Supporting Information

Fabrication of Ultra-thin Polyrotaxane based Films via Solid-state Continuous Assembly of Polymers

Shereen Tan,1 EunHyung Nam,1 Jiwei Cui,1 ChenLong Xu,1 Qiang Fu,1 Jing M. Ren,1 Edgar H. H. Wong,1 Katharina Ladewig,1 Frank Caruso,1 Anton Blencowe,2,* Greg G. Qiao1,*

1Department of Chemical and Biomolecular Engineering, The University of Melbourne, Parkville, Victoria 3010, Australia.

2Mawson Institute, Division of ITEE, The University of South Australia, Mawson Lakes, South Australia, 5095, Australia

Correspondence to: Email: gregghq@unimelb.edu.au; Tel.: +613 83448665
Email: anton.blencowe@unisa.edu.au; Tel.: +618 83023490
1. Experimental section

1.1 Materials:

α-Cyclodextrin (α-CD, 98%), poly(ethylene glycol) (MALDI TOF MS: $M_n = 11.1$ kDa and $M_n \approx 400$ Da), $N,N'$-dicyclohexylcarbodiimide (DCC, 99%), 5-hexynoic acid (97%), tetra-n-butylammonium hydrogen sulphate (TBAHS) (99+%), 3-chloro-1-propanol (98%), copper (I) bromide (Cu(I)Br, purum), $N,N,N',N''$-pentamethyldiethylenetriamine (PMDETA, 99%), 5-norbornene-2-methanol (mixture of endo and exo, 99%), 5-norbornene-2-carboxylic acid (mixture of endo and exo, 98%), Norbornylene (99%), succinic anhydride (>99%), triethylamine (TEA, >99%), allyl bromide (99%), poly(ethylene imine) (PEI) ($M_w \approx 25.0$ kDa) and di(ethylene glycol) vinyl ether (98%) were purchased from Sigma-Aldrich and used as received. 9-Anthracenecarboxylic acid (purum, Fluka), thionyl chloride (Merck), magnesium sulphate (MgSO$_4$) (anhydrous, Merck), sodium azide (99%, Chem-Supply), ethylenediaminetetraacetic acid (EDTA, 99%, Adrich), 4-(dimethylamino)pyridine (DMAP, 99%, Fluka), pyridine (AR grade, >99.5 %, Scharlau), $N,N$-dimethylformamide (DMF, anhyd. 99.8%, Acros Organics) and $N$-(3-(dimethylamino)propyl)-$N$-ethylcarbodiimide hydrochloride (EDCI, 98+, Acros Organics) were all used as received. Metathesis catalyst (IMesH$_2$)(Cl)$_2$(C$_5$H$_5$N)$_2$Ru=CHPh (C1) was prepared from the 2nd generation Grubbs catalyst (Aldrich), as described in the literature.\textsuperscript{1} SnakeSkin dialysis tubing (MWCO = 3500 and 7000 g.mol$^{-1}$) was obtained from Thermo Scientific. Dimethyl sulfoxide (DMSO), diethyl ether (DEE), dichloromethane (DCM), methanol (MeOH), hexane and ethyl acetate were obtained from Chem-Supply and used as received. Anhydrous and deoxygenated DCM and tetrahydrofuran (THF) were obtained by distillation under argon from CaH and sodium benzophenone ketyl, respectively. Deuterated dimethylsulfoxide (d$_6$-DMSO), methanol (CD$_3$OD) and chloroform (CDCl$_3$) were obtained from Cambridge Isotope Laboratories and used as received. Dulbecco’s Phosphate-Buffered Saline (DPBS) and Calcein AM were purchased from Molecular Probes (Australia). Dulbecco’s Modified Eagles’ Medium (DMEM) with 1% of glutamax and fetal bovine serum (FBS) were obtained from Invitrogen. 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 (sulphuric acid : hydrogen peroxide = 7 : 3). \textbf{Caution!}
Piranha solution is highly corrosive and extreme care should be taken during preparation and use. The slides were then washed thoroughly with Milli-Q water between each step.

