EXPERIMENTAL SECTION

Materials

Silicon wafers ([100] orientation, boron-doped, 0-100 Ω cm) were obtained from Compart Technology (Peterborough, UK). Circular glass cover slips (13 mm diameter, thickness no. 1) were obtained from VWR international (Leighton Buzzard, UK). Deionized water was obtained from an Elga Pure Nanopore 15.0 MΩ water purification system. All chemicals were analytical reagent grade and were used as received from the manufacturer. 3-Aminopropyltriethoxysilane (APTES) (>98%), 2-bromoisoobutyryl bromide (BIBB) (98%), triethylamine (99%), dimethylphenyl phosphine (DMPP) (99.0%), phosphate buffered saline (PBS), L-cysteine (97%), deuterium oxide (99.9%), 3-(acryloyloxy)-2-hydroxypropyl methacrylate (99%), methoxy-capped oligo(ethylene glycol) methacrylate (480 g mol⁻¹), potassium chloride (>99%), water (HPLC grade) and 2-amino-1,1,1-trifluoroethane (TFEA) (98%) were purchased from Sigma-Aldrich UK (Gillingham, UK). Hydrogen peroxide (30%), sulfuric acid (95%), ethanol (99.8%, HPLC grade), ammonium hydroxide (Analar) and dichloromethane (HPLC grade) were obtained from Fisher Scientific (Loughborough, UK). Copper(I) bromide (>98%), copper(II) bromide (>99%) and 2,2’-bipyridine (>99%) (BiPy) were obtained from Sigma-Aldrich UK (Gillingham, UK). 2-(Methacryloyloxy) ethyl phosphorylcholine monomer (MPC, >99% purity) was kindly donated by Biocompatibles Ltd. (UK). Aqueous HCl and NaOH solutions were used to adjust the solution pH as desired.

Synthesis of Cysteine Methacrylate (CysMA)

In a 250 mL round-bottom flask, L-cysteine (15.13 g, 124.88 mmol) was dissolved in deionized water (100 mL). 3-(Acryloyloxy)-2-hydroxypropyl methacrylate (29.43 g, 137.36 mmol) was added to this stirred aqueous cysteine solution, then dimethylphenyl phosphine (20 µL, 147 µmol)
was added and the aqueous reaction mixture was stirred for 2 h at 20°C. The reaction solution was washed twice with ethyl acetate (50 mL) and dichloromethane (2 x 50 mL) and the final CysMA monomer product was isolated as a pure white solid (39.6 g, 94% yield) by freeze-drying the concentrated aqueous solution overnight.

1H NMR (400.13 MHz, D2O, 298 K) δ (ppm): 1.89 (s, 3H, -CH3); 2.68-3.17 (m, 6H, -S-CH2-CH2-COO-); 3.79 (m, 1H, CHOH); 3.90 (m, 1H, -CH(COO-)NH3+); 4.20-4.30 (m, 4H, -CH2-CHOH-CH2-); 5.70 (s, 1H, vinyl), 6.13 (s, 1H, vinyl).

13C NMR (400.13 MHz, D2O, 298 K) δ (ppm): 17.31 (-CH3); 26.28 (-S-CH2-CH2-); 32.04 (-S-CH2-); 33.85 (-S-CH2-CH2-); 53.47 (-CH2-CHOH-CH2-); 65.17, 65.26 (2C, -CH2-CHOH-CH2-); 66.81 (-CH(COO-)NH3+); 127.39, 135.57 (2C, vinyl); 169.38, 172.70, 174.07 (3C, carbonyls).

(M+H⁺): Calculated: 336.1117. Found: 336.0

Elemental microanalysis: Calculated: C: 46.56 %; H: 6.31 %; N: 4.18 %; S: 9.56 %. Found: C: 46.31 %; H: 6.33 %; N: 4.30 %; S: 9.58 %

Preparation of initiator-functionalized silicon wafers

All glassware and substrates were cleaned via immersion in ‘piranha’ solution (a 3:7 mixture of hydrogen peroxide and concentrated sulfuric acid) for 2 h. (Caution: Piranha solution is an extremely strong oxidizing agent that has been known to detonate spontaneously upon contact with organic material). The glassware and the substrates were washed with deionized water for several times then sonicated for 10 min and rinsed with deionized water. Glassware and substrates were dried in a 120 °C oven for 1 h. The silicon wafers were submerged in a 1:1:5 solution of ammonium hydroxide, 30% hydrogen peroxide and deionized water (The Radio Cooperative America (RCA)). This solution was heated to 85 °C for 30 min and then allowed to cool. The samples were rinsed with deionized water, sonicated and then dried in an oven before use.1-2

