Electronic Supplementary Material (ESI) for Biomaterials Science.

Supporting Information

SURFACE SULFONATES LOCK SERUM ALBUMIN INTO A "HARD" CORONA

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^{1}H-NMR Characterization

Determination of monomer conversion:

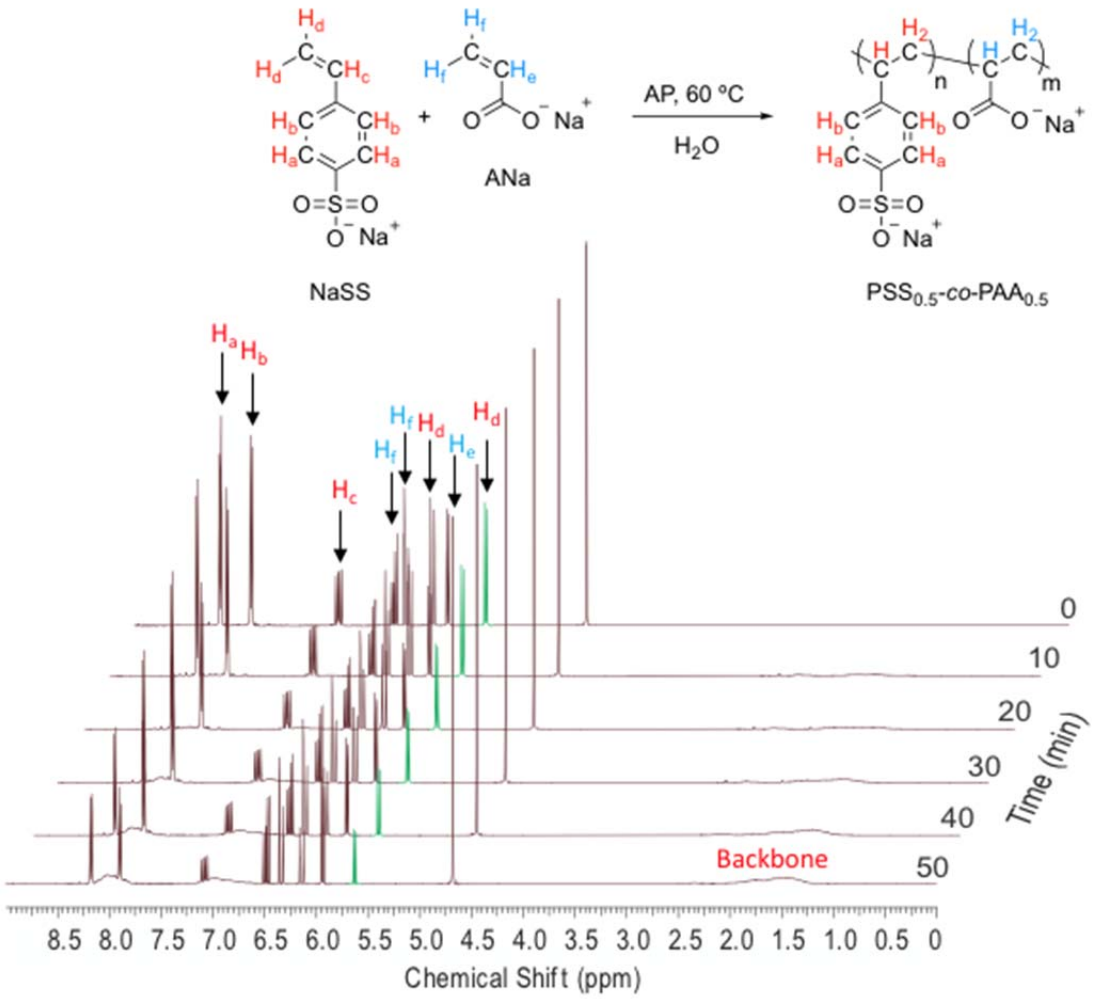

Figure S1. Example of ^{1}H-NMR spectra (600 MHz, D_2O) for *in situ* kinetic analysis at the indicated reaction times during the copolymerization of ANa and NaSS. In a similar way, the conversion for the other copolymers was evaluated. Signal at 4.7 ppm corresponds to the solvent (water in D_2O).