1.2 Methods:

*Synthesis of 3-azidopropyl anthracene-9-carboxylate*

3-Azidopropyl anthracene-9-carboxylate was synthesised according to the literature.\(^1\) \(^2\) \(^3\) \(^4\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ\(_H\) 2.09 (quin, 2H, \(J = 6.4\) Hz, CH\(_2\)), 3.45 (t, 2H, \(J = 5.2\) Hz, OCH\(_2\)), 4.67 (t, 2H, \(J = 5.2\) Hz, CH\(_2\)N\(_3\)), 7.44-7.54 (m, 4H, 4ArH), 7.99-8.01 (m, 4H, 4ArH), 8.48 (s, 1H, ArH) ppm.

*Synthesis of \(\alpha,\omega\)-dialkyne PEG\(_{10k}\)*

\(\alpha,\omega\)-Dialkyne PEG\(_{10k}\) was synthesised according to the literature.\(^1\) \(^2\) \(^3\) \(^4\)

\(^1\)H NMR (400 MHz, d\(_6\)-DMSO): δ\(_H\) 1.69 (quin, \(J = 7.2\) Hz, CH\(_2\)CH\(_2\)CH\(_2\) end-group), 2.20 (dt, \(J = 2.8\) & 7.2 Hz, \(\equiv CCH\(_2\) end-group), 2.40 (t, \(J = 7.2\) Hz, CH\(_2\)CO end-group), 2.80 (t, \(J = 2.8\) Hz, C\(\equiv CH\) end-group), 3.69-3.30 (m, CH\(_2\)O), 4.14-4.11 (m, CH\(_2\)OCO end-group) ppm. MALDI ToF MS: \(M_n\) = 11.3 kDa, GPC-MALLS (DMF): PDI = 1.32.

*Synthesis of bisnorbornyl terminated poly(ethylene glycol)PEG\(_{400Da}\) M2*

Bisnorbornyl terminated poly(ethylene glycol)PEG\(_{400Da}\) was synthesised according to the literature.\(^1\) \(^2\) \(^3\) \(^4\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) δ\(_H\) 1.04-1.98 (m, 4H, CH\(_2\)CHCH\(_2\)), 3.24-2.86 (m, 3H, CHCH\(_2\)CH\(_2\)), 4.35-3.50 (m, 4H, OCH\(_2\)CH\(_2\)), 6.23-5.89 (m, 2H, CH=CH) ppm. \(T_g\) was -30 °C as determined by DSC.

*Synthesis of norbornylene methoxy-4-oxobutanoic acid*

5-Norbornene-2-methanol (1.00 mL, 8.27 mmol, 1 equiv.), succinic anhydride (1.66 g, 16.5 mmol, 2 equiv.) and TEA (0.61 mL, 8.27 mmol, 1 equiv.) were dissolved in distilled THF (20 mL) and the mixture was stirred at 30 °C for 18 h. TLC on silica plates (1 : 1 hexane : ethyl acetate) revealed one major product with an \(R_f\) value of 0.23. The crude product was concentrated *in vacuo* (20 mbar, 40 °C) and the residue was purified by flash chromatography on a silica gel column (5 cm diameter × 40 cm length) eluting with hexane : ethyl acetate, 1 : 1 (0.5 L). The fractions containing pure product we collected and concentrated *in vacuo* (20 mbar, 60 °C) to obtain a viscous clear liquid, 1.2
g (73%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta_{^1}$H 0.52-0.57 (dd, 4H, $J = 1.6, 7.2, CH_2CHCH_2$), 1.12-1.46 (m, 4H, $J = 1.6, 7.2, CH_2CHCH_2$), 2.61-2.87 (m, 5H, CHCHCH, COCH$_2$CH$_2$CO), 3.66-3.91 (m, 2H, CHCH$_2$CH), 5.91-6.16 (m, 2H, CHCH) ppm.