A 2.0 % v/v solution of 3-aminopropyltriethoxysilane (APTES) in ethanol was aged for 5 min at 20°C. The silicon wafers were immersed in this ethanolic solution for 30 min then rinsed with ethanol, dried under N2 and annealed for 30 min at 120 °C.1-3 Then the wafers were immersed in a solution of 2-bromoisobutyryl bromide (BIBB) (0.37 mL, 3 mmol) and triethylamine (0.41 mL, 3 mmol) in dichloromethane (DCM; 60 ml) for 30 min. Subsequently, the wafers were rinsed with ethanol and DCM and dried under nitrogen prior to use.4-7

Surface photopatterning

A Coherent Innova 300C FreD frequency-doubled argon ion laser (Coherent U.K., Ely, UK) with an emission wavelength of 244 nm was used for the UV photodegradation experiments. The laser power output was adjusted to be 100 mW. The area illuminated by the laser beam was 0.2 cm². Micro-patterned brushes were obtained by irradiating uniform polymer brush layers on silicon wafer substrates using a copper electron microscopy grid (Agar, Cambridge, UK as a
photomask. For nano-patterned brushes, interferometric lithography (IL) was conducted using a Lloyd’s mirror two-beam interferometer. [Brueck, S. R. J. Proc. IEEE 2005, 93, 1704; Lu, C.; Lipson, R. H. Laser Photon. Rev. 2009, 1]

Preparation of poly(cysteine methacrylate) (PCysMA) brushes

Initiator-functionalized silicon wafers were placed in Schlenk tubes within a Carousel 12 Reaction Station (Radleys, UK), degassed via three vacuum/refill cycles, then filled with dry N₂. CysMA (5.0 g, 15.0 mmol) was dissolved in deionized water (12.0 mL) at 20°C and degassed for 30 min. Bipy (234 mg, 1.50 mmol), Cu(I)Br (71.4 mg, 0.50 mmol) and Cu(II)Br₂ (55.6 mg, 0.25 mmol) were added to this aqueous solution. This reaction mixture was degassed for 10 min, and then briefly sonicated. To commence the surface ATRP of the CysMA, an aliquot of this reaction solution (2.0 mL) was transferred into each Schlenk tube. At specific desired reaction times, the substrates were removed from each Schlenk tube, sonicated in water and rinsed with ethanol to remove unreacted monomer, and then dried using a dry N₂ purge.

Surface Derivatization

The surface aldehyde groups generated via UV irradiation were derivatized by reaction with 2-amino-1,1,1-trifluoroethane (TFEA). The UV-irradiated PCysMA-coated silicon wafer was immersed in a 1.0 mM ethanolic solution of TFEA for 24 h. Then the wafer was removed, rinsed with ethanol and dried using a dry N₂ purge.

Protein Patterning

The protein resistance of UV-irradiated PCysMA brushes was studied using green fluorescent protein (GFP). Unpatterned and patterned PCysMA brush-coated silicon wafers were immersed in an aqueous solution containing 10.0 mg dm⁻³ of GFP in PBS solution at 4 °C for 12 h. The wafers were removed from the solution and rinsed with copious amounts of buffer and then deionized water, and gently dried under a stream of N₂.

Characterization Techniques

Ellipsometric studies were conducted using a Alph-SE ellipsometer (J. A. Woollam Co., Lincoln, NE) equipped with a He-Ne laser (λ = 633 nm) at an incident angle (Φ) of 70° from the normal. A refractive index of 1.50 was assumed for dry PCysMA brushes. Measurements of brushes immersed in various aqueous solutions were conducted using a liquid cell. The sample cell was rinsed several times with deionized water between each measurement in order to ensure that the desired pH was obtained. Ellipsometric data were fitted to a single slab with a refractive index given by a linear effective medium approximation (EMA) between the polymer and water. Three measurements were recorded for each sample and the mean and standard deviation were determined in each case.
AFM studies were carried out in Tapping Mode using a Digital Instruments Nanoscope IV Multimode Atomic Force Microscope (Veeco, Santa Barbara, USA) with a ‘J’ scanner (0 - 125 µm). Silicon nanopores (Bruker, UK) with nominal force constants of 20-80 Nm⁻¹ and tip radii of between 20 and 60 nm were used. Topographic imaging was performed in air, and also in aqueous solutions of varying solution pH. Prior to AFM measurements, each substrate was immersed in the aqueous solution within the fluid cell for at least 5 min to reach equilibrium. Brush heights are reported as the mean ± standard deviation.

XPS data were acquired using a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK) with a monochromatized Al Kα X-ray source operating at 150 W with an emission current of 8 mA. The base pressure was typically 10⁻⁸ to 10⁻¹⁰ mbar. Electron energy analyzer pass energies of 20 eV and 160 eV were used to acquire both high resolution scans and survey scans, respectively. The energy resolution was selected to be 1.0 eV for survey spectra and 0.10 eV for high resolution spectra. The latter spectra were peak-fitted using CasaXPS software and all binding energies were referenced relative to the main hydrocarbon C1s signal centred at 285 eV.

Malvern Zetasizer NanoZS model ZEN 3600 instrument equipped with a Malvern streaming potential dip cell attachment was used to determine surface zeta potentials. Surface zeta potentials were measured at 25°C in the presence of 1 mM KCl using sterically-stabilized polystyrene nanoparticles as a tracer. The steric stabilizer was selected to be poly(2-(methacryloyloxy)ethyl phosphorylcholine) (PMPC) since its highly hydrophilic, permanently zwitterionic character should ensure no interaction with the PCysMA brush chains at any solution pH. The synthesis of PMPC stabilized polystyrene nanoparticles was reported previously by Armes and co-workers (see supporting information).

Fluorescence images were obtained with a LSM510 meta laser scanning confocal microscope (Carl Zeiss, Welwyn Garden City, UK). Both patterned and non-patterned planar substrates were placed on microscope slides followed by Citifluor mounting as an anti-fade reagent (glycerol-PBS solution, AF1) (Citifluor Ltd., London, UK). A 63x magnification oil immersion lens were used to image the samples. The 488 nm band of a 1.5 mW argon ion laser was used to excite the yellow-green fluorescence emitted by green fluoresce protein (GFP), and this fluorescence was recorded at wavelengths above 515 nm. The captured images were analyzed using Zeiss LSM image browser software.

**MTT Assay**

PCysMA brush samples (approximately 0.5 x 0.5 cm) were disinfected in a sterile environment using ice-cold 70% ethanol for 10 minutes and then washed three times using sterile PBS solution. Afterwards, cell viabilities were assessed via MTT assay (MTT = 3-(4,5-dimethylthiazol-2-yl)-2,5 diphenyl tetrazolium bromide; Sigma-Aldrich, St Louis, MO). Briefly, each brush-coated
surface was removed, cells were washed with PBS and then incubated with MTT solution (0.50 g dm\(^{-3}\) MTT in PBS, 1.0 ml per well in a 24-well plate) for 45 min at 37°C in a humidified incubator (5% CO\(_2\), 95% air). In healthy viable cells, MTT is reduced to a purple colored formazan salt by the activity of the mitochondrial enzyme, succinyl dehydrogenase. After 45 min, the solution was aspirated and the insoluble intracellular formazan product was solubilized and released from cells by adding acidified 2-propanol (0.50 ml per well in a 24-well plate or 1 mL per cm\(^2\) of cultured tissue) and incubated for 10 min. The optical absorbance at 540 nm was then measured using a UV/Vis spectrophotometer equipped with a plate reader and a 630 nm reference filter.

Mean cell viability data and SEM were normalized relative to a negative control (planar glass surfaces containing no polymer brush, 100% cell viability) and expressed as a percentage viability ± SEM. Experiments were performed in triplicate well samples with n = 3 independent experiments. For statistical analysis, a student’s paired t-test was used for the raw data to assess the significance of differences between the various treatments and the control group.

**Cell adhesion test**

Polymer brushes were grown from identical 13 mm diameter circular glass slides to evaluate cellular adhesion, with uncoated glass slides being used as a control. Both PCysMA brush-coated and uncoated glass slides were disinfected using ice-cold ethanol as described above and placed at the bottom of 24-well plates. Then HDF cells were added to the surface (1 x 10\(^5\) cells per well and surface). Cells were incubated for 24 h to allow sufficient time for possible cell adhesion onto the brush surface. The cell viability MTT test was used to assess the extent of cell adhesion. HDFs cells are adherent cells, and it is well recognized that surface attachment is a requirement for such cells viability.\(^{12}\) Therefore lack of viability (low MTT values) after cell contact with the brush coated and uncoated surfaces reflected poor adhesion.

**Complement depletion assay**

Complement activation was assessed as the lytic capacity of a normal human serum (NHS) (Sigma-Aldrich, UK) towards antibody-sensitized sheep erythrocytes after exposure to PCysMA brush surfaces (see Supporting Information, Figure S1). The methodology was adapted from traditional CH50 tests\(^{13}\) for use on polymer brushes. Sheep erythrocytes (Oxoid, UK) were sensitized by rabbit anti-sheep erythrocytes antibodies (Abcam, UK) and diluted by the veronal-buffered saline (VBS++) at a final concentration of 2 x 10\(^9\) cells per mL. Veronal-buffered saline containing 0.15 mM Ca\(^{2+}\) and 0.5 mM Mg\(^{2+}\) (VBS++) were purchased from Lonza, UK. Aliquots of NHS (100 µl) were incubated with 13 mm diameter glass surfaces with polymer brushes of varying thickness (small 4-7 nm, medium 13-16 and long 24-28 nm ). Afterwards, NHS supernatants were removed and mixed with fresh antibody-sensitized erythrocytes.
After incubation for 45 min at 37 °C, the reaction mixture was lightly centrifuged at 1000 rcf for 10 min. The absorbance of the carefully decanted supernatant was determined at a fixed wavelength of 415 nm using a microplate reader (Biotek, UK) and compared to the results obtained using control serum in order to evaluate the extent of hemolyzed erythrocytes. Positive and negative controls were prepared for each series of experiments in order to account for any difference in the hemoglobin response for a given erythrocyte preparation. When using diluted serum, a control for the serum lysis capacity was performed (see Figure 14), whereby aliquots of the diluted serum were compared to the 100% lysis water control. In order to eliminate false positives, only dilutions that correlated with the 100% lysis control were used for this study. Furthermore, corrections for background noise and spontaneous erythrocyte hemolysis were estimated from UV/VIS spectra recorded for blanks containing only brushes in buffered solution and only erythrocytes, respectively.

For clarity, mean data and SEM were normalized to the 100% serum lysis control (also 0% depletion control) and expressed as a percentage of depletion ± SEM. Experiments were performed in duplicate well samples with n = 3 independent experiments. The Student’s paired t-test was used to analyze the raw data to assess the significance of differences between the various treatments and the control group.

Synthesis of PMPC-PS nanoparticles

Preparation of 2-(dimethylamino)ethyl-2-bromoisobutyrylamide ATRP initiator. 2-Dimethylethylenediamine (5.95 g, 0.068 mol) and triethylamine (27.27 g, 0.27 mol) were dissolved in dichloromethane (120 mL) and degassed for 30 min. 2-Bromoisobutyryl bromide (15.49 g, 0.067 mol) was added to the reaction mixture and stirred for 5 h, before filtering to remove the precipitate. The solution was dried over MgSO₄ and filtered once more. Solvent was removed under reduced pressure to produce a pale-brown liquid.

Preparation of PMPC homopolymer. 2-(Dimethylamino)ethyl-2-bromoisobutyrylamide initiator (0.134 g, 0.56 mmol), bpy (0.177 g, 1.12 mmol), and MPC (5.00 g, 16.8 mmol) were placed in a round-bottomed flask and degassed using three vacuum/nitrogen cycles. Methanol (5.13 mL) was degassed separately and transferred into the reaction flask under a nitrogen atmosphere. Then CuCl (0.055 g, 0.56 mmol) was added to the polymerization solution under a nitrogen atmosphere. The reaction solution was diluted with methanol after 6 h to deactivate the ATRP catalyst, then passed through a silica column to remove the catalyst. A white powder of PMPC was obtained after drying on a vacuum line overnight.

Quaternization of tertiary amine-terminated PMPC homopolymer. The PMPC homopolymer (4.23 g, 0.47 mmol) was dissolved in methanol (13 mL); then 4-vinylbenzyl chloride (4-VBC) (0.237 g, 1.41 mmol) was added and stirred for 48 h at 20°C. The solvent was removed under vacuum and the resulting solid was dissolved in water, then the excess 4-VBC was extracted three
times with cyclohexane. Finally, the aqueous phase was freeze-dried from water overnight to produce a white powder.

**Synthesis of PMPC-stabilized PS latex.** PMPC macromonomer (0.50 g) was dissolved in water (45.0 g), and then styrene (5.0 g) was added. This solution was degassed by five evacuation/nitrogen purge cycles and then heated to 60°C. 2,2′Azobis(isobutyramidine) dihydrochloride (AIBA) initiator (0.050 g) was dissolved in water (5.0 g) and degassed, then transferred into the reaction vessel. The polymerization solution was stirred for 24 h at 60°C. The resulting milky-white latex was purified by three centrifugation/redispersion cycles to remove excess macromonomer and unreacted styrene monomer.

**Preparation of poly[2-(methacryloyloxy)ethyl phosphorylcholine] (PMPC) brushes**

2-(Methacryloyloxy)ethyl phosphorylcholine monomer (MPC) (6.0 g, 20 mmol) was placed in a flask under a nitrogen atmosphere after four pump/refill cycles. Water and methanol were degassed separately (for at least 60 min) via a stream of nitrogen gas. Water (5.0 mL) and methanol (5.0 mL) were added to this MPC solution via syringe at 20°C. CuBr (48.4 mg, 0.338 mmol), CuBr$_2$ (36.8 mg, 0.165 mmol), and 2,2′-bipyridine (157.5 mg, 1.014 mmol) were added, the mixture was stirred under nitrogen for 10 min. and then briefly immersed in an ultrasonic bath to aid catalyst dissolution. Initiator-functionalized surfaces were sealed in Schlenk tubes, degassed, then filled with nitrogen. An aliquot (2.0 mL) of the polymerization solution was syringed into each Schlenk tube. After 25 min., the samples were washed with water and methanol. The PMPC brush-coated wafers were briefly sonicated, removed and then rinsed thoroughly with water and methanol, and dried under a nitrogen stream.$^{10}$

**Preparation of poly(oligo(ethylene glycol) methyl ether methacrylate) brushes**

Poly(oligo(ethylene glycol) methyl ether methacrylate) (480 g mol$^{-1}$) (5.00 g, 10 mmol) was dissolved in water (5 dcm$^3$) at 20°C and degassed by passing a continuous stream of nitrogen through the solution for 30 min. Bipy (0.070 g, 0.454 mmol), CuBr (0.023g, 0.16 mmol) and CuBr$_2$ (0.011 g, 0.047 mmol) were added to the solution. The mixture was degassed with a stream of nitrogen for 30 min. Initiator-functionalized patterned planar substrates were sealed in Schlenk tubes and degassed (three vacuum/refill cycles). The reaction solution (2.00 mL) was syringed into each Schlenk tube. The samples were removed after polymerization for 45 min., washed with water and ethanol, and then dried under a stream of nitrogen gas.$^{14}$

**Brush sterilization and bioburden assay**

After disinfection, a few representative samples were characterized by contact angle, ellipsometry and XPS to confirm retention of the original PCysMA brush layer.
For the bio-burden assay, each sterilized brush sample was submerged into 5.0 mL of bacteria growth medium (comprising dextrose, 1.0 g dm$^{-3}$; tryptone, 5.0 g dm$^{-3}$; yeast extract, 2.5 g dm$^{-3}$) (at a solution pH of 7.0 ± 0.2. Samples were grown overnight at 37°C with continual shaking. Higher turbidity over time indicates bacteria growth. A negative control (no glass slide) was also prepared.

*Viability of primary human dermal fibroblasts after exposure to polymer brushes*

Primary human dermal fibroblasts (HDF) were obtained in batches from the ATCC, LGC standards (UK). Fibroblasts were routinely cultured in T75 flasks using standard culture medium (DMEM supplemented with 10% FCS, 2 mM L-glutamine, 625 µg dm$^{-3}$ amphotericin B, 100 IU/ml penicillin and 100 mg dm$^{-3}$ streptomycin). HDF cells were used for testing between passages 4 and 9. HDF cells were seeded at a density of 3 x 10$^4$ cells per well in a standard 24-well plate and cultured for 48 h prior to testing in a standard culture medium.

Brush-coated surfaces were evaluated over 24 h using 80% confluent HDF cells using a non-contact set-up to identify any toxic low molecular weight species. Brush-coated surfaces were placed inside 24-well plate Thincerts$^{TM}$ (8 µm diameter pore size) and placed onto the HDF monolayers. Cells were maintained within normal culture media (1.0 mL) and the brush-coated silicon wafers (roughly 0.5 cm x 0.5 cm) were submerged in normal culture media (300 µL) for 24 h.
**Figure S1.** Scheme representing the methodology of the complement consumption/depletion assays. Briefly, 13-mm diameter glass surfaces with different thickness polymer brushes were incubated with 100 ml of human serum. Afterwards, the supernatants (SN) were removed and mixed with fresh antibody sensitized erythrocytes. Complement proteins will bind the erythrocytes, and produce lysis. If the surfaces promote complement adhesion (CA), these proteins will be depleted from the serum and in contact with sensitized erythrocytes they will produce low hemolysis. No depletion will result in high hemolysis. Quantification can be done via reading absorbance at 415 nm. Comparative controls are included in the test to normalize the data.

**BIBB-APTES films**

The C1s spectrum comprised three peaks with binding energies of 285.0, 286.2 and 288.3 eV, which are attributable to C-C, C-Br/C=N and O=C, respectively. The relative peak areas were 4.3 : 1.8 : 1, which is close to the 4 : 2 : 1 theoretical ratio. The N1s signal at 400 eV was assigned to the O=C–N species. The Br3d spectrum was resolved into two components at 70.3 and 71.3 eV,
with relative intensities of 1.4:1, corresponding to Br3d5/2 and Br3d3/2, respectively. The Br/N atomic ratio suggested that 80-90% of surface amine groups had reacted with 2-bromoisobutyryl bromide, generating the desired BIBB-APTES.

Surface zeta potential vs. pH curves were constructed for both APTES- and BIBB-APTES-functionalized silicon wafers (Figure S3, see supporting information). The former substrate is cationic between pH 2 and pH 7 (with zeta potentials of 35 ± 10 mV) owing to protonation of the surface primary amine groups. Anionic character was observed in alkaline media, with an isoelectric point at around pH 7.5-8.5; these observations are consistent with previous studies.\textsuperscript{15-16} The BIBB-APTES silicon wafer exhibits rather lower surface zeta potentials (8 ± 5 mV) at low pH, and negative values above pH 9. This is consistent with our XPS observations, which indicated that a minor fraction of surface primary amine groups had not reacted with 2-bromoisobutyryl bromide.

\textbf{Figure S2.} Curve-fitted XPS spectra recorded for BIBBAPTES functionalized Si wafers: (A) C1s core-line spectrum. (B) N1s core-line spectrum. (C) Br3d core-line spectrum
Figure S3. The surface zeta potential of APTES and BIBB-APTES functionalized Si wafers immersed in aqueous solution as a function of solution pH. (■) APTES film. (●) BIBB-APTES film.

Figure S4. AFM tapping mode height images of PCysMA brushes grown by SI-ATRP on Si. Image size: 2 µm × 2 µm. The z-range is 0-5 nm in both images.
Figure S5. AFM tapping mode height images recorded for (A) dry PCysMA brush, (B) the same brush immersed in pH 1.5, (c) the same brush immersed in pH 7, and (D) the same brush immersed in pH 10.5 aqueous solution of various pH. Image size: 50 × 50 µm, Z-range 0 - 100 nm.
Figure S6. In situ ellipsometric dry thickness of PCysMA brushes as a function of immersion time at 20°C (original dry thickness = 10 nm). (■) immersed in aqueous solution at pH 8. (●) immersed in aqueous solution at pH 9. (♦) immersed in aqueous solution at pH 10. (▲) immersed in aqueous solution at pH 11.
Figure S7. X-ray photoelectron core-line spectra recorded for PCysMA brush after pH degradation (3 nm dry thickness). (A) C1s spectrum obtained for PCysMA brush. (B) S2p spectrum obtained for the same PCysMA brush. (C) N1s spectrum obtained for the same PCyMA brush.
Figure S8. Height images of PCysMA brushes fabricated by interferometric lithography using a Lloyd’s mirror two-beam interferometer and a UV dose of 13.2 J.cm⁻²: (A) at θ = 10°; (B) at θ = 20°; (C) at θ = 30°; and (D) at θ = 45°. Image size: 5 µm × 5 µm. The z-range is 0-10 nm in all cases.

Figure S9. Confocal fluorescence image obtained for PCysMA brushes subjected to a green fluorescent protein (GFP) challenge. No protein adsorption is detected for the pristine PCysMA brush.
Disinfection was achieved by rinsing the brush samples with ice-cold ethanol to minimize the initial bioburden (see supporting information, Figure S8) and XPS studies confirmed that this protocol produced no discernible change in the PCysMA brush layer. A non-contact set-up (involving immersion of brush samples in cell media using 24-well plate Thincerts™) was used as an initial biocompatibility screen. Since the cells are attached to the bottom of each well plate, they were exposed to the PCysMA brush layers via the aqueous cell media, but not by direct contact. Cellular viabilities were very high for each PCysMA brush, regardless of its thickness (see Figure S11).

**Figure S10. Disinfection of the brushes and bioburden assay.** Polymer brush surfaces of approximately 0.5x0.5 cm were disinfected in a sterile environment. The disinfected surfaces were submerged in bacterial growth medium and were grown overnight under shaking at 37°C. Increased turbidity over time indicates bacteria growth (*). A negative control (No glass slide) was also prepared.
Figure S11 Cellular viability of primary human dermal fibroblasts (HDFs) after exposure to the polymer brush. A series of PCysMA brushes of varying mean dry thickness (relatively thin brushes of 4-7 nm, intermediate brushes of 13-16 nm and relatively thick brushes of 24-28 nm) were evaluated for their biocompatibility when exposed to HDF cells: (a) an indirect contact set-up (using a polycarbonate membrane with a mean pore diameter of 8 µm) was used to avoid any surface effects on cell adhesion in order to focus on the possible presence of low molecular weight toxins (diagram not to scale); (b) MTT assays confirmed high cell viabilities for all brush samples investigated (N = 3 independent experiments conducted in triplicate).
References

(1) Ahmad, S. A.; Leggett, G. J.; Hucknall, A.; Chilkoti, A. *Biointerphases* **2011**, *6*, 8.
(2) Janssen, D.; De Palma, R.; Verlaak, S.; Heremans, P.; Dehaen, W. *Thin Solid Films* **2006**, *515*, 1433.
(3) Alang Ahmad, S.; Hucknall, A.; Chilkoti, A.; Leggett, G. J. *Langmuir* **2010**, *26*, 9937.
(4) Marsh, A.; Khan, A.; Garcia, M.; Haddleton, D. M. *Chem. Comm.* **2000**, *2083*.
(5) Brown, A. A.; Khan, N. S.; Steinbock, L.; Huck, W. T. S. *Eur. Polym. J.* **2005**, *41*, 1757.
(6) Ma, H.; Li, D.; Sheng, X.; Zhao, B.; Chilkoti, A. *Langmuir* **2006**, *22*, 3751.
(7) Ma, H.; Wells, M.; Beebe Jr, T. P.; Chilkoti, A. *Adv. Funct. Mater.* **2006**, *16*, 640.
(8) Edmondson, S.; Vo, C.-D.; Armes, S. P.; Unali, G.-F. *Macromolecules* **2007**, *40*, 5271.
(9) Fielding, L. A.; Edmondson, S.; Armes, S. P. *J. Mater. Chem.* **2011**, *21*, 11773.
(10) Edmondson, S.; Nguyen, N. T.; Lewis, A. L.; Armes, S. P. *Langmuir* **2010**, *26*, 7216.
(11) Thompson, K. L.; Bannister, I.; Armes, S. P.; Lewis, A. L. *Langmuir* **2009**, *26*, 4693.
(12) Frisch, S. M.; Ruoslahti, E. *Curr. Opin. Cell Biol.* **1997**, *9*, 701.
(13) Meerasa, A.; G Huang, J.; X Gu, F. *Curr. Drug Deliv.* **2011**, *8*, 290.
(14) Brown, A. A.; Khan, N. S.; Steinbock, L.; Huck, W. T. *Eur. Polym. J.* **2005**, *41*, 1757.
(15) van der Maaden, K.; Sliedregt, K.; Kros, A.; Jiskoot, W.; Bouwstra, J. *Langmuir* **2012**, *28*, 3403.
(16) Zhang, H.; He, H.-X.; Wang, J.; Mu, T.; Liu, Z.-F. *Appl. Phys. A* **1998**, *66*, S269.