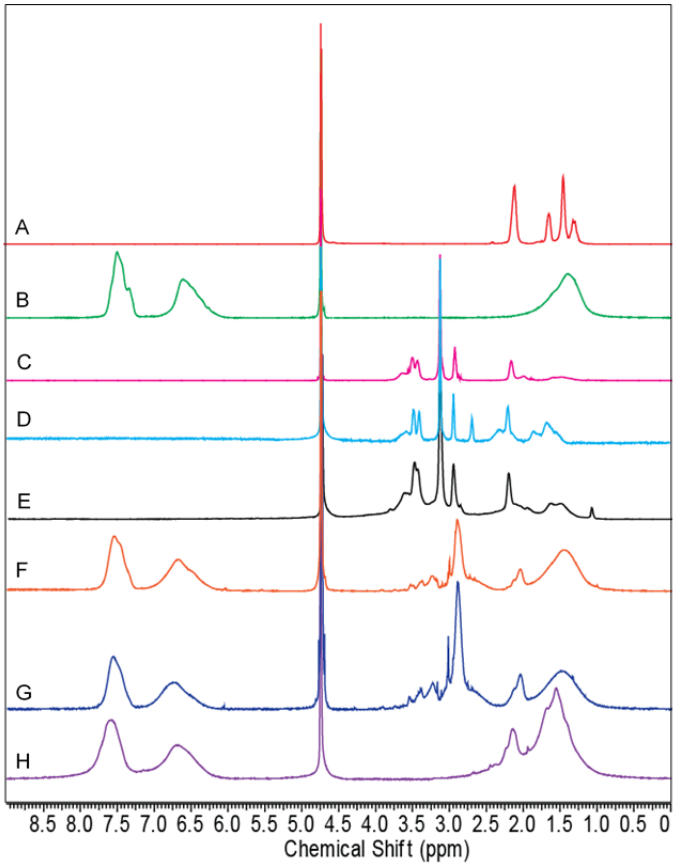

Figure S2. ^{1}H-NMR spectra (600 MHz, D_2O) of PAA; (B) PSS; and (C) PAEDAPS; (D) $PAA_{0.75}$-*co*-$PAEDAPS_{0.25}$; (E) $PAA_{0.5}$-*co*-$PAEDAPS_{0.5}$; (F) $PSS_{0.75}$-*co*-$PAEDAPS_{0.25}$; (G) $PSS_{0.5}$-*co*-$PAEDAPS_{0.5}$; and (H) $PSS_{0.5}$-*co*-$PAA_{0.5}$ after purification. Signal at 4.7 ppm corresponds to the solvent (water in D_2O).

Size Exclusion Chromatography (SEC)

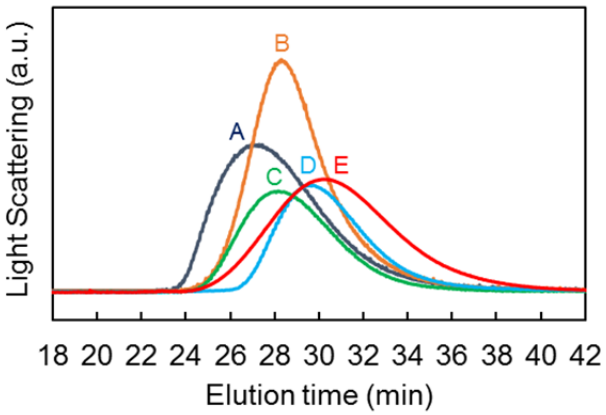

Figure S3. SEC chromatograms for (A) $PAA_{0.5}$-*co*-$PAEDAPS_{0.5}$; (B) $PAA_{0.75}$-*co*-$PAEDAPS_{0.25}$ (C) $PSS_{0.5}$-*co*-$PAEDAPS_{0.5}$; (D) $PSS_{0.75}$-*co*-$PAEDAPS_{0.25}$; and (E) $PSS_{0.5}$-*co*-$PAA_{0.5}$ at 25 °C in 0.2 M $NaNO_3$ eluent solution at a flow rate of 0.5 mL min^{-1}.