Synthesis of poly(ethylene glycol)PEG$_{10K}$-α-CD based polyrotaxane

(i) Formation of polypseudorotaxanes:

α,ω-Dialkyne PEG$_{10K}$ (1 g, 0.09 mmol, 1 equiv.) was dissolved in Milli-Q (5 mL) at 60 °C with stirring and an aqueous solution of α-CD (2.55 g, 0.22 M) was added drop-wise. The mixture was stirred for 18 h at 60 °C before being brought back to 30 °C for a further 48 h. The solution was then lyophilised (0.1 mbar) to afford the polypseudorotaxane as a white solid.

(ii) Formation of polyrotaxanes:

The polypseudorotaxane (3.55 g, 0.09 mmol, 1 equiv.), 3-azidopropyl anthracene-9-carboxylate (0.16 g, 0.52 mmol, 5.8 equiv.) and PMDETA (0.07 g, 0.04 mmol, 0.5 equiv.) were dissolved in DMF (100 mL) and the mixture was degassed by bubbling argon through it for 1 h. Cu(I)Br (0.03 g, 0.04 mmol, 0.4 equiv.) was then added and the mixture was stirred at 30 °C for 48 h. The crude reaction mixture was then concentrated in vacuo (0.1 mbar, 40 °C), redissolved in DMSO (5 mL) and dialyzed (MWCO = 7000 g.mol$^{-1}$) against EDTA solution (0.04 M), followed by water and methanol for 4 d to remove the copper complexes. The dialyzed product was then precipitated into DEE and dried in vacuo (0.1 mbar, 60 °C) to afford the polyrotaxane as a white powder, 1.33 g (37%). $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta_{^1}$H 1.79 (quin, 2H, $J = 7.2$ Hz, CH$_2$CH$_2$CH$_2$), 2.20 (dt, 2H, $J = 2.8 & 7.2$ Hz, =CCCH$_2$H$_2$), 2.34-2.41 (m, 4H, COCH$_2$CH$_2$, CH$_2$CH$_2$O), 3.29-3.69 (m, CH$_2$O), 4.11-4.14 (m, 4H, CH$_2$CH$_2$O), 4.80 (d, 6H, OCHCH$_2$ of α-CD), 5.38-5.64 (s, 12H, CH$_2$OH of α-CD), 7.61 (q, 4H, ArH), 7.90 (s, 1H, =CHN), 8.01 (d, 2H, ArH), 8.20 (d, 2H, ArH), 8.80 (s, 1H, ArH) ppm.

Synthesis of norbornene functionalized polyrotaxanes P1

The polyrotaxane (0.30 g, 0.02 mmol, 1 equiv.), norbornylene methoxy-4-oxobutanoic acid (0.70 g, 0.31 mmol, 14 equiv.), EDCI (0.66 g, 0.31 mmol, 14 equiv.) and DMAP (0.04 g, 0.03 mmol, 1.5 equiv.) were dissolved in anhydrous DMF (5 mL) and stirred at 30 °C for 36 h. The crude reaction mixture was then concentrated in vacuo (0.1 mbar, 50 °C),
redissolved in methanol (3 mL) and dialyzed (MWCO = 7000 g.mol\(^{-1}\)) against methanol for 3 d. The dialyzed product was then precipitated into DEE and dried in vacuo (0.1 mbar, 60 °C) to afford **P1** as a slight yellow powder, 210 mg (70 %). \(^1\)H NMR (400 MHz, \(d_6\)-DMSO): \(\delta_H\) 1.79 (quin, 2H, \(J = 7.2\) Hz, \(\text{CH}_2\text{CH}_2\text{CH}_2\)), 2.20 (dt, 2H, \(J = 2.8\) & 7.2 Hz, =\(\text{CH}_2\text{CH}_2\)), 2.34-2.41 (m, 4H, \(\text{COCH}_2\text{CH}_2\), \(\text{CH}_2\text{CH}_2\)O), 3.29-3.69 (m, \(\text{CH}_3\text{O}\)), 4.11-4.14 (m, \(\text{CH}_3\text{O}\)), 4.80 (d, 6H, \(\text{OC}\text{H}\text{CH}_2\text{O}\) of \(\alpha\text{-CD}\)), 5.38-5.64 (s, 12H, \(\text{CH}_2\text{OH}\) of \(\alpha\text{-CD}\)), 7.61 (q, 4H, ArH), 7.90 (s, 1H, =\(\text{CHN}\)), 8.01 (d, 2H, ArH), 8.20 (d, 2H, ArH), 8.80 (s, 1H, ArH) ppm.

