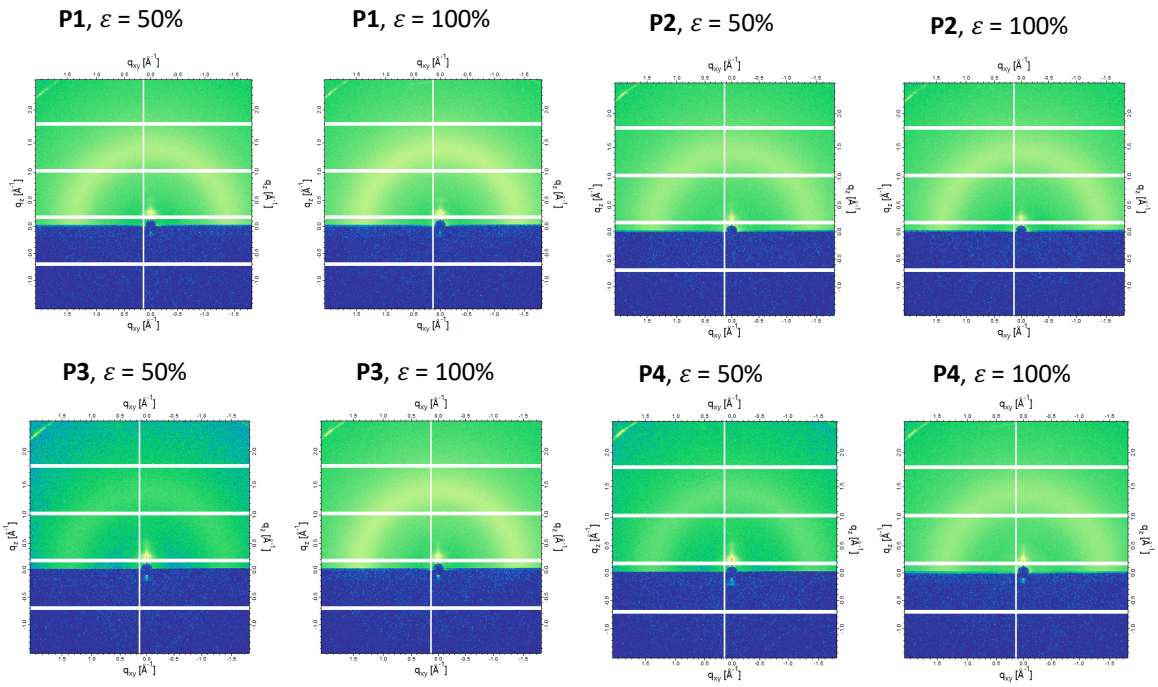

Figure S20. Grazing incidence XRD patterns of **P1** to **P4** spin-cast on SiO_2 substrate, at 50% and 100% strain elongation.