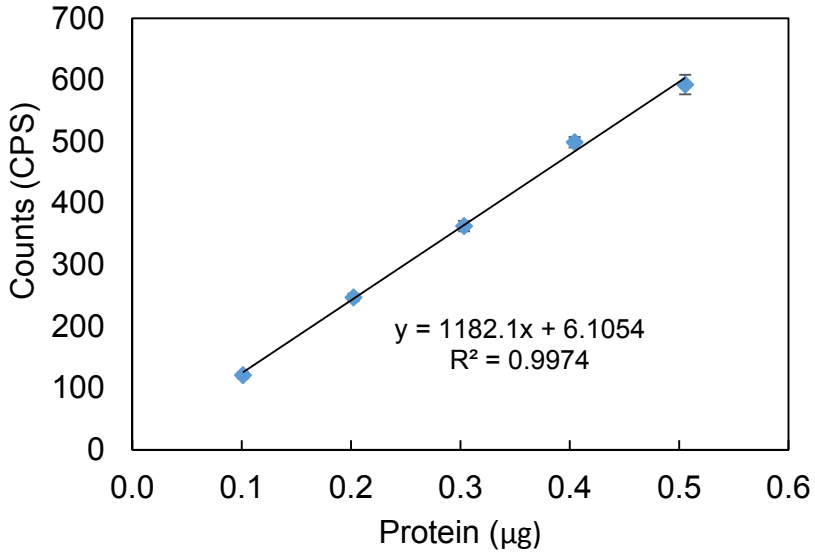

Figure S4. Calibration curve for [^{125}I]-bovine serum albumin (CPS vs. µg) constructed by drying 1.0 to 5.0 µL droplets of the 0.1 mg mL^{-1} [^{125}I]-bovine serum albumin solution between clean Si wafer and the scintillator and laying the side with the dried droplet facing the scintillator.

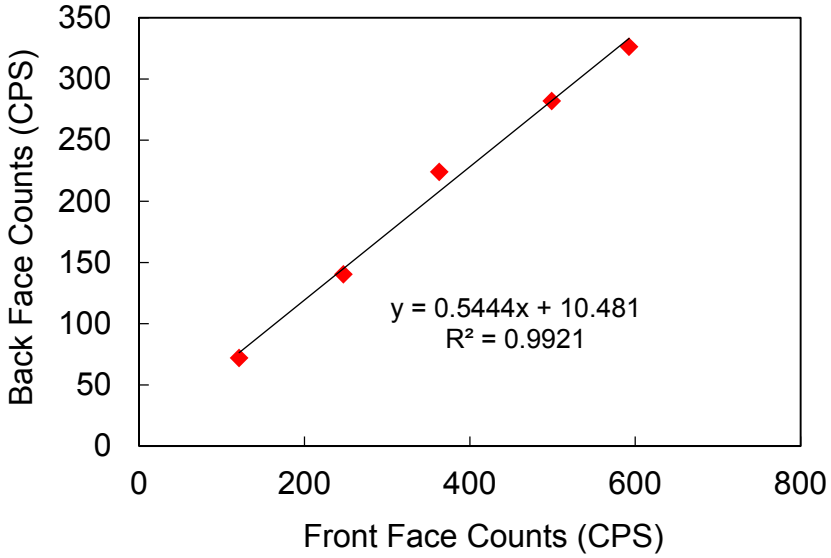

Figure S5. The "backface" effect of [^{125}I] occurs because γ's cannot be stopped by the Si-wafer/film sample, therefore particles coming from the back of the wafer (the side that is not facing the plastic scintillator) also give signal. This calibration curve adds this contribution.

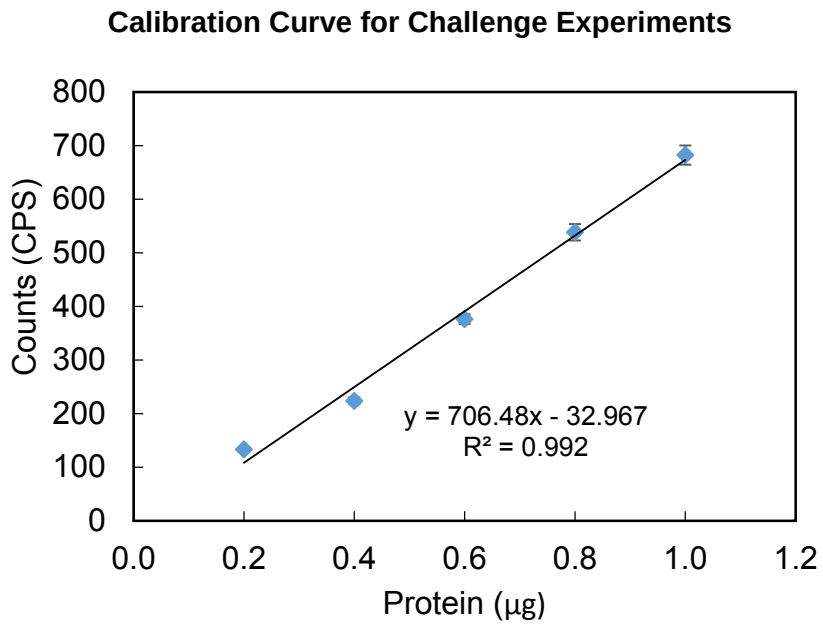

Figure S6. Calibration curve (CPS vs. µg) was constructed by drying 1.0 to 5.0 µL droplets of the 0.2 mg mL^{-1} [^{125}I]-bovine serum albumin solution between clean Si wafer and the scintillator.

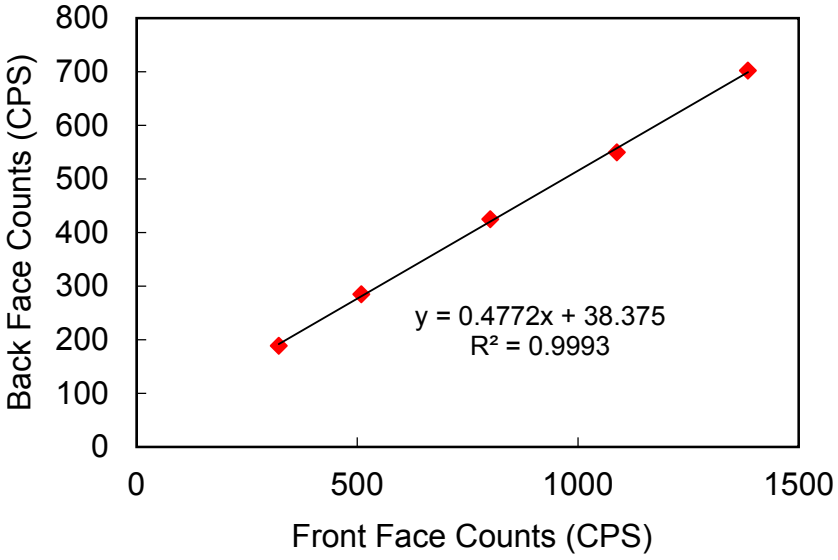

Figure S7. The "backface" effect of [^{125}I] occurs because γ's cannot be stopped by the Si-wafer/film sample, therefore particles coming from the back of the wafer (the side that is not facing the plastic scintillator) also give signal. This calibration curve adds this contribution.