**Synthesis of norbornene functionalised poly(ethylene oxide-co-glycidol) (P(EO-co-Gly)), P2**

The synthesis of norbornene functionalised P(EO-co-Gly) was adapted from the literature,\(^5\) 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. **Synthesis of copolymer P(EO-co-EEGE)**

Copolymerization was conducted according to the literature under the help of A. Prof. Wang (Fudan University, China).\(^4\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta_H\): 1.20-1.15 (m, 3H, \(\text{CH}_3\text{CH}_2\)), 1.30-1.22 (m, 3H, O(\(\text{CH}_3\))CHO), 3.79-3.41 (m, 4H, \(\text{CH}_2\text{CH}_2\)O), 4.74-4.62 (s, 1H, O(\(\text{CH}_3\))CHO-) ppm. GPC-MALLS (DMF)-\(M_n\) = 22.7 kDa, PDI = 1.08.

2. **Synthesis of copolymer P(EO-co-Gly)**

Deprotection of P(EO-co-EEGE) was conducted according to the literature.\(^3\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta_H\): 3.79-3.41 (m, 4H, \(\text{CH}_2\text{CH}_2\)O). GPC-MALLS (DMF)-\(M_n\) = 21.1 kDa, PDI = 1.10.

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 redissolved 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 %). $^1$H NMR (400 MHz, CDCl₃) $\delta$H: 1.54-1.26 (m, 4H, CH₂CHCH₂), 3.04-2.89 (m, 3H, CH₂CHCH₂), 4.32-3.94 (m, 2H, OCH₂CH), 6.19-5.91 (m, 2H, CH=CH) ppm. GPC-MALLS (DMF) $M_n$ = 20.6 kDa, PDI = 1.81.

### 1.2.1 Planar template preparation:

Planar template preparation was adapted from the literature.³

*(i) Allyl functionalization of Si wafer by deposition of allyl-PEI*

A Si wafer (*ca.* 1 × 1 cm) was added to a 7 mL vial containing 1 mL of allyl-PEI 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 30 min 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 functionalization with Ru catalyst.

*(ii) Surface immobilization of Ru catalyst initiating moieties on allylated Si wafer*

To a dry 5 mL round bottom flask equipped with magnetic stirrer bar and 3-way stopcock was added the catalyst (IMes)Cl₂(C₅H₅N)₂Ru=CHPh C1 (2.9 mg, 4 μmol) and DCM (1 mL) under argon to yield a 4 mM stock solution. Separately, the allylated Si wafer (from method 2.1) was added to a 7 mL vial (dried and backpurged with argon). This was followed by the addition of 1 mL of the catalyst stock solution to the vial using a gas-tight syringe. The Si wafer and stock solution were allowed to stand at room temperature for 30 min. The catalyst-functionalized wafers were washed with DCM (2 × 20 mL) and coated with the macrocross-linkers.
(iii) Film assembly via solid state CAP$_{\text{ROMP}}$

The catalyst-functionalised wafer was spin-coated with the macrocross-linker, or a mixture of the macrocross-linker and additive, in $d$-MeOH (50 μL, 10 mg·mL$^{-1}$, 1500 rpm, 33 s) and then annealed at 70 °C under argon for 24 h. The ssCAP$_{\text{ROMP}}$ reaction was stopped by soaking the wafer in MeOH (5 mL) containing 2% v/v DEVE for 1 h. The polymer-coated wafer was subsequently washed with and soaked in MeOH (1 mL) for 12 h to remove any non-cross-linked polymers, and dried in vacuo before analysis.