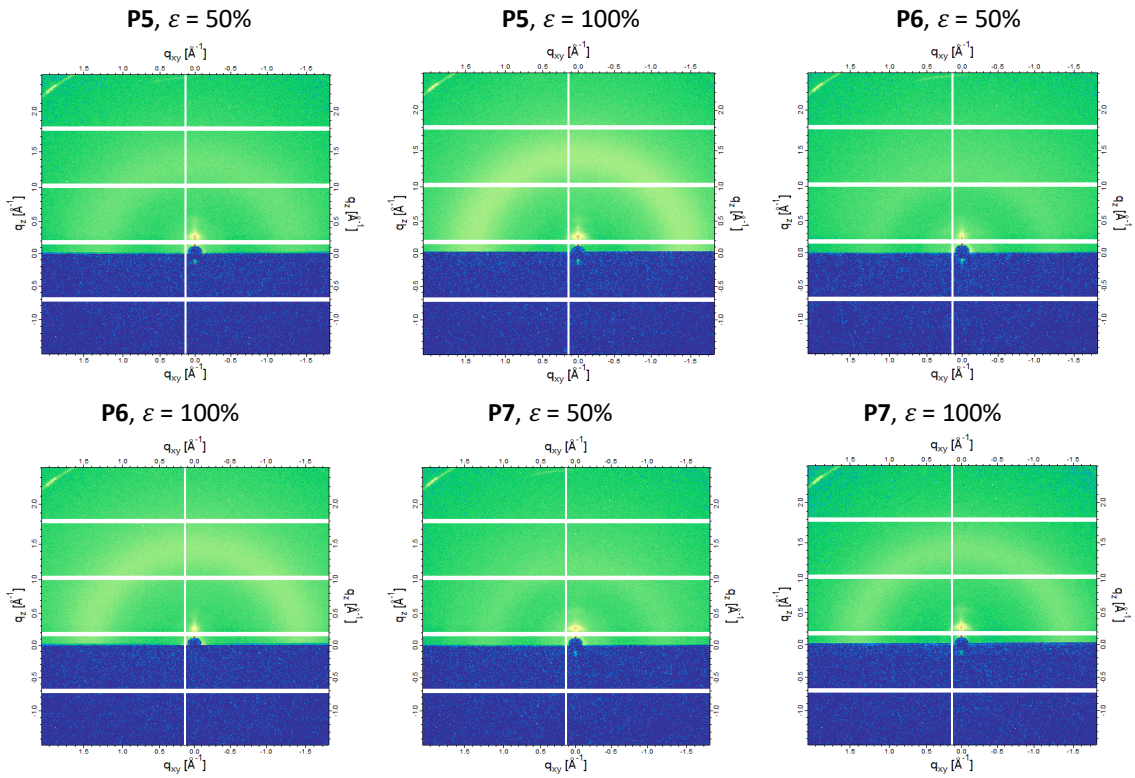

Figure S21. Grazing incidence XRD patterns of **P5** to **P7** spin-cast on SiO_2 substrate, at 50% and 100% strain elongation.

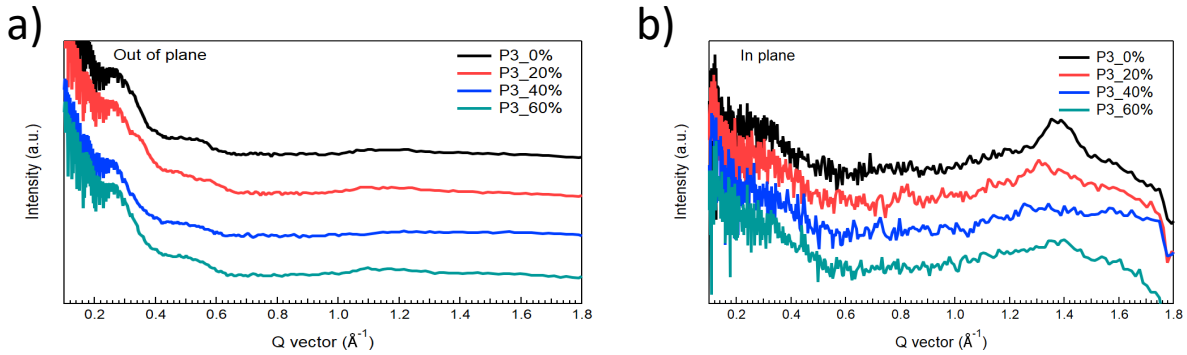

Figure S22. Grazing-incident X-Ray diffraction (GIXD) of **P3** from 0 to 60% strain, measured a) out of plane and b) in plane.

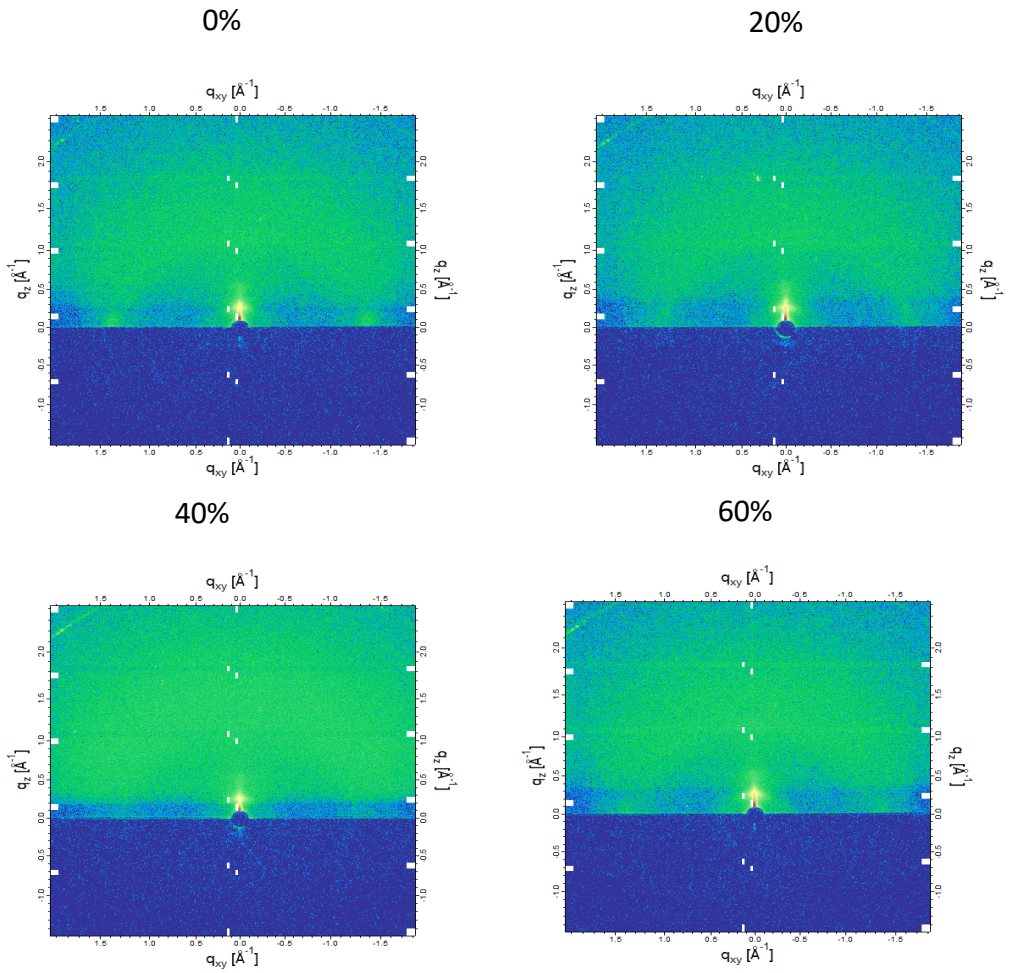

Figure S23. Grazing incidence XRD patterns of **P3** spin-cast on SiO_2 substrate, from 0 to 60% strain elongation.

Table S1. GIXD results for **P3** from 0 to 60% strain elongation

Sample	q (Å^{-1})	d spacing (nm)
P3 (ε = 0%)	0.264	2.380
P3 (ε = 20%)	0.265	2.371
P3 (ε = 40%)	0.258	2.435
P3 (ε = 60%)	0.261	2.407

Table S2. Previously reported average and maximum hole mobility (μ_h^{ave}, μ_h^{max}**)**, threshold voltages (V_{th}), I_{on}/I_{off}, and ratios for OFETs fabricated from **P1** to **P4** before and after thermal annealing.[1] The device performances were averaged from 20 devices, from four different batches. [a] Evaluated by AFM.

Polymer	**Annealing Temperature [°C]**	**Thickness (nm)[a]**	***W/L***	**μ_h^{ave} / μ_h^{max} [$cm^2V^{-1}s^{-1}$]**	**I_{ON}/I_{OFF}^{ave}**	**V_{th}^{ave} [V]**
P1 (0 mol%)	170	40-50	20	1.52±0.25/1.91	10^5	-4.32
P2 (5 mol%)	170	40-50	20	2.02±0.35/2.46	10^6	-5.50
P3 (10 mol%)	170	40-50	20	0.46±0.16/0.67	10^6	-4.75
P4 (20 mol%)	170	40-50	20	0.74±0.17/1.06	10^5	-5.93

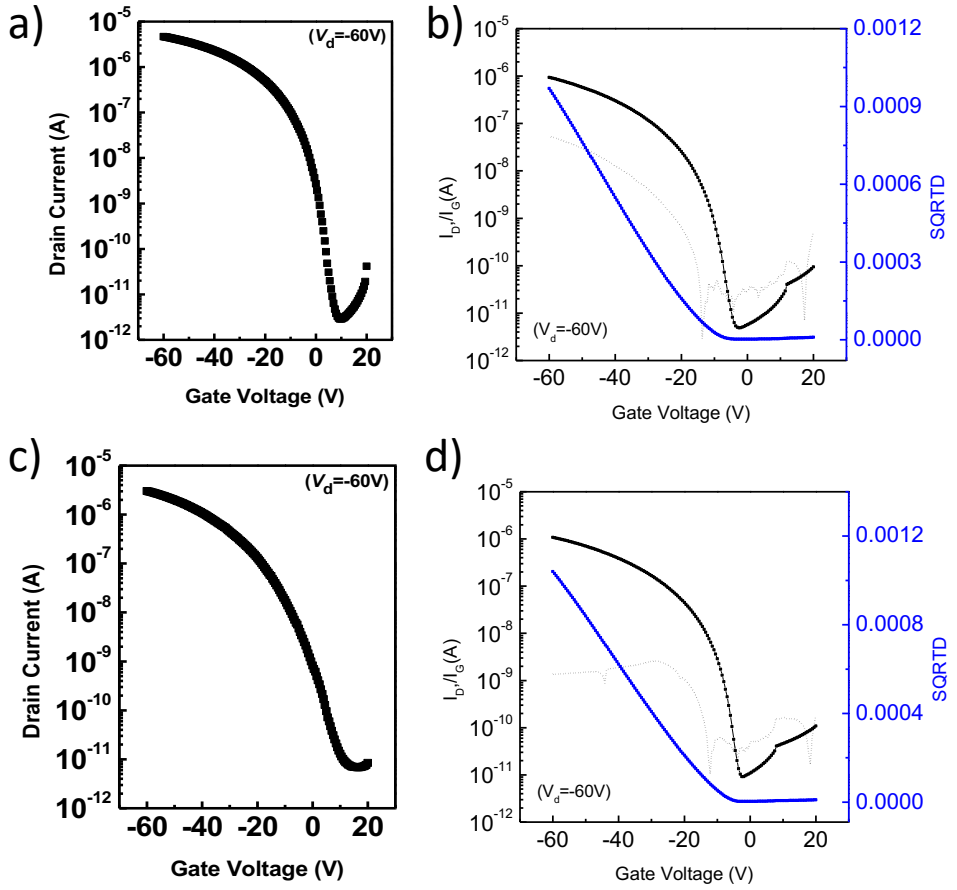

Figure S24. Transfer curves of FET devices from a) **P3** at 50% strain elongation, b) **P3** at 100% strain elongation, c) **P6** at 50% strain elongation, and d) **P6** at 100% strain elongation. All devices were fabricated on SiO_2 from laminated stretched polymer film, without annealing treatment. Drain voltage = -60V

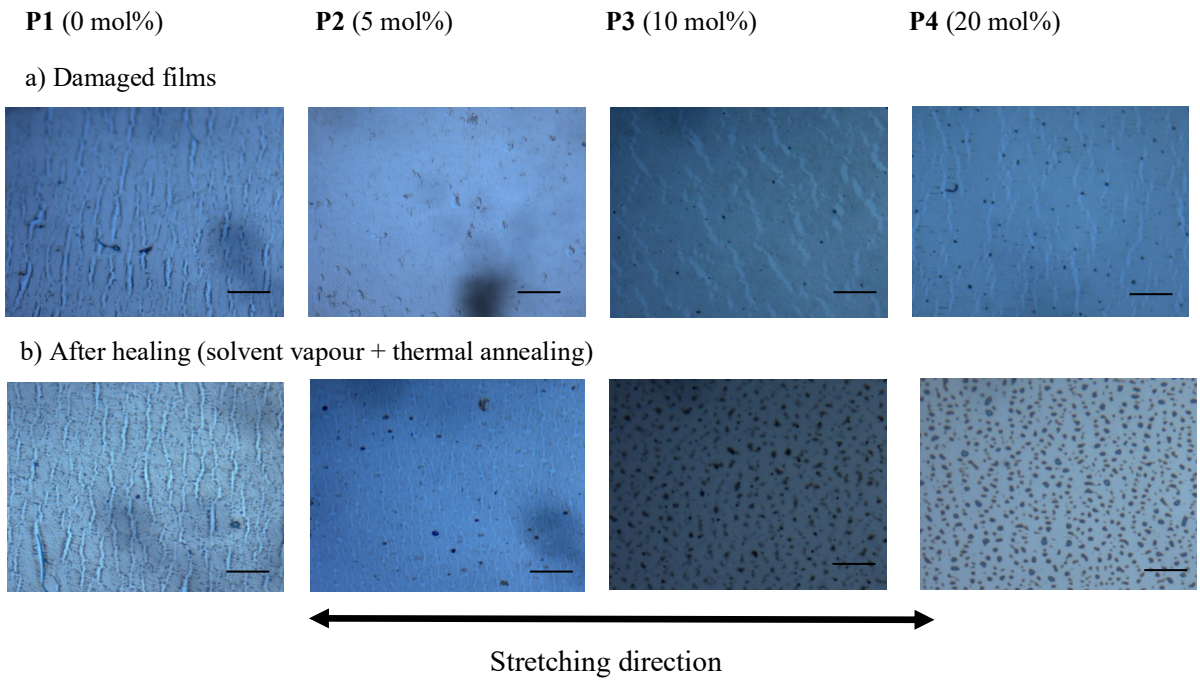

Figure S25. Optical microscope images of a) damaged thin films of **P1** to **P4** (100% strain applied and released before transfer on SiO_2) and b) Thin films of **P1** to **P4** after exposure to solvent vapour (chlorobenzene) and thermal annealing for 30 minutes. Scale bar, for all images, is 20 µm

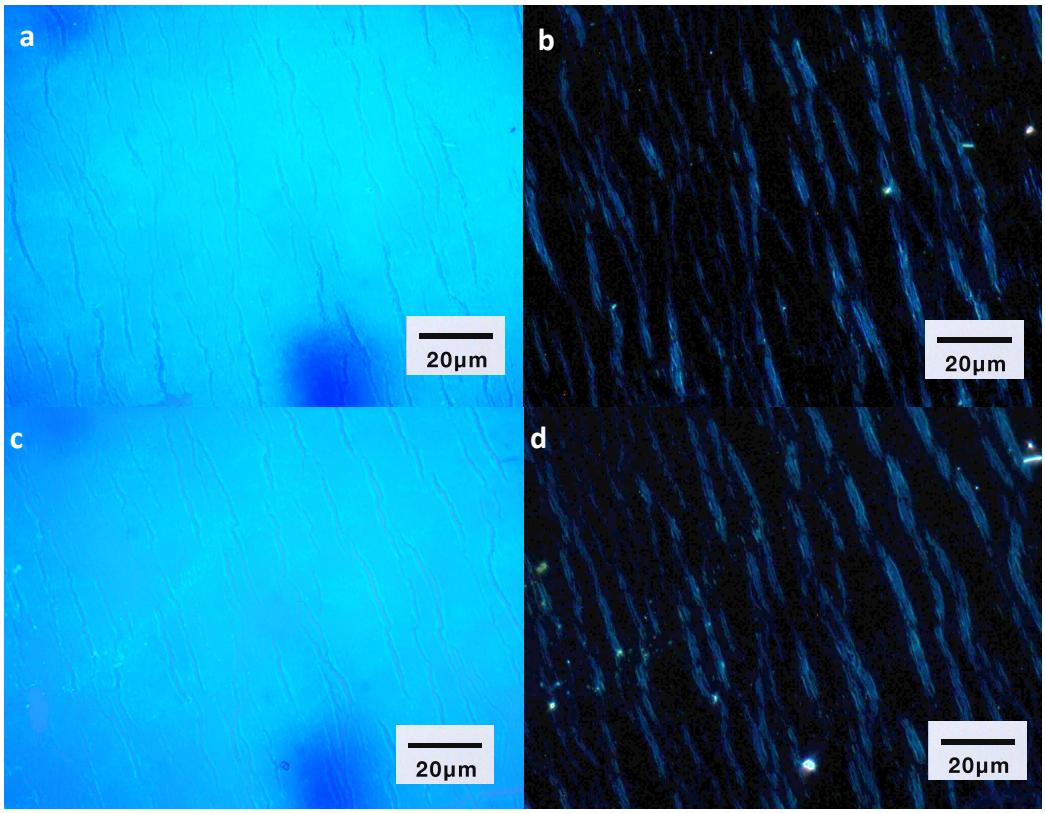

Figure S26. a) Optical microscope images of a) damaged thin films of **P6**, containing 10 mol% of dodecyl side-chains (100% strain applied and released before transfer on SiO_2); b) Optical microscope images of damaged thin films of **P6**, containing 10 mol% of dodecyl side-chains in dark field (100% strain applied and released before transfer on SiO_2); c) Optical microscope images of thin films of **P6** after exposure to solvent vapour (chlorobenzene) and thermal annealing for 30 minutes and d) optical microscope images of thin films of **P6** in dark field after exposure to solvent vapour (chlorobenzene) and thermal annealing for 30 minutes. Scale bar, for all images, is 20 µm

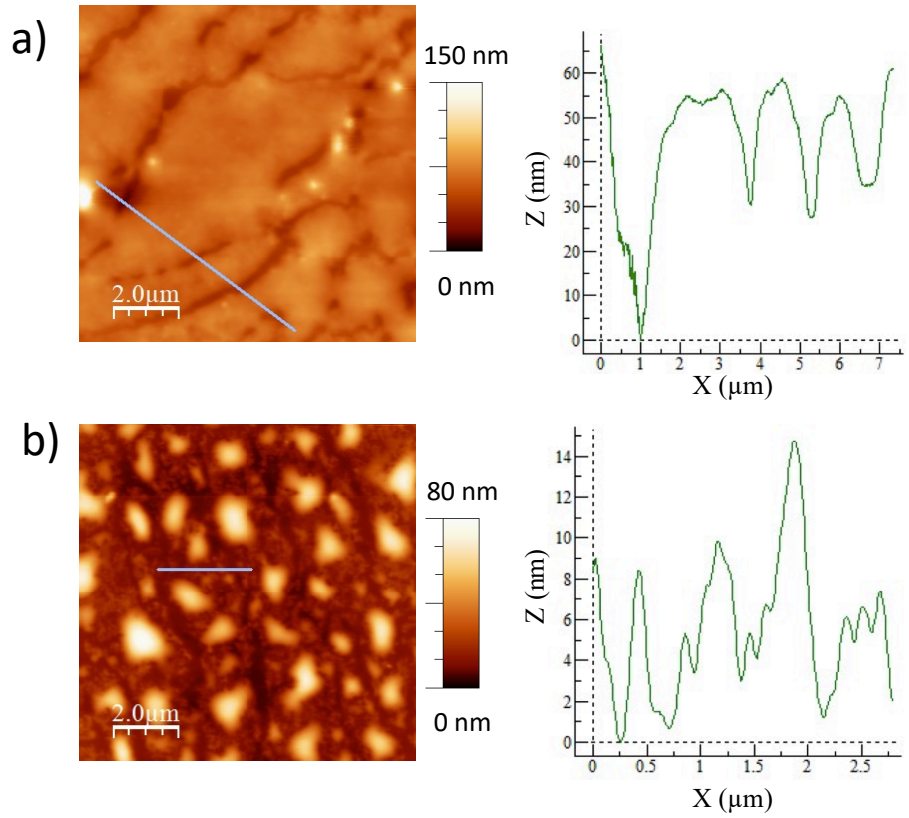

Figure S27. Height images and profiles, determined by AFM, of a) Thin films of **P3** after exposure to solvent vapour (chlorobenzene, 10 min. at 40°C) and thermal annealing (30 min. at 150°C), and b) Thin films of **P4** after exposure to solvent vapour (chlorobenzene, 10 min. at 40°C) and thermal annealing (30 min. at 150°C). Scale bar is 2 µm.

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