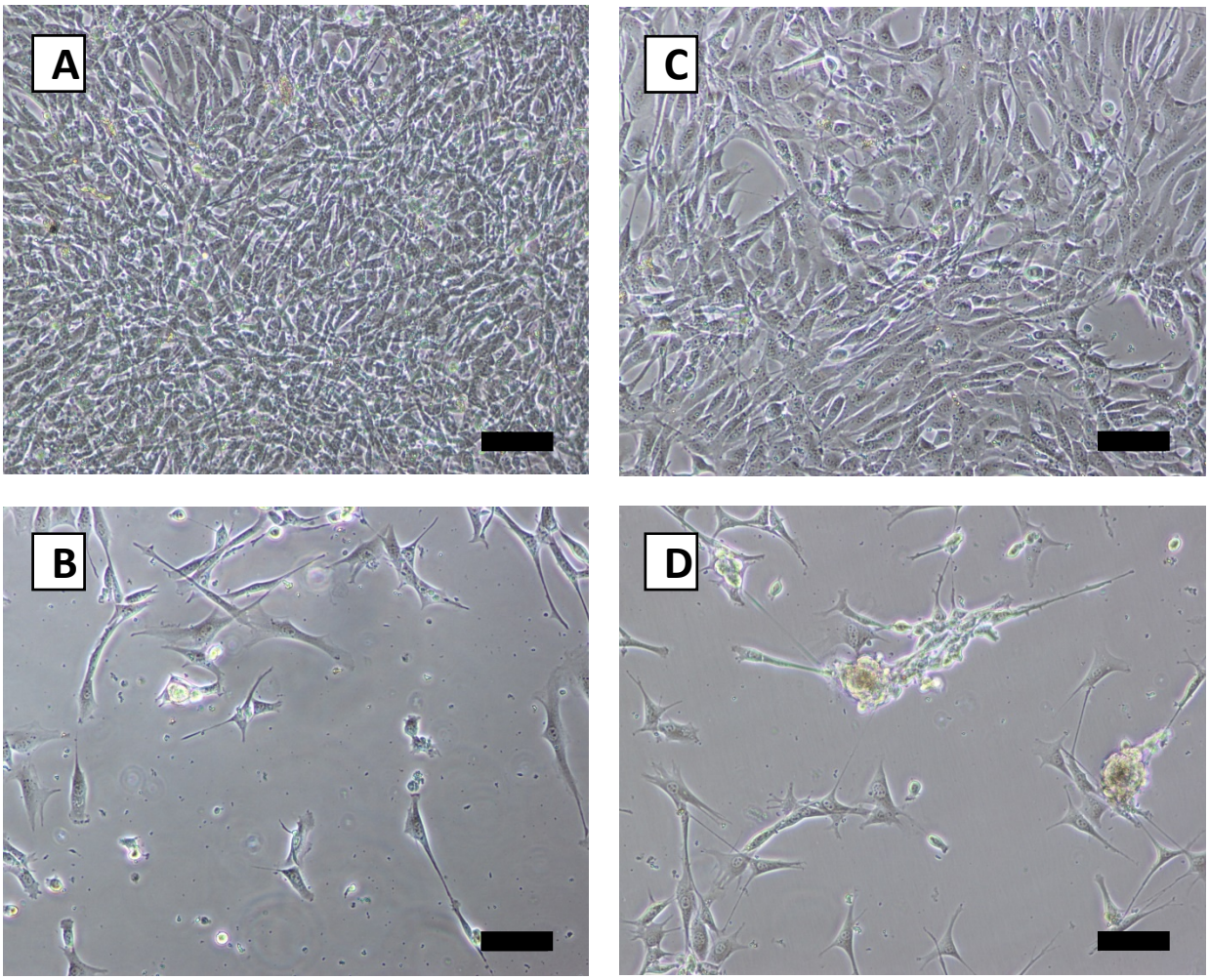

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Figure S8. Phase contrast micrographs obtained on day 3 of live 3T3 fibroblasts seeded at 10000 cells per well after plates were pre-coated with BSA by rinsing in 1 mg/mL of BSA in PBS for 1 hour and then rinsing in PBS for 30 minutes. (A) TCP, (B) untreated polystyrene, (C) $[PAH/PAA, 0.15]_5$, and (D) $[PAH/PSS, 0.15]_5$. Scale bar 100 μm.

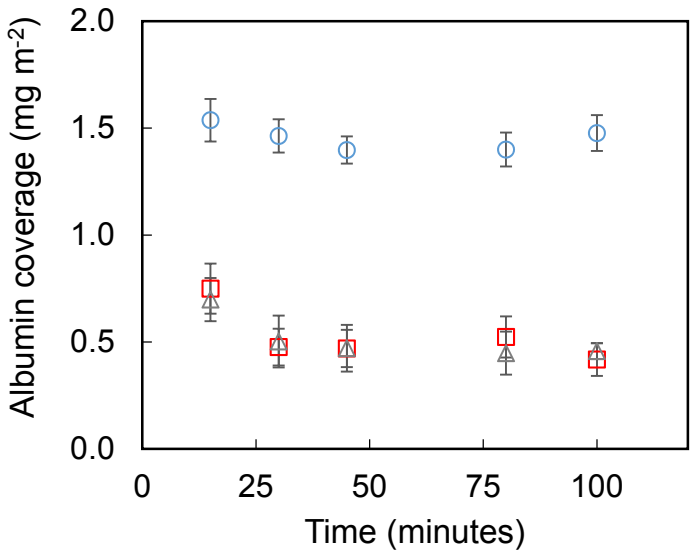

Figure S9. Kinetics of albumin loss from Si wafers. Wafers were immersed in the 0.2 mg mL^{-1} [^{125}I]-bovine serum albumin solution for 60 min then placed on the scintillator to record albumin coverage. The initial starting albumin coverage at 0 min was 4 to 8 mg m^{-2} for all trials. Substrate was then rinsed consecutively for intervals in three adsorption-challenging solutions resulting in a total rinse time of 100 min. Samples were only ever rinsed in one of the challenge solutions. The three challenge solutions were: (○) PBS (0.15 M NaCl), (□) 1.0 M NaCl buffered with phosphate, and (△) 1% unlabeled BSA in PBS (0.15 M NaCl).

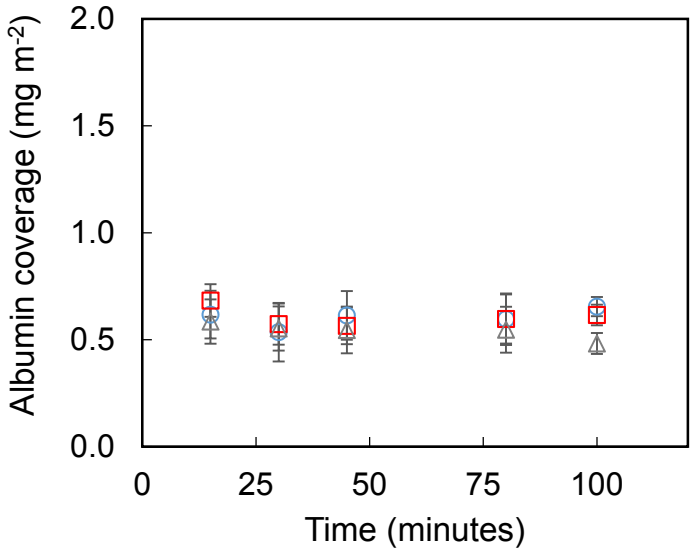

Figure S10. Kinetics of albumin loss from PAA-terminated PEMUs. PAA-terminated films on Si wafers were immersed in the 0.2 mg mL^{-1} [^{125}I]-bovine serum albumin solution for 60 minutes and then placed on scintillator to record albumin coverage. The initial starting albumin coverage at 0 minutes was 4 to 8 mg m^{-2} for all trials. Substrate was then rinsed consecutively for timed intervals in three adsorption-challenging solutions resulting in a total rinse time of 100 minutes.

Samples were only ever rinsed in one of the challenge solutions. The three challenge solutions were: (○) PBS (0.15M NaCl), (□) 1.0M NaCl buffered with phosphate, and (△) 1% unlabeled BSA in PBS (0.15M NaCl).

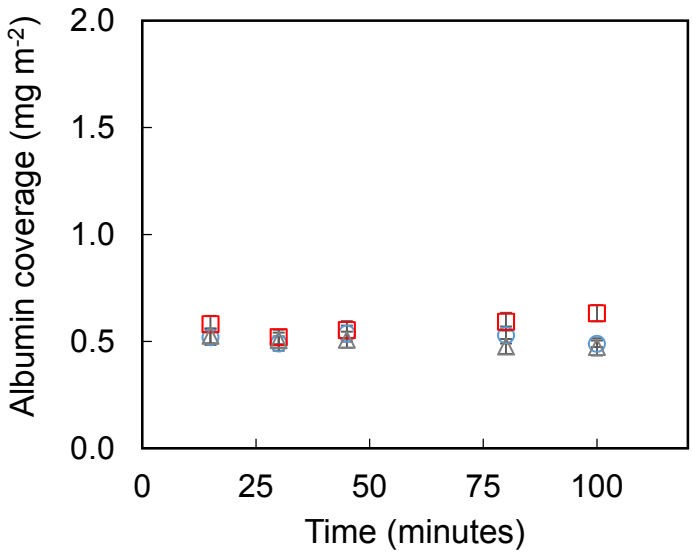

Figure S11. Kinetics of albumin loss from TCP. TCP substrates were immersed in the 0.2 mg mL^{-1} [^{125}I]-bovine serum albumin solution for 60 minutes and then placed on scintillator to record albumin coverage. The initial starting albumin coverage at 0 minutes was 4 to 8 mg m^{-2} for all trials. Substrate was then rinsed consecutively for timed intervals in three adsorption-challenging solutions resulting in a total rinse time of 100 minutes. Samples were only ever rinsed in one of the challenge solutions. The three challenge solutions were: (○) PBS (0.15 M NaCl), (□) 1.0 M NaCl buffered with phosphate, and (△) 1% unlabeled BSA in PBS (0.15 M NaCl).

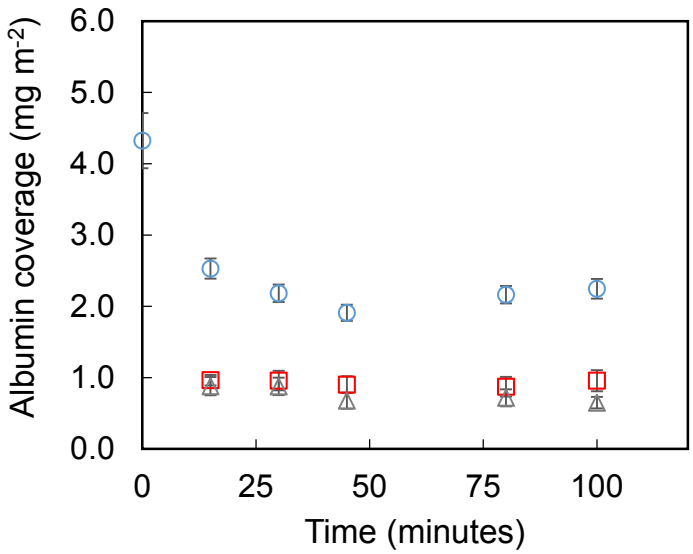

Figure S12. Kinetics of albumin loss from PS. PS substrates were immersed in the 0.2 mg mL^{-1} [^{125}I]-bovine serum albumin solution for 60 minutes and then placed on scintillator to record albumin coverage. The initial starting albumin coverage at 0 minutes was 4 to 9 mg m^{-2} for all trials. Substrate was then rinsed consecutively for timed intervals in three adsorption-challenging solutions resulting in a total rinse time of 100 minutes. Samples were only ever rinsed in one of the challenge solutions. The three challenge solutions were: (○) PBS (0.15 M NaCl), (□) 1.0 M NaCl buffered with phosphate, and (△) 1% unlabeled BSA in PBS (0.15 M NaCl).

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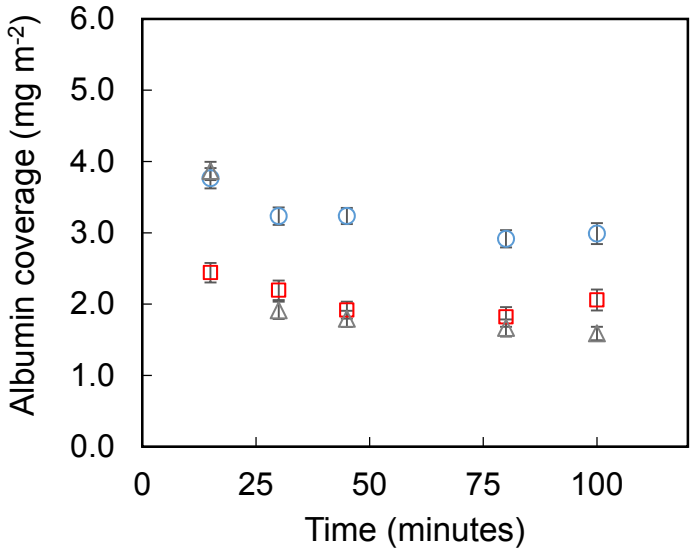

Figure S13. Kinetics of albumin loss from PSS-terminated PEMUs. PSS-terminated films were immersed in the 0.2 mg mL^{-1} [^{125}I]-bovine serum albumin solution for 60 minutes and then

placed on scintillator to record albumin coverage. The initial starting albumin coverage at 0 minutes was 6 to 8 mg m^{-2} for all trials. Substrate was then rinsed consecutively for timed intervals in three adsorption-challenging solutions resulting in a total rinse time of 100 minutes. Samples were only ever rinsed in one of the challenge solutions. The three challenge solutions were: (○) PBS (0.15 M NaCl), (□) 1.0 M NaCl buffered with phosphate, and (△) 1% unlabeled BSA in PBS (0.15 M NaCl).