(iv) CAP re-initiation on planar substrates

The previously assembled CAP film (i.e., L1) on Si wafer was added to a vial containing 1 mL of a solution of catalyst (IMes)(Cl$_2$)(C$_5$H$_5$N)$_2$Ru=CHPh C1 (4 μmol in DCM). After 30 min of soaking, the catalyst refunctionalized substrate was removed, washed with DCM (2 × 20 mL) and spin-coated with the macrocross-linker, or a mixture of the macrocross-linker and additive, in $d$-MeOH (50 μL, 10 mg·mL$^{-1}$, 1500 rpm, 33 s). After annealing at 70 °C under argon for 24 h, the substrate was immersed in 2% v/v DEVE in MeOH (5 mL) for 1 h and then washed with MeOH as previously described. After drying in vacuo the CAP films (i.e., L2) were analyzed and used for subsequent layering experiments (i.e., L3 to L4) via repetition of the above procedure.

1.2.2 Film Swelling Studies

ssCAP films (L4) were swelled in distilled water for 2 d and thickness measurements of the films before (dry-state) and at the swollen (wet) state were measured using AFM scratch analysis. The degree of swelling of the films was measured by calculating each films equilibrium swelling ratio (ESR %) according to the formula below:

$$ESR(\%) = \frac{\text{thickness}_{\text{swollen}} - \text{thickness}_{\text{dry}}}{\text{thickness}_{\text{dry}}} \times 100$$  \hspace{1cm} \text{Equation 1}

1.2.3 Cell attachment studies

NIH/3T3 cells (ATCC CRL-2752) were maintained at 37 °C with 5% CO$_2$ in DMEM containing 10% (v/v) of FBS and 1% (v/v) of glutamax. Disk glass slides (diameter 18
mm) were cleaned with piranha solution (7:3 v/v mixture of concentrated sulfuric acid and 30% hydrogen peroxide), rinsed with water and dried with nitrogen gas. *Caution!* *Piranha solution is highly corrosive and extreme care should be taken during preparation and use.* CAP films were fabricated on disk glass slides for cell attachment studies. Prior to the experiments, substrates were rinsed with ethanol and copious amounts of DPBS. Disk glass slides with different surface chemistry were transferred into a 12-well plate. Each well was seeded with $8 \times 10^4$ cells in DMEM (pH 7.4). After 24 h incubation at 37 °C in 5% CO$_2$ and 100% relative humidity, unattached cells were removed by gently washing with DPBS, and the cells on different substrates were stained with 600 µL of Calcein AM solution for 10 min (1 µL of dye with a concentration of 1 mg.mL$^{-1}$ diluted with 2 mL of DPBS). Finally, each well was gently rinsed with DPBS. The attachment and morphology of the cells was observed using fluorescence microscopy (Olympus IX71). The number of attached cells was determined by visually counting cells present in the microscopy images (10× objective magnification).

### 1.2.4 Film Degradation Studies

ssCAP films (L4) were incubated with fetal bovine serum (10%) and DMEM (90 %) at 37 °C for 1 and 7 d. Prior to AFM measurements in the wet-state, the ssCAP films were rinsed with distilled water and re-submerged in distilled water for thickness analysis.

