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Spatial-Controlled Nanoengineered Films Prepared via Rapid Catalyst Induced Cross-Linking

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Materials

Azobis(2-methyl-propionitrile) (AIBN) was purchased from Acros Organics and was used as received. Allyl bromide (99%), [1,3-bis(diphenylphosphino)propane]dichloronickel(II), 1,3-bis(trimethylsilyl)urea (95%), 3-bromothiophene (97%), calcium hydride (CaH$_2$), N,N'-dicyclohexylcarbodiimide (DCC, 99%), diethyl ether (DEE, anhydrous), 1,4-dioxane ($\geq$ 99%), 2-hydroxyethyl methacrylate (97%), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDCI, $\geq$ 98%), 4-(dimethylamino)pyridine (DMAP, $\geq$ 99%), Ethylene glycol diethyl ether (98%), Grubbs catalyst (2nd generation), 3-(2-hydroxyethyl)thiophene (99%), N-bromo succinimide (99%), 5-norbornene-2-carboxylic acid (mixture of *endo* and *exo*, 98%), poly(ethylene imine) (PEI) (M_w ~ 25 kDa) and *tert*-butylmagnesium chloride solution (1 M in THF) were obtained from Aldrich and used without further purification. Oligo(ethylene glycol) methyl ether methacrylate (M_n ~ 500 Da) was obtained from Aldrich and passed through basic aluminium oxide prior to use. Aluminium oxide (basic), cyclohexanone, ethanol, isopropanol, magnesium sulfate (MgSO$_4$, anhydrous), *n*-hexane, poly(vinyl alcohol) (PVA) (M_w ~ 27 kDa) and toluene were obtained from Merck and used directly. Diethyl ether (DEE), N,N-dimethylformamide (DMF), chloroform (CHCl$_3$), sodium bicarbonate (NaHCO$_3$) and sodium hydroxide (NaOH) were obtained from Chem-Supply and used directly. Anhydrous, deoxygenated dichloromethane (DCM) and tetrahydrofuran (THF) were obtained by distillation under argon from CaH$_2$ and sodium benzophenone ketyl, respectively. Deuterated chloroform (CDCl$_3$) was obtained from Cambridge Isotope Laboratories. High-purity water with a resistivity greater than 18 MΩ·cm was obtained from an in-line Millipore RiOs/Origin water purification system. Silicon wafers (MMRC Pty. Ltd., Melbourne, Australia) were cut to approximately 1 × 1 cm slides and cleaned with Piranha solution (sulfuric acid:hydrogen peroxide = 7:3) – *Caution! Piranha solution is highly corrosive and extreme care should be taken during preparation and use*. The slides were then sonicated in isopropanol:water (1:1) solution for 15 min and finally heated to 60 °C for 20 min in RCA solution (water:ammonia:hydrogen peroxide = 5:1:1). The slides were washed thoroughly with Milli-Q water between each step.

Characterization Methods

Polymer molecular weight characterization was carried out via gel permeation chromatography (GPC) using either toluene, THF or DMF as the mobile phases. GPC analysis using toluene as the eluent was conducted on a Viscotek GPC Max VE2001 solvent/sample module equipped with a Viscotek VE3580 refractive index detector and a sample injection volume of 200 μL. Samples were passed through three 30 cm, PL gel (5 μm) mixed C columns and one 30 cm, PL gel (3 μm) mixed E column at 0.6 mL·min^{-1}. Molecular mass distributions were calculated relative to narrow polystyrene reference standards. GPC analysis using THF as the eluent was carried out on a Shimadzu liquid chromatography system equipped with a Wyatt DAWN-HELEOS MALS detector (λ = 690 nm, 30 mW), Wyatt OPTILAB DSP interferometric refractometer (λ = 690 nm) and Shimadzu SPD-10AVP UV-Vis detector using three Phenomenex Phenogel columns (500, 104, and 106 Å porosity; 5 μm bead size) operating at 45 °C. THF was used as the eluent at a flowrate of 1 mL·min^{-1}. The molecular weights of the samples were determined using polystyrene standards. GPC analysis using DMF as the eluent was conducted on a Shimadzu liquid chromatography system equipped with a PostNova PN3621 MALS detector (λ = 532 nm), Shimadzu RID-10 refractometer (λ = 633 nm) and Shimadzu SPD-20A UV-Vis detector, using three Phenomenex Phenogel columns in series (500, 10^4 and 10^6 Å porosity, 5 μm bead size) operating at 75 °C. DMF with 0.05 mol·L^{-1} LiBr (> 99%, Aldrich) was employed as the mobile phase at a flow rate of 1 mL·min^{-1}. NovaMALS software (PostNova Analytics) was used to determine the molecular weight characteristics using calculated dn/dc values.

^{1}H nuclear magnetic resonance (NMR) spectroscopy was conducted on a Varian Unity 400 MHz spectrometer at 400 MHz using deuterated solvent (CDCl$_3$) as reference and at a sample concentration of ~ 20 mg·mL^{-1}.

Atomic force microscopy (AFM) images of air-dried films on silicon wafers were acquired with an MFP-3D Asylum Research instrument. Typical scans were conducted in AC mode with ultrasharp SiN gold-coated cantilevers (MikroMasch, Bulgaria). Image processing and surface roughness analysis were performed using the Nanoscope and Igor Pro software programs, respectively. Film thicknesses were estimated by film scratching (mechanical removal) and by

tracing a profile along the film and the scratched zone. The thickness measurements reported represent mean values over 3 different analysis sites per substrates.

The surface morphology of free standing films and the films on silicon wafers were imaged by SEM using a FEI Quanta 200 ESEM FEG. Samples were pre-coated with gold using a Dynavac Mini sputter coater prior to imaging.
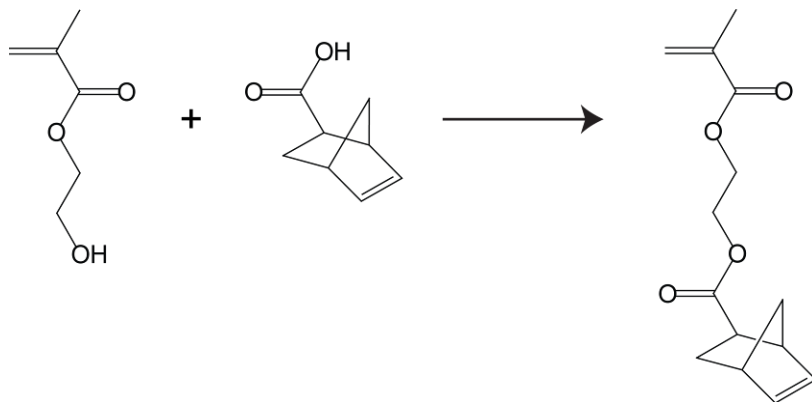
Contact angle measurements were conducted with a Data Physics OCA 20 Tensiometer. Measurements were recorded with OCA software, using a sessile drop profile.

Experimental Methods

**1. Monomer and polymer preparation**

*1.1 Synthesis of **P1***

1.1.1 Synthesis of 2-(methacryloyloxy)ethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate

To a solution of 2-hydroxyethyl methacrylate (1.30 g, 10.0 mmol) and 5-norbornene-2-carboxylic acid (1.45 g, 10.5 mmol) dissolved in anhydrous DCM (50 mL), was added EDCI (2.30 g, 12.0 mmol) and DMAP (146 mg, 1.2 mmol). The reaction mixture was stirred at 25 °C for 4 h, and then washed with saturated $NaHCO_3$ (2 x 30 mL), 0.5 M HCl solution (2 x 30 mL), brine (30 mL), and water (30 mL). The organic phase was then dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford the monomer as a light yellow oil, 2.22 g (81 %). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ_H 6.15-6.05 & 5.86-5.83 (*m*, 2H, **CH**=**CH**), 6.08 (*s*, 2H, CH**H**=CCH₃), 5.55 (*s*, 2H, C**H**H=CCH₃), 4.34-4.16 (*m*, 4H, **CH₂**OC(=O)), 3.15 (*s*, 1H, **CH**), 2.90 (*m*, 1H, **CH**),

2.85 (*m*, 1H, **CH**), 2.21-2.17 & 1.86-1.82 (*m*, 1H, **CH**H), 1.90 (*s*, 3H, **CH₃**), 1.46-1.44 & 1.38-1.34 (*m*, 1H, C**H**H), 1.36-1.34 (*m*, 1H, **CH**H), 1.31-1.29 & 1.23-1.21 (*m*, 1H, C**H**H) ppm.

*1.1.2 Synthesis of **P1***

P1
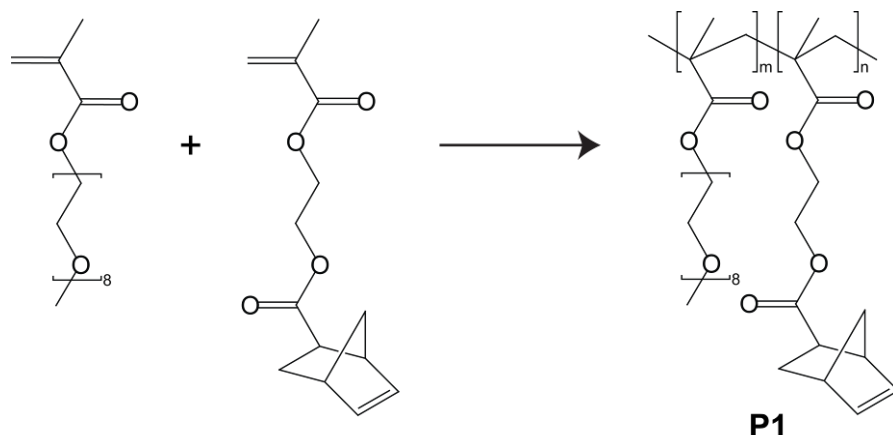
A solution of oligo(ethylene glycol) methyl ether methacrylate (0.576 g, 1.2 mmol), 2-(methacryloyloxy)ethyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (0.075 g, 0.3 mmol) and AIBN (0.005 g, 0.03 mmol) in 1,4-dioxane (4 mL) was degassed by bubbling nitrogen through the mixture for 20 min at room temperature. The reaction mixture was then heated to 100 °C for 2 h under nitrogen. The reaction mixture was cooled to room temperature, and precipitated into DEE:hexane (7:2) solution (45 mL). The precipitate was isolated by centrifugation, re-dissolved in THF (3 mL), and then re-precipitated into DEE:hexane (7:2) solution (45 mL). The precipitate was isolated by centrifugation, and dried *in vacuo* (20 mbar, 25 °C) for 24 h to yield [POEGA-*co*-NB] **P1** as a white viscous liquid, 0.46 g (71 %). GPC-DRI (THF): M_n = 31.6 kDa, M_w/M_n = 1.8; ¹H NMR (400 MHz, CDCl₃, 25 °C) δ_H 6.19-6.14 & 5.91 (*m*, 2H, **CH**=**CH**), 4.20-4.00 (*m*, 2H, **CH₂**OC(=O), ester groups), 3.63 (*m*, 4H, **CH₂CH₂**O, ethylene glycol groups), 3.05-2.90 (*m*, 3H, **CH** + **CH** + **CH**), 2.22 (*m*, 1H, **CH**H), 2.13 (*m*, 3H, **CH₃**), 1.92-1.76 (*m*, 1H, **CH**HCH₃), 1.51-1.29 (*m*, 3H, C**H**H + C**H**H + C**H**H), 1.10-0.70 (*m*, 1H, C**H**HCH₃) ppm. Pendant norbornene functionality was 18 mol% as determined by ¹H NMR spectroscopic analysis.

*1.2 Synthesis of **P2***

The synthesis of norbornene functionalised P(EO-*co*-Gly) **P2** was adapted from the literature,[1] and involved three steps: (i) the copolymerization of ethylene oxide (EO) and 2,3-epoxypropyl-1-ethoxyethyl ether protected glycidol (EEGE) to prepare the copolymer P(EO-*co*-EEGE); (ii)

hydrolysis of the copolymer to form poly(ethylene oxide-*co*-glycidol) (P(EO-*co*-Gly)), and; (iii) the partial esterification of P(EO-*co*-Gly) with norbornene carboxylic acid.

1.2.1 Synthesis of copolymer P(EO-co-EEGE)

Copolymerization was conducted according to the literature under the guidance of A. Prof. Wang (Fudan University, China).[1] GPC-MALLS (DMF): M_n = 22.7 kDa, M_w/M_n = 1.08; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ_H 1.20-1.15 (*m*, 3H, C*H₃*CH$_2$O), 1.30-1.22 (*m*, 3H, O(C*H₃*)CHO), 3.79-3.41 (*m*, 4H, **CH₂CH₂O**), 4.74-4.62 (*s*, 1H, O(CH$_3$)**CHO**-) ppm.

1.2.2 Synthesis of copolymer poly(ethylene oxide-co-glycidol) [P(EO-co-Gly)]

Deprotection of P(EO-*co*-EEGE) was conducted according to the literature.[1] GPC-MALLS (DMF): M_n = 21.1 kDa, M_w/M_n = 1.10; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ_H 3.79-3.41 (*m*, 4H, **CH₂CH₂O**) ppm

*1.2.3 Synthesis of copolymer P(EO-co-NB) **P2***

P(EO-*co*-Gly) (500 mg, 0.03 mmol, 1 equiv.), norbornene-2-carboxylic acid (69.1 mg, 0.5 mmol, 20 equiv.), EDCI (95.9 mg, 0.5 mmol, 20 equiv.) and DMAP (6.11 mg, 0.05 mmol, 2 equiv.) were dissolved in DCM (10 mL) and stirred at 30 °C for 18 h. The crude reaction mixture was then concentrated *in vacuo* (1 mbar, 30 °C), redissolved in MeOH (2 mL) and dialyzed (MWCO = 3500 g·mol⁻¹) against H$_2$O and subsequently methanol for 2 d. The solution was then concentrated *in vacuo* (1 mbar, 50 °C), and the residue was re-dissolved into DCM (2 mL) and precipitated into DEE (20 mL). The product was collected by centrifugation and dried *in vacuo* (1 mbar, 30 °C) to afford **P2** as a white powder, 307 mg (62 %). GPC-MALLS (DMF): M_n = 20.6 kDa, M_w/M_n = 1.81; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C) δ_H 1.54-1.26 (*m*, 4H, **CH₂**CHC**H₂**), 3.04-2.89 (*m*, 3H,**CH**CHCH$_2$**CH**), 4.32-3.94 (*m*, 2H, OC**H₂**CH), 6.19-5.91 (*m*, 2H, **CH=CH**) ppm. Pendant norbornene functionality was 5 mol% as determined by ^{1}H NMR spectroscopic analysis.

*1.3 Synthesis of **P3***

The synthesis of norbornene functionalised P3HT **P3** was adapted from the literature.[2]

2. Planar template preparation

2.1 Deposition of allyl-PEI

A Si wafer (~ 1 × 1 cm) was added to a 7 mL vial containing 1 mL of allyl-PEI[3] solution (1 mg·mL^{-1} in 0.5 M NaCl, passed through a 0.45 μm filter). The Si wafer was allowed to stand for 1 h at room temperature, removed and washed with water (1 × 20 mL), THF (2 × 20 mL) and DCM (3 × 20 mL). The obtained allylated Si wafer was then ready for immediate use in the CIC process.

2.2. Film assembly and CIC

As a general example, the allyl-functionalised wafer (from method 2.1) was spin-coated with macrocross-linker in CHCl$_3$ (50 μL, 20 mg·mL^{-1}, 2000 rpm, 33 s), then immersed in Ru catalyst solution (1 mL, 0.05-0.5 mg·mL^{-1} in dry DEE) for a predetermined period of time. The wafer was then washed with and soaked in DCM for 12 h to remove any non-cross-linked polymers, and dried *in vacuo* prior to analysis. Different concentrations of polymer solutions were used in the spin-coating step to obtain various film thicknesses (i.e., 10 ~ 30 mg·mL^{-1}).

3. Multi-layering

Multi-layering of films on planar substrates

As a general example, the previously assembled CIC film (i.e., L1) on Si wafer was spin-coated with macrocross-linker in CHCl$_3$ (50 μL, 20 mg·mL^{-1}, 2000 rpm, 33 s). The wafer was soaked in 2nd Gen. Grubbs catalyst solution (1 mL, 0.5 mg·mL^{-1} in dry DEE) for 30 min, and washed with and soaked in DCM as previously described. The wafer was dried *in vacuo* and the cross-linked films (i.e., L2) were analyzed. This process was repeated to obtain multi-layered films.

4. Patterning

1.1 Patterning via selective CIC

As a general example, the allyl-functionalised wafer (from method 2.1) was spin-coated with macrocross-linker **P3** in CHCl$_3$ (50 μL, 20 mg·mL^{-1}, 2000 rpm, 33 s), dried, then a solution of

the modified Ru catalyst (0.5 mg·mL^{-1} in cyclohexanone) was placed onto selected regions of the spin-coated film using a micropipette. After 3min, the film was washed with and soaked in chloroform for 12 h to remove any non-cross-linked polymers, and dried *in vacuo* prior to analysis.
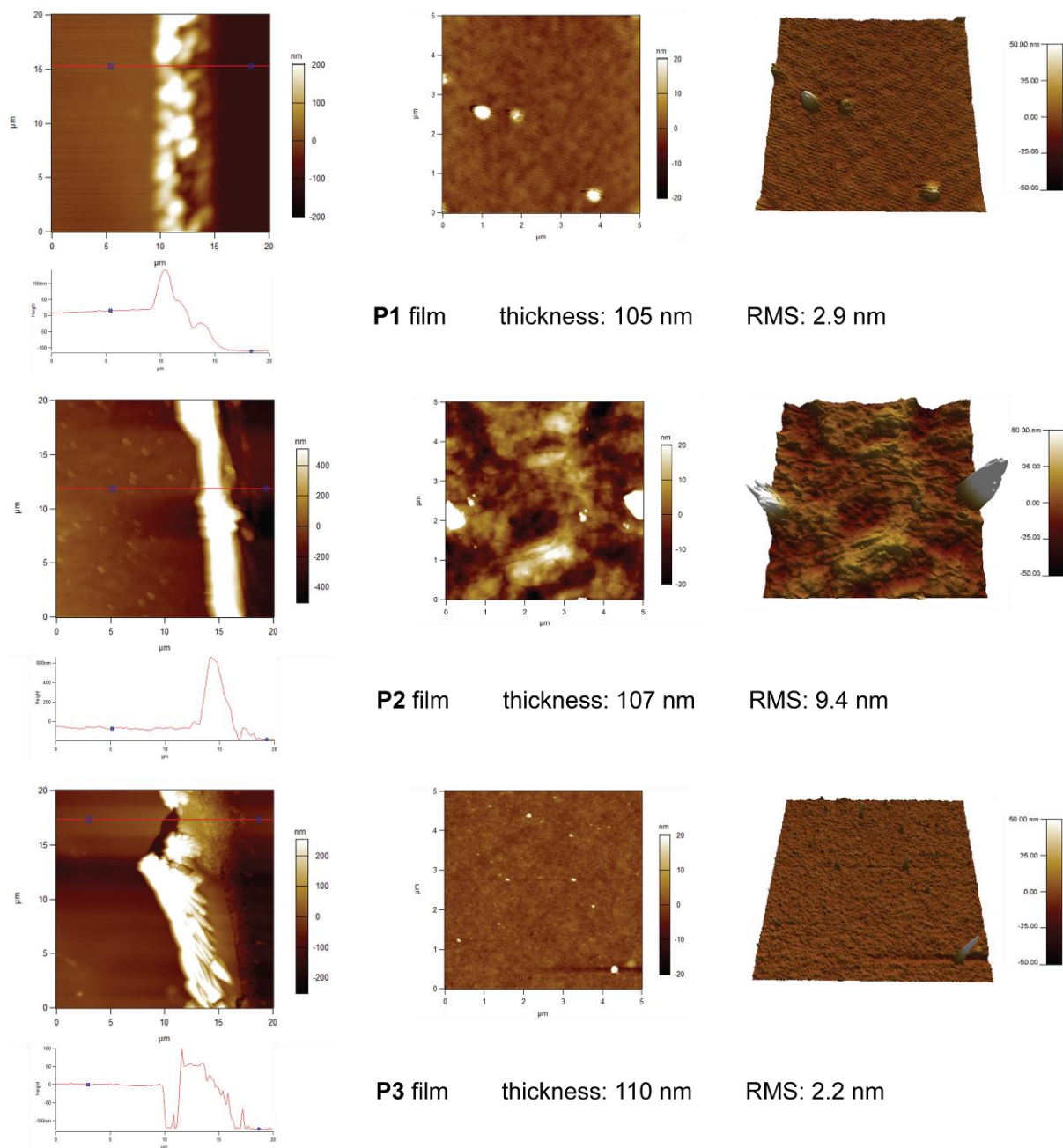
1.2 Microcontact printing

A robotic contact plotter (XactII Compact Microarrayer System, Labnext, USA) equipped with a hollow pin (Xtend microarray pin) with a diameter of 80 μm was used to dispense the catalyst solution (5 mg·mL^{-1} modified catalyst in 1:1 v/v diethyl ethylene glycol: dibutylphthalate) onto the P3HT **P3** coated substrate in a square microarray format (6 × 7 spots). The centre-to-centre distance between spots was set to 700 μm to avoid spot overlapping. After 24 h the substrates were washed to remove non-cross-linked polymer and the pattern was analysed via AFM.

4. Supporting Figures

P1 film
thickness: 100 nm

P2 film
thickness: 109 nm

P3 film
thickness: 107 nm
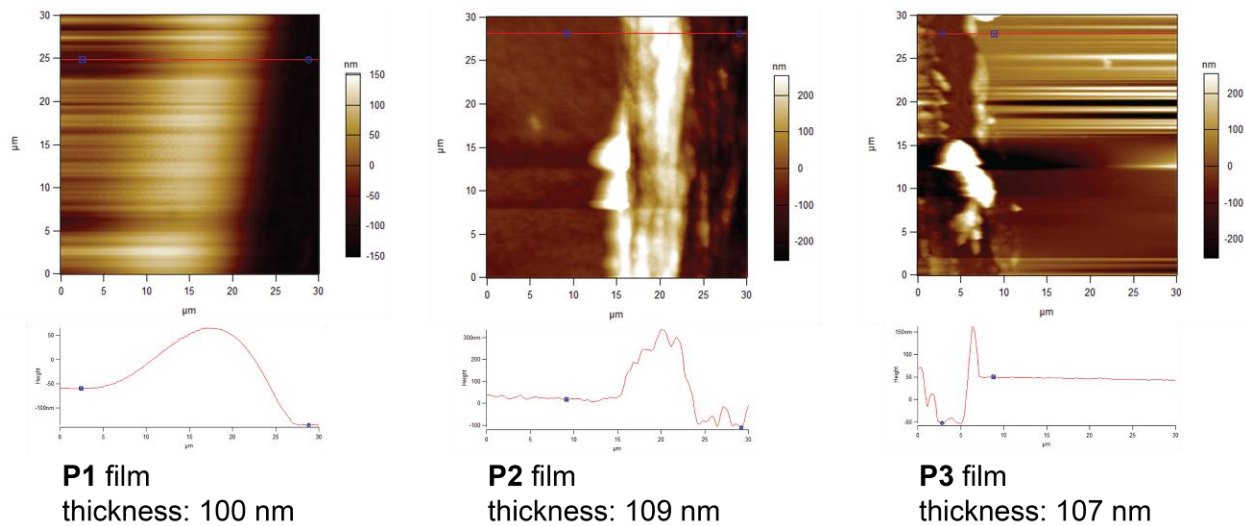
Figure S1. AFM height mode images (30 × 30 μm) and z-profile of the scratched zone of POEGMA **P1**, PEG **P2** and P3HT **P3** spin-coated films.

**P1** film   thickness: 105 nm   RMS: 2.9 nm

P2 film   thickness: 107 nm   RMS: 9.4 nm

P3 film   thickness: 110 nm   RMS: 2.2 nm

Figure S2. AFM height mode images (20 × 20 µm) and z-profile of the scratched zone (left), and (3D) height mode images (5 × 5 µm; middle and right) of POEGMA **P1**, PEG **P2** and P3HT **P3** cross-linked films.
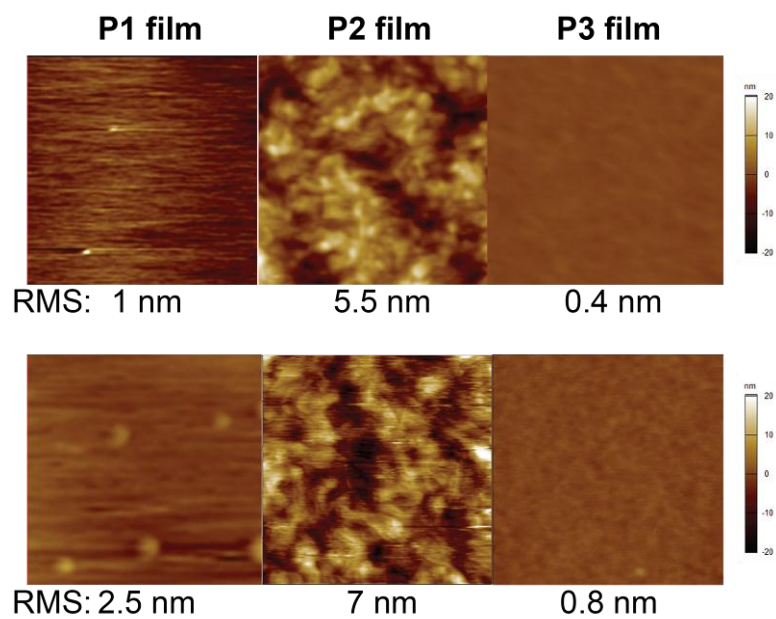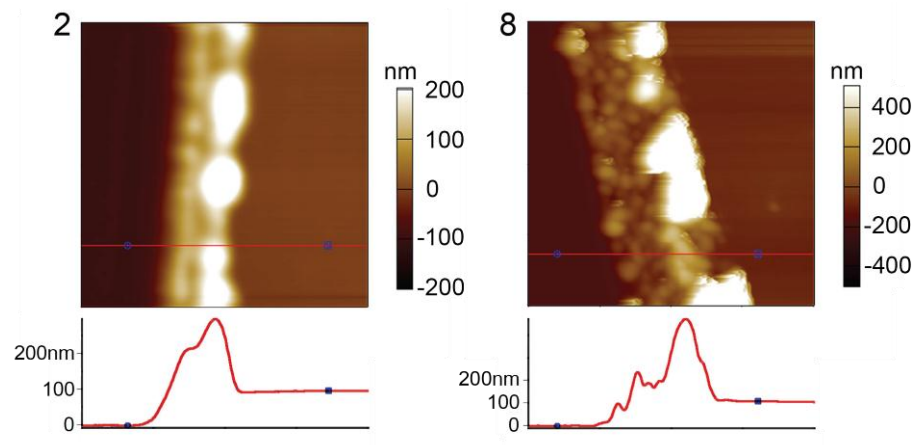
Figure S3. AFM height mode images (5 × 5 μm) of POEGMA **P1**, PEG **P2** and P3HT **P3** non-cross-linked films before (top) and after (bottom) soaking in DEE.
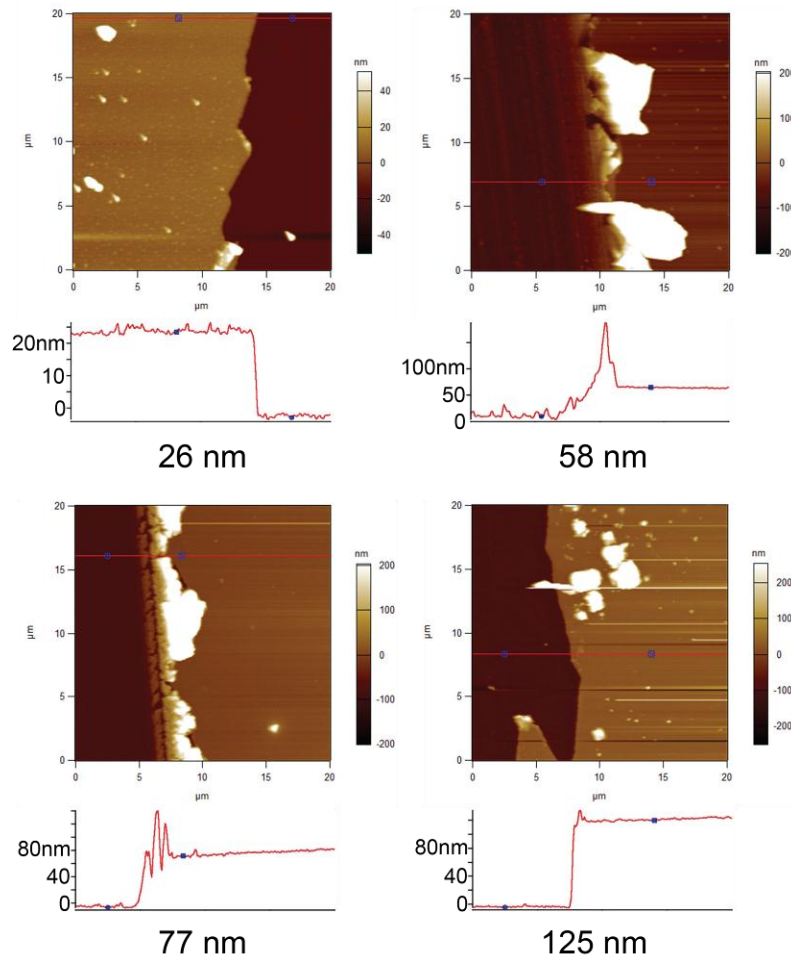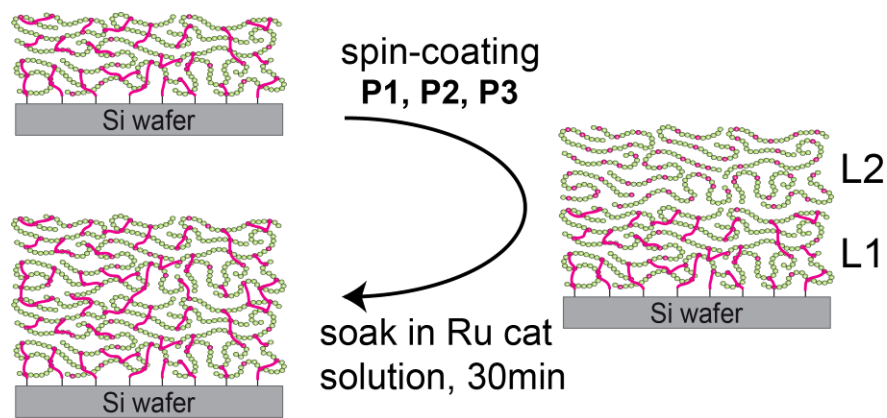
Figure S4. AFM height mode images (20 × 20 μm) and z-profile of the scratched zone of P3HT **P3** cross-linked films with different film thicknesses.

(a)

(b)

A 0.50 mg·mL⁻¹, 3 min   B 0.50 mg·mL⁻¹, 30 min

C 0.25 mg·mL⁻¹, 30 min   D 0.05 mg·mL⁻¹, 30 min
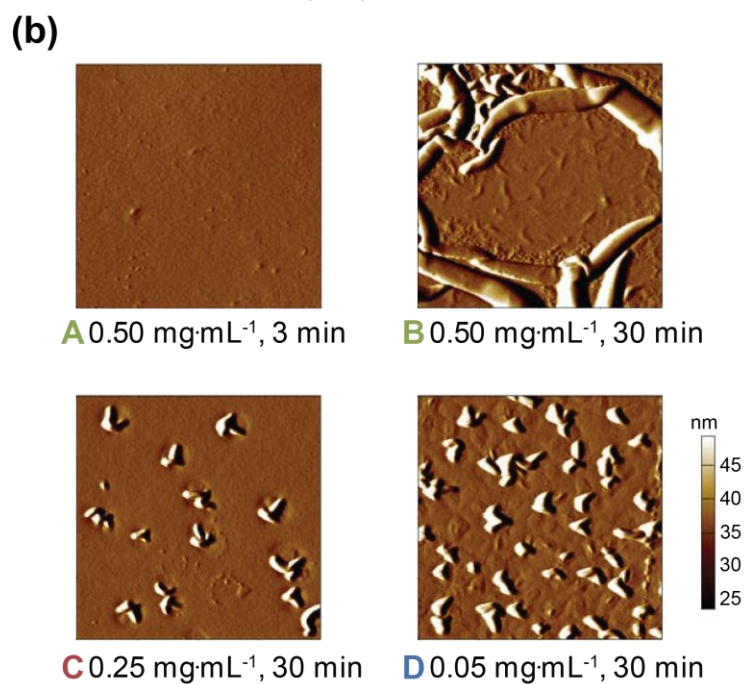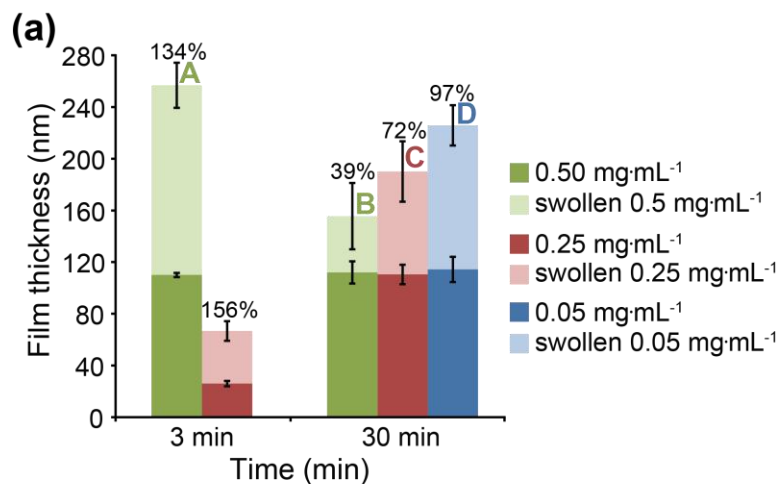
Figure S5. a) Thicknesses of swollen POEGMA **P1** films formed via CIC at different catalyst concentrations and reaction (contact) times, as determined by solution AFM analysis. All experiments were completed in triplicate. b) 20 × 20 μm AFM amplitude retrace images of swollen **P1** films in water for 21 h.

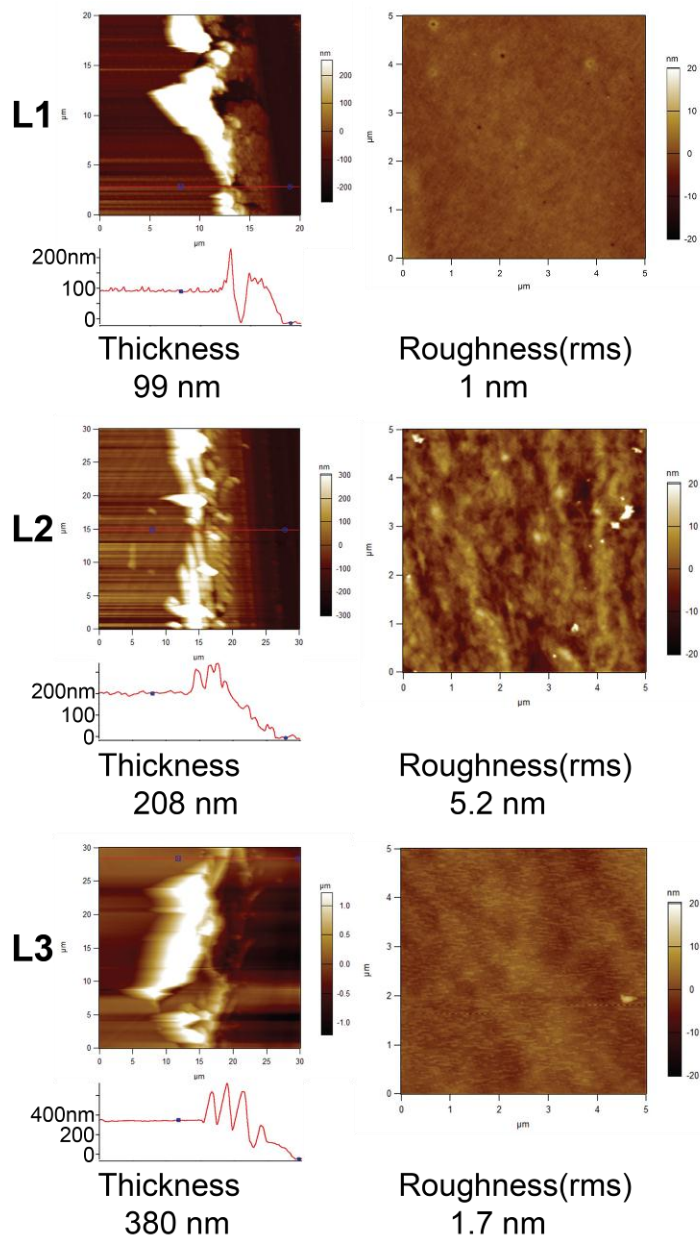**Figure S6.** AFM height mode images (20 × 20 μm) and z-profiles of the scratched zones of POEGMA **P1** films on the second and eighth substrates prepared using the same catalyst solution (0.5 mg·mL^{-1} in DEE, 1 mL).
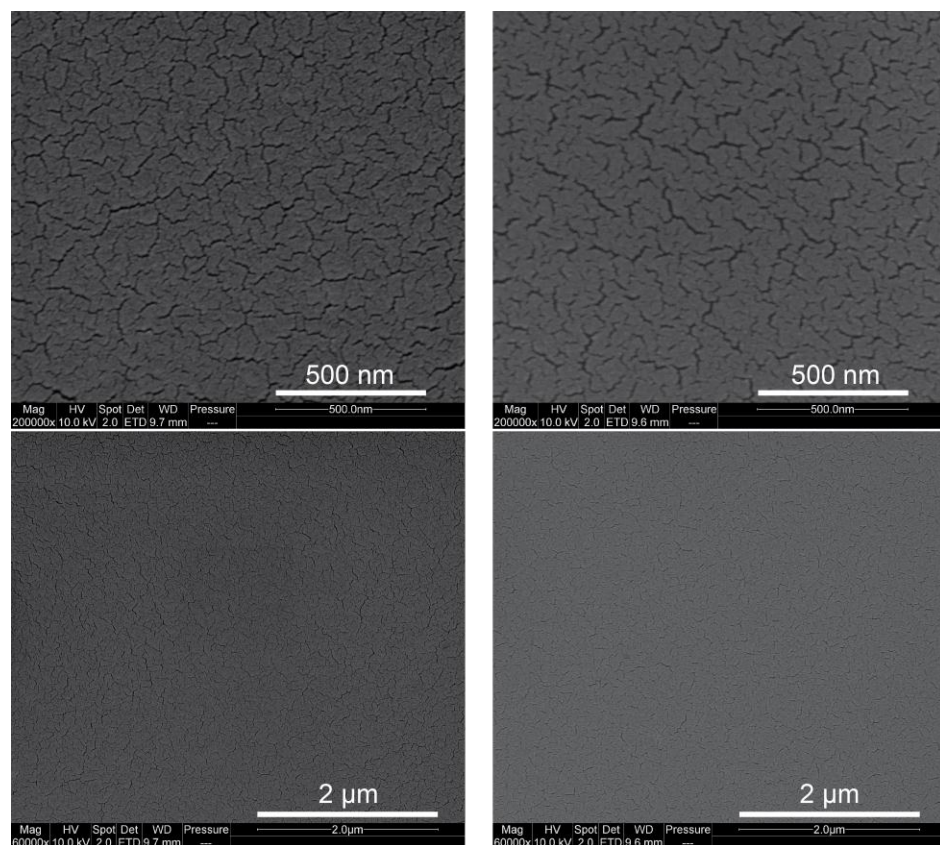

Figure S7. General scheme showing the formation of multi-layered, cross-linked films through consecutive CIC cycles.

Figure S8. AFM height mode images (20 × 20 μm) and z-profiles (left), and height mode images (5 × 5 μm) (right) of each layer of the **P3-P2-P3** multi-layered film prepared from PEG **P2** (L2) and P3HT **P3** (L1 and L3).

Figure S9. SEM images of cross-linked free-standing P3HT **P3** film (left) and cross-linked **P3** film attached on Si wafer (right).

References

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3. T. K. Goh, S. N. Guntari, C. J. Ochs, A. Blencowe, D. Mertz, L. A. Connal, G. K. Such, G. G. Qiao and F. Caruso, *Small*, 2011, **7**, 2863.