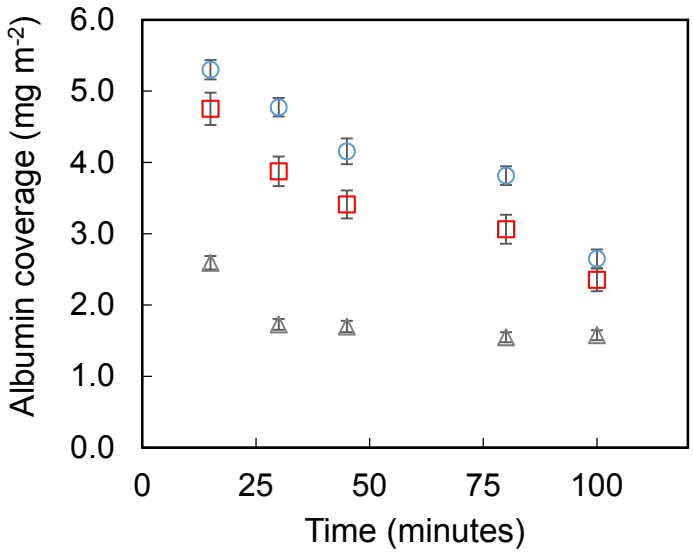

Figure S14. Kinetics of albumin loss from PVS-terminated PEMUs. PVS-terminated films were immersed in the 0.2 mg mL^{-1} [^{125}I]-bovine serum albumin solution for 60 minutes and then placed on scintillator to record albumin coverage. The initial starting albumin coverage at 0 minutes was 6 to 9 mg m^{-2} for all trials. Substrate was then rinsed consecutively for timed intervals in three adsorption-challenging solutions resulting in a total rinse time of 100 minutes. Samples were only ever rinsed in one of the challenge solutions. The three challenge solutions were: (○) PBS (0.15 M NaCl), (□) 1.0 M NaCl buffered with phosphate, and (△) 1% unlabeled BSA in PBS (0.15 M NaCl).

Table S1. Examples of PSS/PAH and PAA/PAH films used in cell adhesion studies on PEMUs

Surface parameters	Multilayer	Thickness (nm)	Cell type	Capping layer	Capping charge[a]	Multilayer post treatment	Cell Adhesion[b]	Reference
Surface charge	PAH/PSS	38	Human umbilical vein endothelial cells	PAH	+	--	G	1
Surface Charge PSS M_W	PAH/PSS	~ 57	C2C12 skeletal muscle cells	PSS PAH	- +	--	G P	2
Stiffness	PAH/PAA	~ 50 - 80	NR6WT Fibroblast	PAH/PAA	+/-	Increasing ionic cross-linking	G	3
Stiffness	PAH/PAA	40	Human microvascular endothelial cell	PAA	-	Increasing ionic cross-linking	G	4
Stiffness	PAH/PAA	~100 (hydrated)	Hepatocyte	PAA	-	Increasing ionic cross-linking	G	5
Stiffness	PAH/PAA	---	Mesenchymal stem cells	PAA	-	Increasing covalent cross-linking	G	6
Surface modification	PAH/PAA	---	NR6 Fibroblast	PAH	+	Grafting RGD Peptides to surface	G	7
Surface modification	PAH/PAA	---	MG63 osteoblast	PAH	+	Grafting RGD Peptides to surface	G	8
Surface charge/ Thickness	PAH/PAA	280 - 300	Smooth muscle cell A7r5/ Human osteosarcoma U-2 OS	PAH/PAA	+/-	---	Depends on [polymer]	9
Stiffness	PAH/PAA	~ 200	A7r5 smooth muscle cells	PAH	+	Increasing covalent cross-linking	G	10

[a] Charge of the last layer

[b] Effects on cell adhesion: G=good, P=poor.

References

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