### 1.3 Characterization Methods

**Gel-Permeation Chromatography (GPC)**

Polymer molecular weight characterization was carried out via GPC using DMF as the mobile phase. The GPC analysis was conducted on a Shimadzu liquid chromatography system equipped with a PostNova PN3621 MALS detector ($\lambda = 532$ nm), Shimadzu RID-10 refractometer ($\lambda = 633$ nm) and Shimadzu SPD-20A UV-Vis detector using three Phenomenx columns (500, 10$^4$, and 10$^6$ Å porosity; 5 µm bead size) in series operating at 50 °C. DMF with 0.05 M 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 known $dn/dc$ values or based
upon the assumption of 100 % mass recovery of the polymer where the \( \frac{dn}{dc} \) value was unknown.

**Nuclear Magnetic Resonance (NMR) Spectroscopy**

\(^1\)H NMR spectroscopy was conducted on a Varian Unity 400 MHz spectrometer operating at 400 MHz, using the deuterated solvent as reference and a sample concentration of ca. 20 mg.mL\(^{-1}\).

**Atomic force microscopy (AFM)**

Atomic force microscopy (AFM) images of air-dried and liquid-state ssCAP\(_{\text{ROMP}}\) 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) and films in water were imaged by tapping mode with NP-S10 cantilevers (Bruker, USA). Image processing and surface roughness analysis were performed using the Nanoscope and Igor Pro software programs, respectively. CAP 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 substrate.

**Differential scanning calorimetry (DSC)**

Differential scanning calorimetry (DSC) analysis was carried out with a PerkinElmer Pyris-1 DSC instrument. \textbf{P1} was first heated from 0 to 300 °C at a heating rate of 20 °C.min\(^{-1}\), then cooled to 0 °C at a cooling rate of 20 °C.min\(^{-1}\), and \textbf{P2} was heated from −70 to 150 °C at a heating rate of 20 °C.min\(^{-1}\), then cooled to −70 °C at a cooling rate of 20 °C.min\(^{-1}\).
Figure S1. (a) Spin-coated thickness of P1-based films using 55 µL of a 10 mg/mL macro-cross-linker solution at 1500 rpm, as determined from the AFM z-profile of the scratched zone. (b) 3D height mode AFM image of the spin-coated film.

Figure S2. Differential scanning calorimetry (DSC) curve of P1.
Figure S3. $^1$H NMR spectra ($d_6$-DMSO, 400 MHz) of (a) anthracene end-capped polyrotaxane and (b) anthracene end-capped polyrotaxane P1 conjugated with norbornene.
Figure S4. Control experiment; P1 was spin-coated and annealed at 70 °C in the absence of C1 catalyst. AFM (a) z-profile of the scratched zone and (b) 3D height mode image of the spin-coated film.

Figure S5. Surface morphology (5×5 μm) measured by AFM of nanoscale films (L4) with increasing additive (M1 or M2) in the dry- and swollen-states.
**Figure S6.** $^1$H NMR spectrum ($d_6$-DMSO, 400 MHz) of linear PEG$_{20kDa}$ macro-cross-linker P2 with pendent functional hydroxyl and norbornene groups.

**Figure S7.** ssCAP$_{ROMP}$ film prepared from the linear PEG macro-cross-linker P2 with pendent norbornene groups. AFM (a) z-profile of the scratched zone and (b) 3D height mode image of the cross-linked film.
**Figure S8.** The AFM z-profile of the scratched zones of nanoscale P1 films with different additives (M1 or M2) at various amounts (wt %) in the dry- and swollen-state.
Figure S9. The AFM z-profile of the scratched zones of nanoscale P2 films in (a) the dry-state and (b) the swollen-state.

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Figure S10. The AFM z-profile of the scratched zones of nanoscale P1 films with different additives (M1 or M2) (wt %) at various time points during degradation studies in the swollen-state.
Figure S11. Fluorescence microscopy images of cell (NIH/3T3) attachment on glass surfaces, P1 ssCAP films (L4) and P2 PEG film (L1). Scale bars are 100 μm.
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References:


