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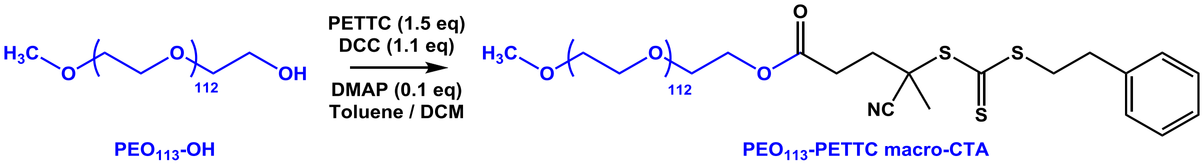
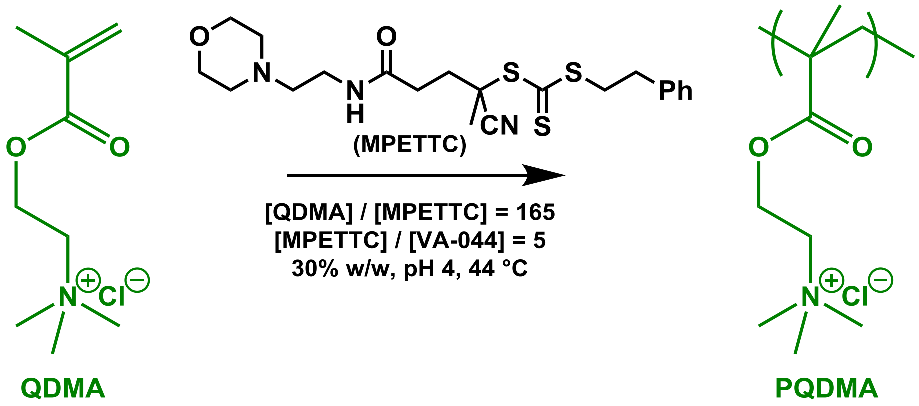
# Electronic Supporting Information:

# Layer-by-Layer Self-Assembly of Polyelectrolytic Block Copolymer Worms on a Planar Substrate

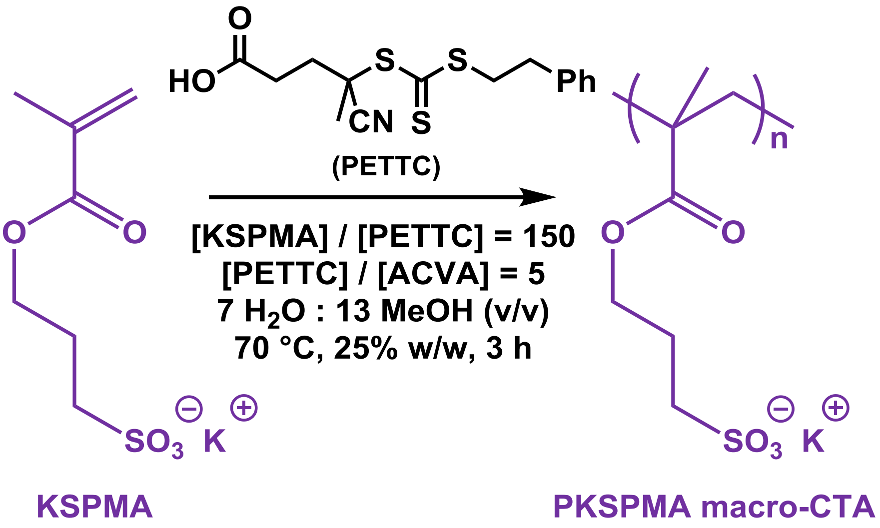
Nicholas J. W. Penfold*, Andrew J. Parnell, Pierre Verstraete, Johan Smets and Steven P. Armes*



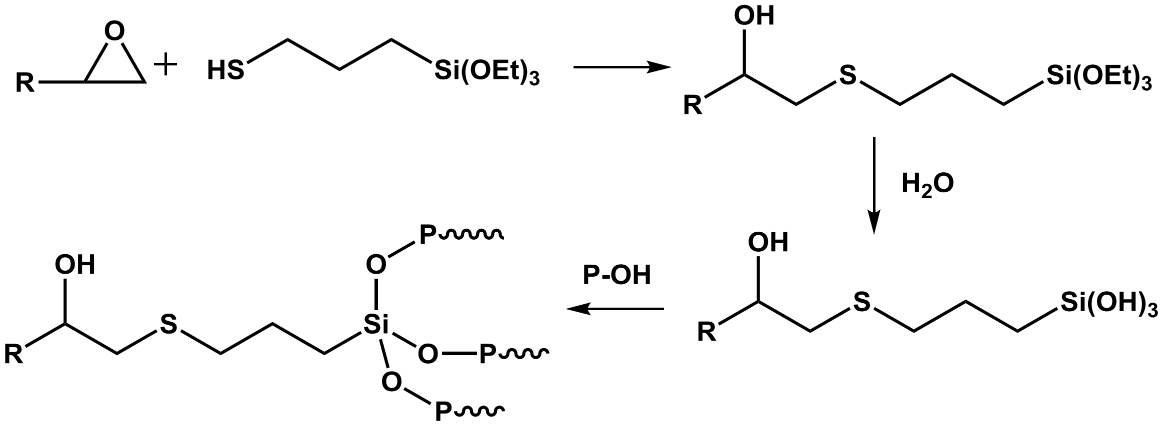
**Scheme S1.** Esterification of monomethoxy poly(ethylene oxide) methyl ether using PETTC to produce the PEO$_{113}$-PETTC macro-CTA. Abbreviations: DCC = N,N′-dicyclohexylcarbodiimide, DMAP = 4-(dimethylamino)pyridine.



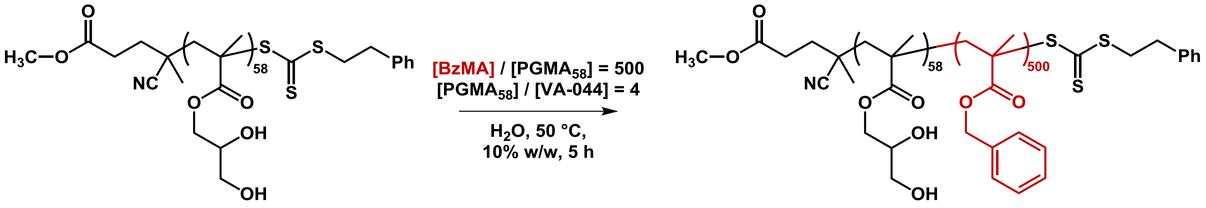
**Scheme S2.** Reaction scheme for the RAFT aqueous solution polymerization of QDMA using the RAFT agent MPETTC at pH 4, 30% w/w solids and at 44 °C using a [MPETTC] / [VA-044] molar ratio of 5.0. The target PQDMA DP is 165.



**Scheme S3.** Reaction scheme for the synthesis of a poly(potassium 3-sulfopropyl methacrylate) macro-CTA by RAFT solution polymerization of KSPMA in a 13:7 (v/v) methanol / water mixture at 70 °C targeting a DP of 150.



**Scheme S4.** Suggested mechanism for the formation of core cross-linked polyelectrolytic block copolymer worms. The epoxide groups on the PGlyMA residues are ring-opened via nucleophilic attack of the MPTES thiol group. Simultaneously, the siloxy groups are hydrolyzed to silanols and subsequently react either with one another or with the secondary hydroxyl groups of the PHPMA residues. The latter species is denoted by P-OH, where P stands for polymer.



**Scheme S6.** Reaction scheme for the RAFT aqueous emulsion polymerization of BzMA using a MePETTC-PGMA$_{58}$ macro-CTA to prepare non-ionic MePETTC-PGMA$_{58}$-PBzMA$_{500}$ nanoparticles.[1] Such nanoparticles serve as a non-adsorbing tracer for the surface zeta potential measurements presented in this work.

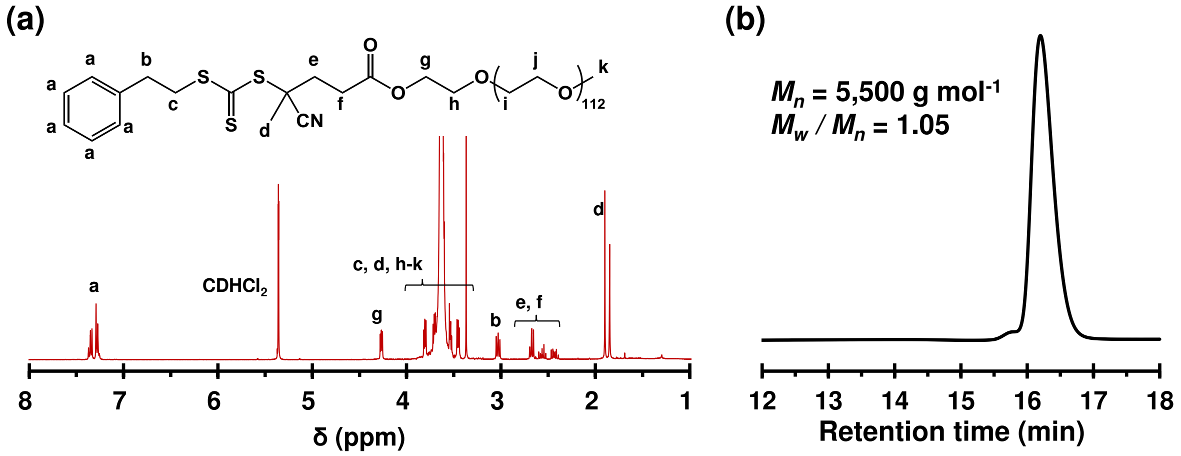


**Figure S1.** (a) Assigned $^1$H NMR spectrum recorded in $CD_2Cl_2$ for PEO$_{113}$PETTC macro-CTA, indicating a degree of esterification of 95% by comparing the integrated signals associated with the aromatic end-groups at 7.2–7.5 ppm with the PEO backbone signals at 3.3 – 4.6 ppm. (b) THF GPC chromatogram and molecular weight data obtained for this PEO$_{113}$PETTC macro-CTA. Molecular weight data are expressed relative to PEO standards.

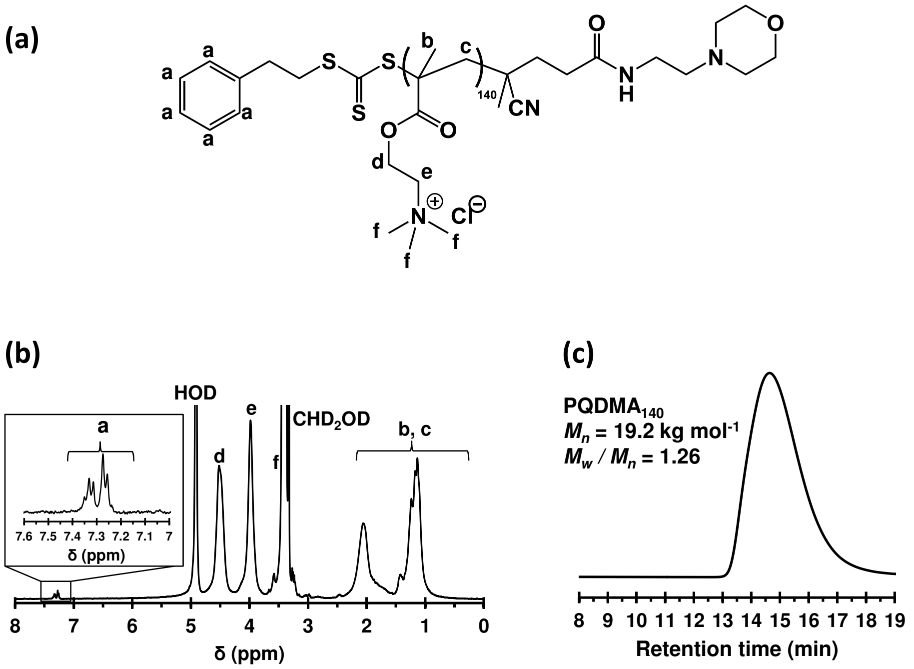


**Figure S2.** (a) Chemical structure of the cationic PQDMA$_{140}$ macro-CTA used in this study. (b) Partially assigned $^{1}$H NMR spectrum recorded in $CD_3OD$ and (c) corresponding aqueous GPC chromatogram obtained at pH 2 (molecular weight data expressed relative to PEO calibration standards).

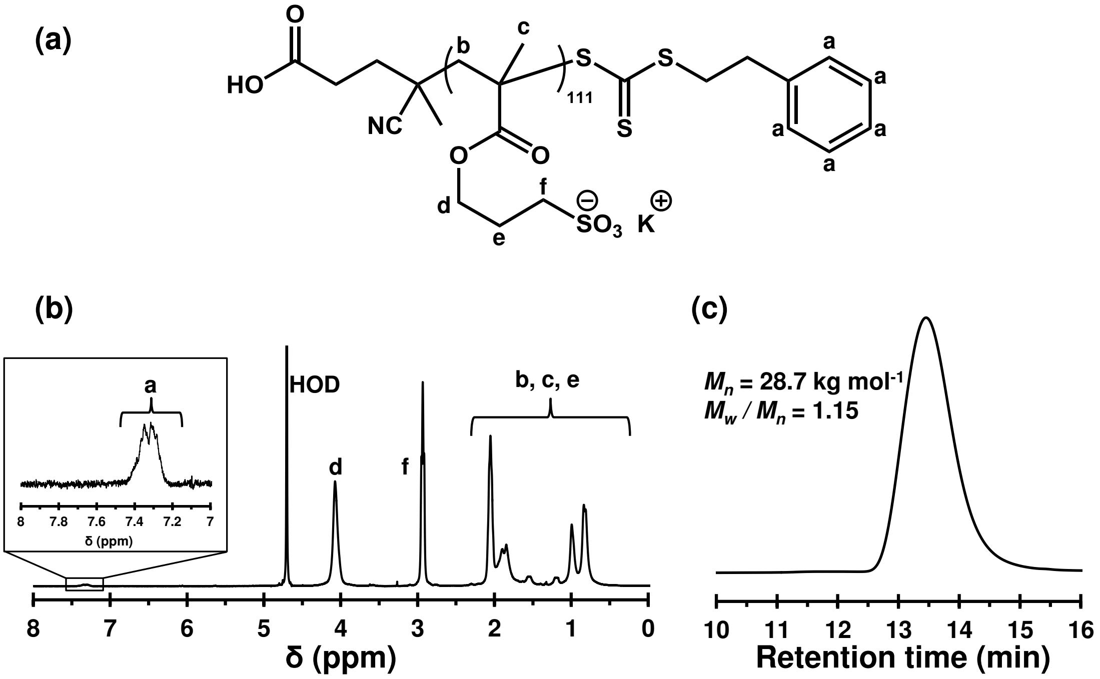


**Figure S3.** (a) Chemical structure of the anionic PKSPMA$_{111}$ macro-CTA used in this study. (b) Partially assigned $^{1}$H NMR spectrum recorded in $D_2O$ and (c) corresponding aqueous GPC chromatogram obtained at pH 9.8 (molecular weight data expressed relative to PEO calibration standards).

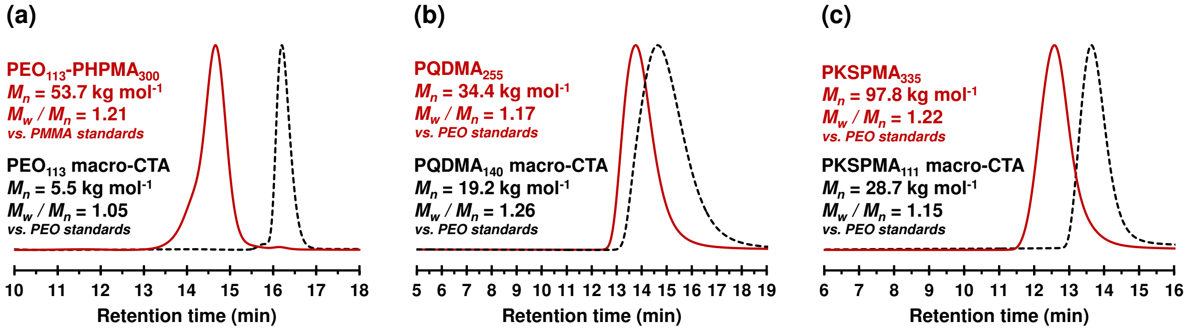


**Figure S4.** (a) THF GPC chromatograms (vs. PMMA standards) obtained for a PEO$_{113}$-PHPMA$_{300}$ diblock copolymer prepared via RAFT aqueous dispersion polymerization of HPMA and the corresponding PEO$_{113}$-PETTC macro-CTA precursor. (b) and (c) Aqueous GPC chromatograms (vs. PEO standards) obtained for PQDMA$_{225}$ and PKSPMA$_{335}$ homopolymers prepared by self-blocking experiments via RAFT aqueous solution polymerization using PQDMA$_{140}$ or PKSPMA$_{111}$ macro-CTAs, respectively.

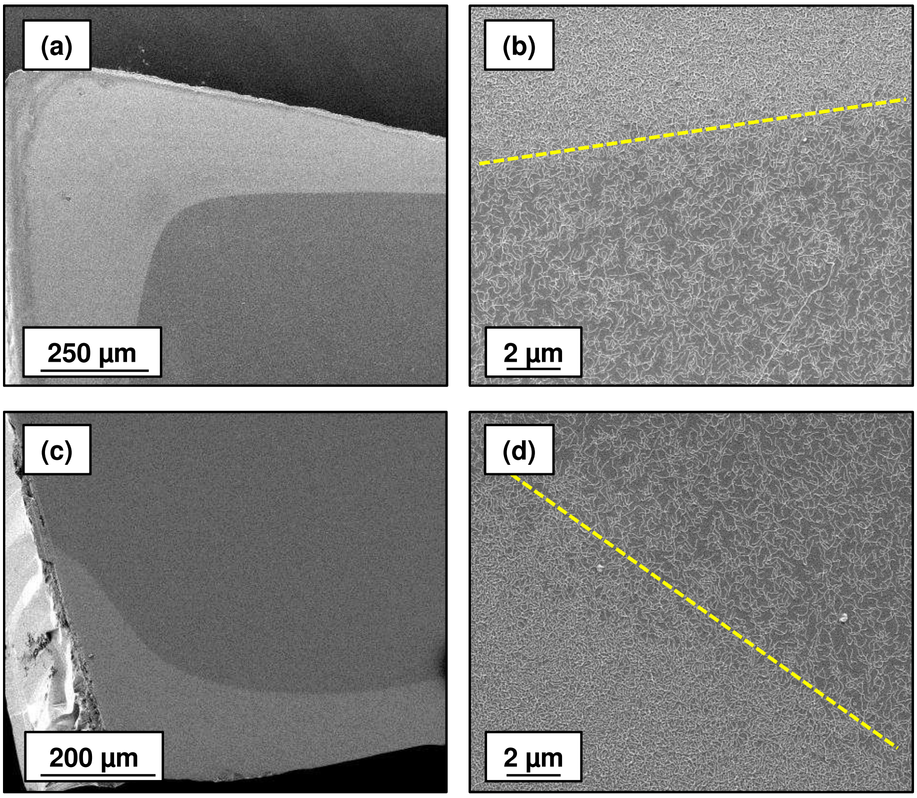


**Figure S5.** Representative SEM images obtained after dipping an anionic planar silicon wafer into a 1.0 % w/w aqueous dispersion of (0.90 PEO$_{113}$ + 0.10 PQDMA$_{140}$)-P(HPMA$_{137}$-stat-GlyMA$_{35}$) cationic cross-linked worms at pH 5 for 20 min at 20 °C in the absence of any added salt. For (a) and (b), wafers were dried under a nitrogen gas stream. However, for (c) and (d) wafers were dried in a 25 °C oven overnight with nitrogen blowing. The dashed yellow line indicates the well-defined boundary between the densely-covered wafer edges and the less densely-coated central section of the wafer.

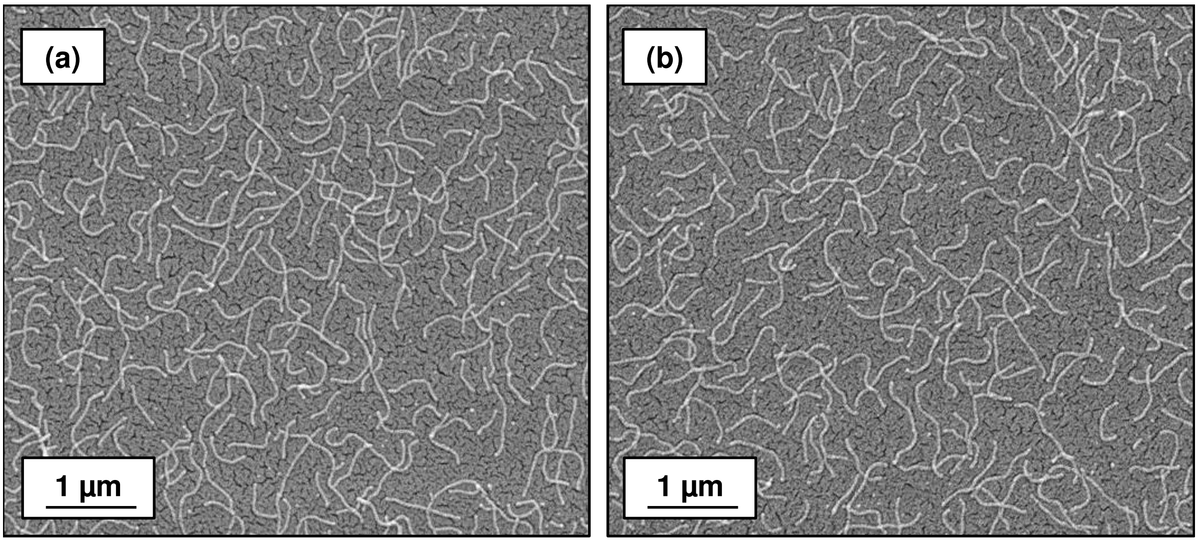


**Figure S6.** Representative SEM images obtained after dipping an anionic silicon wafer facing upside down into a 1.0 % w/w aqueous dispersion of (0.9 $PEO_{113}$ + 0.1 $PQDMA_{140}$)-P($HPMA_{137}$-stat-$GlyMA_{35}$) cationic cross-linked worms for either (a) 20 s or (b) 60 s. Importantly, the silicon surface wafer orientation does not appear to affect either the worm adsorption kinetics or the final surface coverage. Adsorption conditions: pH 5, no added salt, 20 °C.

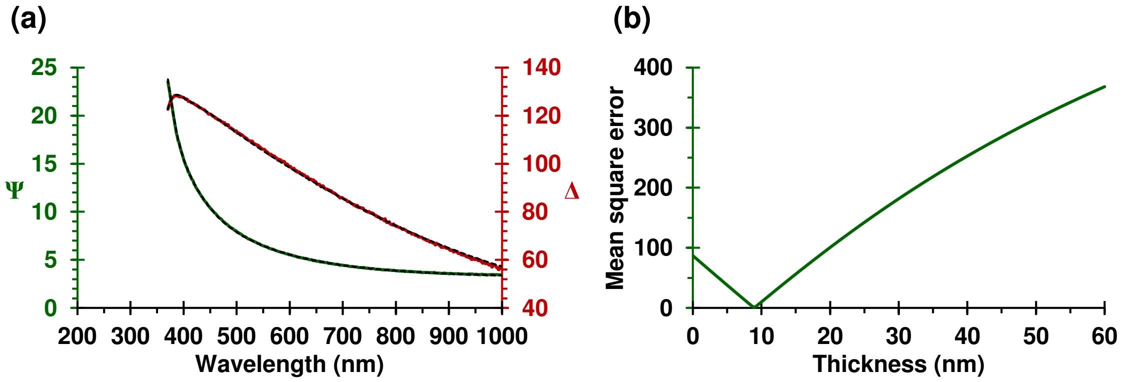


**Figure S7.** (a) Representative plots of the measured ellipsometric parameters Ψ (red line) and Δ (green line) and fitted data modelled using a Cauchy model (black dotted line) for the deposition of cationic cross-linked worms onto an anionic silicon wafer (layer 1). (b) Mean-square error against thickness plot to validate the fit of Ψ and Δ to the model. Adsorption conditions: 1.0% w/w worms, 2 min, pH 5, no salt, 20 °C.

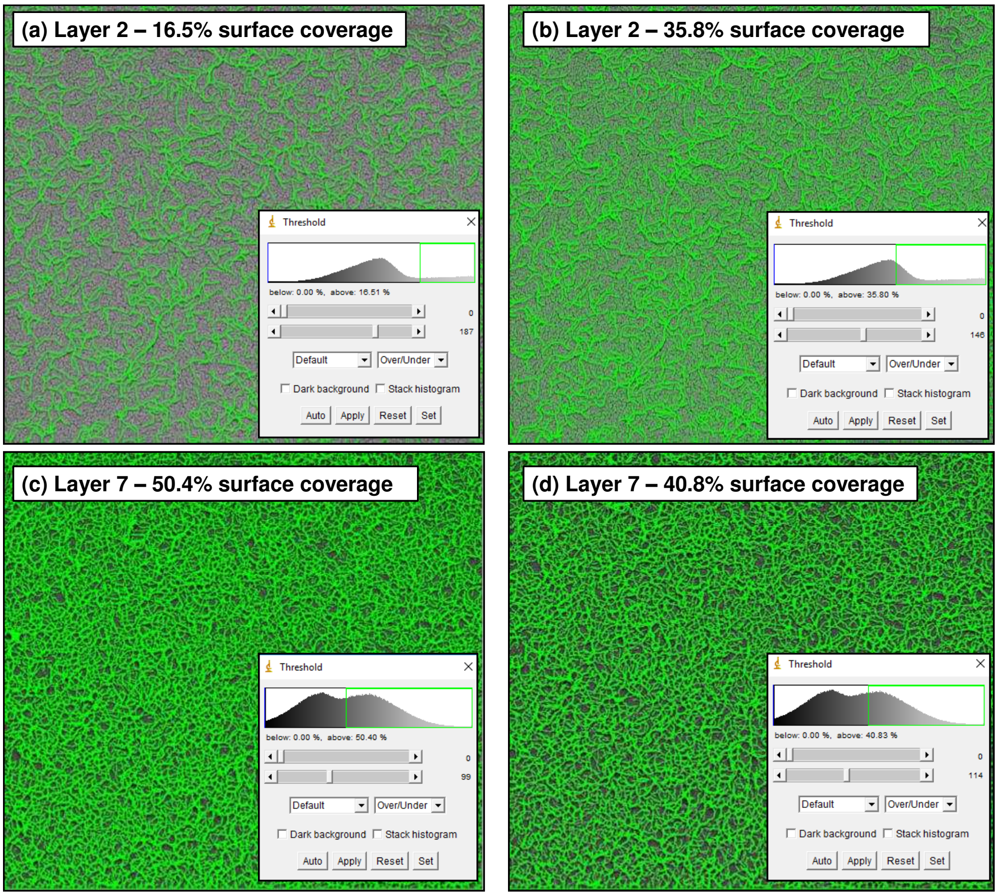


**Figure S8.** Representative ImageJ threshold analyses of SEM images obtained for layer 2 demonstrating (a) an appropriate choice of threshold cut off corresponding to 16% surface coverage and (b) the overestimation of surface coverage (36%) that occurs when the threshold cut off is set too high. Digital image analysis becomes increasingly problematic for larger numbers of adsorbed worm layers. Representative threshold analyses applied to images recorded for seven worm layers are shown in (c) and (d) to illustrate this cut off problem; both threshold values appear reasonable by visual inspection yet they result in a significantly different in surface coverages.

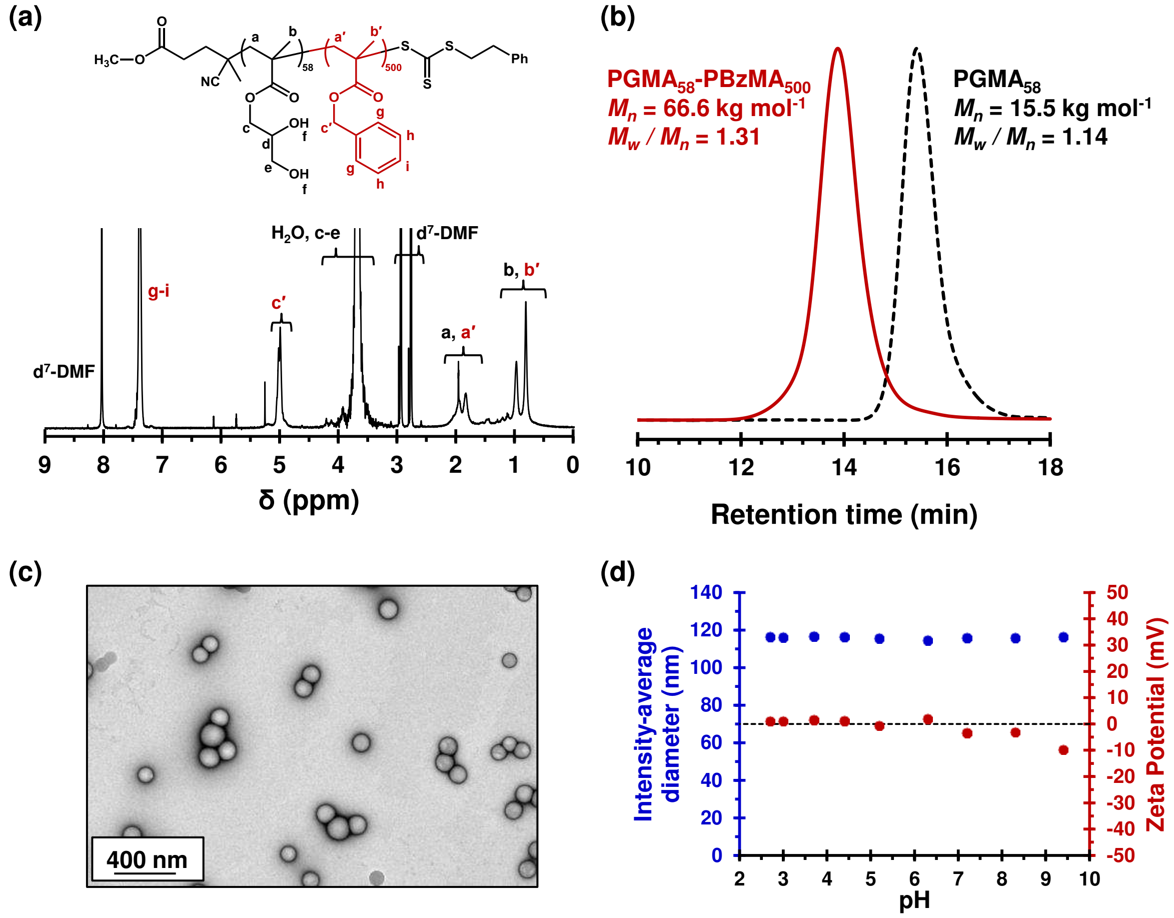


**Figure S9.** (a) Assigned $^1$H NMR spectrum recorded in d$_7$-DMF obtained for a freeze-dried sample of MePETTC-PGMA$_{58}$-PBzMA$_{500}$ diblock copolymer. (b) DMF GPC chromatograms (calibrated using a series of near-monodisperse PMMA standards) recorded for the MePETTC-PGMA$_{58}$ macro-CTA precursor and the MePETTC-PGMA$_{58}$-PBzMA$_{500}$ diblock copolymer. (c) Representative TEM image obtained for a dried 0.10% w/w aqueous dispersion of MePETTC-PGMA$_{58}$-PBzMA$_{500}$ nanoparticles, confirming their spherical morphology and relatively narrow particle size distribution. (d) Intensity-average diameter vs pH and zeta potential vs pH curves obtained for MePETTC-PGMA$_{58}$-PBzMA$_{500}$ diblock copolymer nanoparticles. Measurements were recorded using a 0.10% w/w aqueous dispersion in the presence of 1 mM KCl. The dispersion pH was adjusted using either 0.1 M or 1 M HCl.

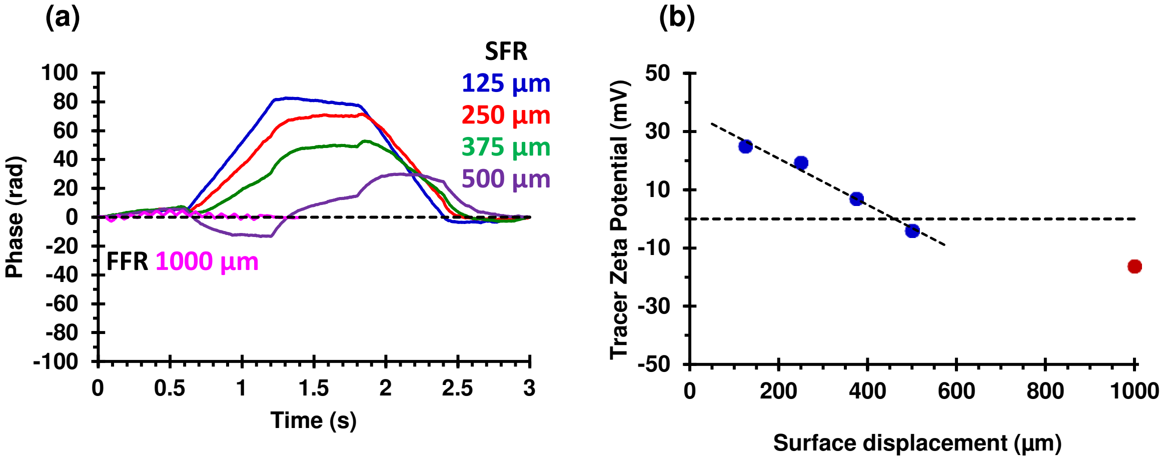


**Figure S10.** (a) Raw phase plot obtained for a clean bare anionic planar silicon wafer illustrating the expected Doppler shift when using non-ionic MePETTC-PGMA$_{58}$-PBzMA$_{500}$ nanoparticles as a tracer. Slow field reversal (SFR) measurements were performed at displacements of 125 µm, 250 µm, 375 µm and 500 µm from the surface of the silicon wafer. A fast field reversal (FFR) measurement was performed at a displacement of 1000 µm from the surface of the silicon wafer. (b) From these phase data, the tracer nanoparticle zeta potential is plotted against displacement and the surface zeta potential is calculated via equation S2. All measurements were performed at 25 °C with a Malvern ZEN1020 Surface Zeta Potential Dip Cell using a 0.0025% w/w aqueous dispersion of MePETTC-PGMA$_{58}$-PBzMA$_{500}$ nanoparticles as a non-adsorbing tracer to determine surface zeta potentials at pH 5 in the presence of 1 mM KCl.

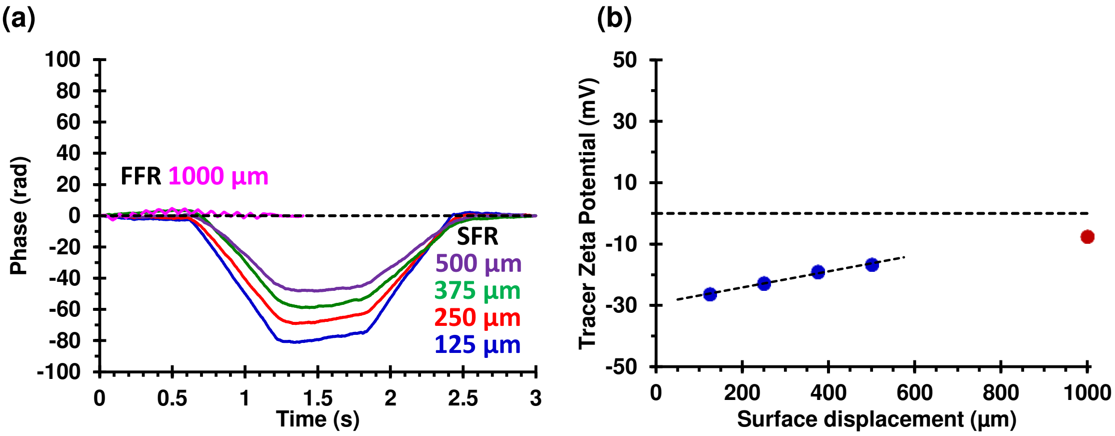


**Figure S11.** (a) Raw phase plot obtained after immersing a clean anionic silicon wafer into an aqueous dispersion of cationic worms (layer 1) illustrating the expected Doppler shift for MePETTC-PGMA$_{58}$-PBzMA$_{500}$ non-ionic tracer nanoparticles. Note the change in sign for this phase data set compared to that shown in Figure S10, indicating surface charge reversal. Slow field reversal (SFR) measurements were performed at displacements of 125 µm, 250 µm, 375 µm and 500 µm from the suface of the worm-coated silicon wafer. A fast field reversal (FFR) measurement was performed at a displacement of 1000 µm from the surface of the silicon wafer. (b) Relationship between tracer particle zeta potential and displacement used to calculate the surface zeta potential via equation S2. All measurements were performed at 25 °C with a Malvern ZEN1020 Surface Zeta Potential Dip Cell using a 0.0025% w/w aqueous dispersion of MePETTC-PGMA$_{58}$-PBzMA$_{500}$ nanoparticles as a non-adsorbing tracer to determine surface zeta potentials at pH 5 in the presence of 1 mM KCl.

# EXPERIMENTAL

## Materials

[2-(Methacryloyloxy)ethyl] trimethylammonium chloride (QDMA, 80% w/w aqueous solution), monomethoxy poly(ethylene oxide) methyl ether (PEO, $M_n$ = 5000 g mol$^{-1}$, mean DP = 113), glycidyl methacrylate (GlyMA, 97%), potassium 3-sulfopropyl methacrylate (KSPMA, 98%), benzyl methacrylate (96%) *N*,*N′*-dicyclohexylcarbodiimide (DCC, 99%) and hydrogen peroxide (30% w/w aqueous solution) were purchased from Sigma Aldrich (UK) and used as received. 2-Hydroxypropyl methacrylate (HPMA; 97%), 3-mercaptopropyltriethoxysilane (MPTES, 95%), 4-(dimethylamino)pyridine (DMAP, 99%) and 4,4′-azobis(4-cyanovaleric acid) (ACVA, 98%) were purchased from Alfa Aesar (UK) and used as received. VA-044 was purchased from Wako Chemicals Ltd. Deuterated methanol ($CD_3OD$; D, 99.8%) and dichloromethane ($CD_2Cl_2$; D, 99.9%) were purchased from Cambridge Isotopes Laboratories Ltd. Dry dichloromethane was obtained from an in-house Grubbs solvent purification system. All other solvents were purchased from either VWR International or Sigma Aldrich and were HPLC-grade quality. Deionised water was obtained from an Elgastat Option 3A water purification unit with a resistivity of 15 MΩ cm. Silicon wafers (Test grade, P(boron), 1-10 Ω cm) were purchased from PI-KEM and cleaned before use (see below).

## Synthesis of Poly(ethylene oxide)-PETTC Macro-CTA

All glassware was dried in a 150 °C oven overnight and then flame-dried under vacuum prior to use. PETTC was synthesised as previously described.[2] A 1 L two-neck round-bottomed flask was charged with a magnetic stirrer bar, poly(ethylene oxide) monomethyl ether (PEO; $M_n$ = 5000 g mol$^{-1}$, 39.9 g, 7.98 mmol) and toluene (ca. 800 mL) and this solution was subjected to azeotropic distillation under a stream of dry nitrogen to remove approximately 500 mL toluene. The flask was cooled to ≈ 0 °C prior to addition of anhydrous dichloromethane (ca. 300 mL) until the solution became clear. A 50 mL round-bottomed flask was charged with DMAP (97.5 mg, 0.789 mmol), PETTC (4.07 g, 12.0 mmol) and anhydrous dichloromethane (ca. 40 mL) then transferred into the PEO solution *via* cannula under a nitrogen atmosphere. A third 100 mL round-bottomed flask was charged with DCC (12.5 g, 60.6 mmol) and anhydrous dichloromethane (ca. 30 mL) then transferred into the reaction solution *via* cannula under a nitrogen atmosphere. The reaction solution was warmed to 20 °C, stirred for 20 h and then filtered to remove the insoluble dicyclohexylurea by-product. After concentrating the yellow solution *via* rotary evaporation under vacuum, the $PEO_{113}$-PETTC product was precipitated into excess diethyl ether (2 L), then dissolved in a minimum amount of dichloromethane (ca. 50 mL). This precipitation protocol was repeated a further three times and then the purified $PEO_{113}$-PETTC was dried in a vacuum oven at 30 °C (40.4 g, 95% yield). $^1$H NMR studies indicated a mean degree of esterification of 95%. THF GPC studies indicated a $M_n$ of 5,500 g mol$^{-1}$ and an $M_w$ / $M_n$ of 1.05 (vs a series of near-monodisperse PEO calibration standards).

## RAFT Aqueous Dispersion Polymerization of 2-Hydroxypropyl Methacrylate using a $PEO_{113}$ Macro-CTA

A 14 mL vial was charged with a magnetic stirrer bar, HPMA (0.770 g, 5.34 mmol), $PEO_{113}$-PETTC macro-CTA (0.100 g, 17.79 μmol, target DP = 300), VA-044 (1.20 mg, 3.71 μmol, [$PEO_{113}$-PETTC] / [VA-044] molar ratio = 5.0) and water (7.83 g) to afford a 20% w/w pale yellow aqueous solution. The sealed vial was placed in ice-cold water, degassed with nitrogen for 30 min and then placed in a preheated oil bath set at 50 °C for 3 h. The HPMA polymerization was quenched by exposure to air and cooling to 20 °C, yielding a free-flowing, milky-white dispersion. $^1$H NMR studies indicated more than 99% HPMA conversion. THF

GPC analysis indicated an $M_n$ of 53,700 g mol$^{-1}$ and a $M_w$ / $M_n$ of 1.21, expressed against a series of near-monodisperse poly(methyl methacrylate) calibration standards.

### Synthesis of poly([2-(methacryloyloxy)ethyl] trimethylammonium chloride) Macro-CTA by RAFT Aqueous Solution Polymerization

MPETTC RAFT agent was synthesised as described previously.[3] A 250 ml round-bottomed flask was charged with MPETTC (0.3413 g, 0.757 mmol) and ([2-(methacryloyloxy)ethyl] trimethylammonium chloride monomer (QDMA) (32.56 g of the as-supplied 80% aqueous solution, corresponding to 26.05 g QDMA monomer, 125 mmol, target DP = 165) and stirred for 10 min. Then 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044, 47.4 mg, 0.147 mmol, [MPETTC]/[VA-044] = 5) and water (55.79 g) were added to afford a 30% w/w cloudy-yellow solution. The pH was lowered to 4.0 by careful addition of 1 M HCl, the cloudy solution became transparent and was stirred for a further 5 min. The yellow solution was degassed under $N_2$ for 30 min while the flask was immersed in an ice/water slurry. The sealed reaction vessel was immersed in a preheated oil bath set at 44 °C for 70 min. The polymerization was quenched by exposure to air and cooling to room temperature. The QDMA conversion was calculated to be 75% by $^1$H NMR. Purification and isolation of the polymer was achieved by precipitation into excess acetonitrile (3 x 500 mL), dissolution into deionised water, removal of residual acetonitrile under vacuum and then freeze-drying from water for 72 h to yield a yellow solid. $^1$H NMR studies indicated a mean DP of 140 by comparing the integrated aromatic end-group signals at 7.1 – 7.4 ppm to that of the methacrylic backbone at 0.4 – 2.5 ppm, suggesting a RAFT agent efficiency of 87%. Aqueous GPC analysis (pH 2, 0.5 M acetic acid, 0.3 M $NaH_2PO_4$) of the purified $PQDMA_{140}$ macro-CTA indicated an $M_n$ of 19,200 g mol$^{-1}$ and an $M_w$ / $M_n$ of 1.26 against a series of near-monodisperse PEO calibration standards.

### Chain Extension of $PQDMA_{140}$ Macro-CTA *via* RAFT Aqueous Solution Polymerization of QDMA

A 14 mL vial was charged with a magnetic stirrer bar, QDMA (1.000 g of an 80% w/w aqueous solution, 0.800 g QDMA, 3.85 mmol), $PQDMA_{140}$ (1.000 g, 33.8 μmol, target DP = 115), VA-044 (2.20 mg, 7.85 μmol, [$PQDMA_{140}$] / [VA-044] molar ratio = 5.0) and water (2.333 g) to afford a 30% w/w pale yellow solution. The sealed vial was placed in ice-cold water, degassed using nitrogen for 30 min and then placed in a preheated oil bath set at 44 °C for 24 h. The QDMA polymerization was quenched by exposure to air and cooling to 20 °C. $^1H$ NMR analysis indicated more than 99% QDMA conversion. Aqueous GPC analysis (pH 2, 0.5 M acetic acid, 0.3 M $NaH_2PO_4$) indicated an $M_n$ of 34.4 kg $mol^{-1}$ and an $M_w / M_n$ of 1.17 against a series of near-monodisperse PEO calibration standards

### Synthesis of Poly(potassium 3-sulfopropyl methacrylate) Macro-CTA by RAFT Solution Polymerization in a Methanol/Water Mixture

PETTC was synthesised as described in a previous protocol.[2] A 50 mL round-bottomed flask was charged with a magnetic stirrer bar, potassium 3-sulfopropyl methacrylate (KSPMA; 9.98 g, 40.4 mmol, target DP = 150), PETTC (91.5 mg, 0.270 mmol), ACVA (15.1 mg, 0.054 mmol, [PETTC] / [ACVA] molar ratio = 5.0). Methanol (17.0 g, 21.5 mL) and water (12.0 g) were added to afford a 25% w/w transparent yellow solution, which was then degassed under nitrogen for 30 min while immersing the flask in an ice/water slurry in order to minimize solvent evaporation. The sealed reaction vessel was then immersed in a preheated oil bath set at 70 °C for 3 h. The polymerization was quenched by exposure to air and cooling to 20 °C, which resulted in the formation of a cloudy solution. $^1H$ NMR studies indicated a KSPMA monomer conversion of 69%. Methanol co-solvent was removed under vacuum using a rotary evaporator to afford a transparent yellow aqueous solution. Purification was achieved by precipitation into excess acetonitrile (250 mL), isolation *via* vacuum filtration, dissolution into a minimum amount of water then precipitated into excess acetonitrile (4 x 250 mL). The isolated purified PKSPMA was dissolved in water, residual acetonitrile was removed under vacuum, and then the aqueous PKSPMA solution was freeze-dried for 48 h to afford a pale yellow powder. $^1$H NMR studies confirmed the absence of any KSPMA monomer and a mean DP of 111 was calculated by comparing the integrated aromatic end-group signals at 7.2–7.5 ppm with that of the oxymethylene proton signal assigned to the polymerized KSPMA residues at 3.7–4.3 ppm. This suggests a RAFT agent efficiency of 94%. Aqueous GPC analysis (pH 9.8, 0.2 M $NaNO_3$, 0.01 M $NaH_2PO_4$) of this $PKSPMA_{111}$ macro-CTA indicated an $M_n$ of 19,200 g mol$^{-1}$ and an $M_w / M_n$ of 1.26 against a series of near-monodisperse PEO calibration standards.

### Chain Extension of $PKSPMA_{111}$ Macro-CTA by RAFT Aqueous Solution Polymerization of KSPMA

A 14 mL vial was charged with a magnetic stirrer bar, KSPMA (0.667 g, 2.70 mmol), $PKSPMA_{111}$ macro-CTA (0.3333 g, 12.0 µmol, target DP = 224), ACVA (0.70 mg, 2.38 µmol, [$PKSPMA_{111}$] / [ACVA] molar ratio = 5.0) and water (2.333 g) to afford a 30% w/w pale yellow solution. The sealed vial was placed in ice-cold water, degassed under nitrogen for 30 min and then placed in a preheated oil bath set at 70 °C for 24 h. The KSPMA polymerization was quenched by exposure to air and cooling to 20 °C to afford a viscous, pale yellow solution. $^1$H NMR studies confirmed more than 99% KSPMA conversion. Aqueous GPC analysis (pH 9.8, 0.2 M $NaNO_3$, 0.01 M $NaH_2PO_4$) indicated an $M_n$ of 97,800 g mol$^{-1}$ and an $M_w / M_n$ of 1.22 against a series of near-monodisperse PEO calibration standards.

### Synthesis of Core Cross-linked Cationic Copolymer Worms by RAFT Aqueous Dispersion Copolymerization of 2-Hydroxypropyl Methacrylate and Glycidyl Methacrylate

A 14 ml sample vial was charged with a magnetic stirrer bar, $PQDMA_{140}$ macro-CTA (0.0700 g, 2.37 μmol), $PEO_{113}$ macro-CTA (0.1267 g, 22.5 μmol), VA-044 (1.60 mg, 4.94 μmol), HPMA (0.4963 g, 3.42 mmol), GlyMA (0.1223 g, 0.86 mmol) and deionised water (3.2451 g) to afford a 20% w/w aqueous solution. The sealed vial was degassed under nitrogen in an ice-water slurry for 30 min and placed in a preheated oil bath at 50 °C for 4 h. This statistical copolymerization was quenched by exposure to air followed by cooling to 20 °C. The cationic copolymer worm dispersion was diluted to 5.0 % w/w by adding deionised water and gently stirred for 24 h at 20 °C. Core cross-linking of these cationic worms was achieved at 20 °C by adding (3-mercaptopropyl)triethoxysilane (200 mg, 202 μL, 0.84 mmol, [GlyMA]/[MPTES] molar ratio = 1.0) with continuous stirring for 48 h. These cross-linked cationic worms were characterized by aqueous electrophoresis, TEM and SEM.

### Synthesis of Core Cross-linked Anionic Worms Copolymer Worms by RAFT Aqueous Dispersion Copolymerization of 2-Hydroxypropyl methacrylate and Glycidyl methacrylate

A 14 ml sample vial was charged with a magnetic stirrer bar, $PKSPMA_{111}$ macro-CTA (0.0605 g, 2.35 μmol), $PEO_{113}$ macro-CTA (0.1200 g, 21.4 μmol), VA-044 (1.50 mg, 4.64 μmol), HPMA (0.5746 g, 3.99 mmol), GlyMA (0.1298 g, 0.91 mmol) and deionised water (3.524 g) to afford a 20 % w/w aqueous solution. The sealed vial was immersed in an ice/water slurry bath and degassed under nitrogen for 30 min, before being placed in a preheated oil bath set at 50 °C for 4 h. The statistical copolymerization was quenched by exposure to air and cooling to 20 °C. The aqueous copolymer worm dispersion was diluted to 5.0 % w/w using deionised water and gently stirred at 20 °C for 24 h. Core cross-linking of these anionic worms was achieved at 20 °C by addition of 3-mercaptopropyltriethoxysilane (0.2200 g, 222 μL, 0.92 mmol, [GlyMA]/[MPTES] molar ratio = 1.0) with continuous stirring for 48 h. These cross-linked anionic worms were by aqueous electrophoresis, TEM and SEM.

### Synthesis of MePETTC-PGMA$_{58}$-PBzMA$_{500}$ Tracer Nanoparticles *via* RAFT Aqueous Emulsion Polymerization of Benzyl methacrylate

MePETTC-PGMA$_{58}$ was synthesised according to previous reports.[3] MePETTC-PGMA$_{58}$-PBzMA$_{500}$ nanoparticles were prepared *via* RAFT aqueous emulsion polymerization of benzyl methacrylate (BzMA). A 50 mL round-bottomed flask was charged with a magnetic stirrer bar, BzMA (2.7500 g, 15.6 mmol), MePETTC-PGMA$_{58}$ macro-CTA (0.3000 g, 31.1 μmol, target DP = 500), VA-044 (2.10 mg, 7.70 μmol, [MePETTC-PGMA$_{58}$] / [VA-044] molar ratio = 4.0) and water (27.50 g, affording a 10% w/w dispersion). The sealed flask was immersed in an ice bath, degassed *via* nitrogen bubbling for 30 min and then placed in a preheated oil bath set at 50 °C for 5 h. $^1$H NMR analysis was performed in d$_7$-DMF and a BzMA conversion of 97% was calculated by comparing the integrated residual vinyl monomer signal at 6.3 ppm to the integrated aromatic signals at 7.3 – 7.9 ppm. DMF GPC studies indicated an $M_n$ of 66,600 g mol$^{-1}$ and an $M_w$ / $M_n$ of 1.31 against a series of near-monodisperse PMMA calibration standards, with no evidence for contamination with unreacted macro-CTA. These tracer particles were subsequently used for the determination of the surface zeta potential of silicon wafers.

### Layer-by-Layer Deposition Protocol

Silicon wafers were cut into 4 mm x 5 mm rectangles (for surface zeta potential and SEM analysis) or 15 mm x 7 mm (rectangles for ellipsometric measurements) using glass cutter and placed into individual glass vials. Glassware and silicon wafers were cleaned by immersion in a 1:1 ethanol/water mixture with ultrasonication for 30 min, followed by sonication in deionised water for 30 min. Clean wafers were then immersed in acidic piranha solution, consisting of a 3:1 (v/v) mixture of $H_2SO_4$ and $H_2O_2$ (30% w/w) for 1 h. [**Warning:** Piranha solution is an extremely strong oxidising agent that heats spontaneously on mixing and is also known to detonate upon contact with organic materials]. After cooling to 20 °C, the wafers were washed ten times with deionised water. The wafers were then immersed in an RCA (Radio Corporation of America) solution (70% deionised water, 15% $NH_3$, 15% $H_2O_2$) and boiled for 1 h. Finally, the wafers were rinsed ten times with deionised water and placed in a 120 °C oven to dry overnight. Aqueous dispersions of either cationic or anionic worms were diluted to the desired copolymer concentration (typically 1.0 % w/w) at pH 5, and then a clean silicon wafer was dipped into such worm dispersions for the desired time-period at 20 °C. Afterwards, worm-coated wafers were extensively washed with deionised water to remove excess worms and then dried using a nitrogen stream before being characterized by SEM, ellipsometry and surface zeta potential measurements.

## Copolymer Characterization

### Aqueous Gel Permeation Chromatography

Aqueous GPC analysis of 0.50 % w/w copolymer solutions was performed using either an acidic or basic eluent. The cationic $PQDMA_{140}$ macro-CTA (and also the $PQDMA_{240}$

homopolymer obtaining from the self-blocking experiment) were analysed using an acidic aqueous buffer containing 0.3 M $NaH_2PO_4$, 0.5 M acetic acid and adjusted to pH 2 with concentrated HCl. The anionic $PKSPMA_{111}$ macro-CTA (and also the $PKSPMA_{335}$ homopolymer obtained after the self-blocking experiment) were analysed using a basic aqueous buffer containing 0.2 M $NaNO_3$ and 0.01 M $NaH_2PO_4$ and adjusted to pH 9.8 using NaOH. In both cases the GPC set-up comprised an Agilent 1260 Infinity series degasser and pump, an 8 μm Agilent PL Aquagel-OH 40 column and an 8 μm Agilent PL Aquagel-OH 30 column connected in series to a refractive index (RI) detector. The flow rate was 1.0 mL $min^{-1}$ and the column oven and RI detector was set at 30 °C. Calibration was achieved using a series of eight near-monodisperse poly(ethylene glycol) standards with $M_p$ values ranging from 1,960 g $mol^{-1}$ to 969,000 g $mol^{-1}$.

### THF Gel Permeation Chromatography

The THF GPC set-up comprised an Agilent 1260 Infinity series degasser and pump, two Agilent PLgel 5 μn MIXED-C columns in series, a VWD detector operating at 298 nm and a refractive index detector. THF eluent contained triethylamine (2.0% w/w), butylhydroxytoluene (0.05% w/v). This set-up was operating at a flow rate of 1.0 mL $min^{-1}$ and 30 °C. A series of either seven poly(ethylene glycol) standards ranging from 238 g $mol^{-1}$ to 86,200 g $mol^{-1}$ or twelve near-monodisperse poly(methyl methacrylate) standards ranging from 800 g $mol^{-1}$ to 2,200,000 g $mol^{-1}$ were used for calibration.

### Scanning Electron Microscopy

Both bare silicon wafers and worm-coated wafers were mounted onto SEM stubs using electrically conductive adhesive pads. The stubs were gold-coated for 2 min prior to analysis. SEM studies were performed using an Inspect F microscope operating at 5 kV.

## DMF Gel Permeation Chromatography

Aqueous copolymer dispersions were freeze-dried overnight to obtain pale yellow powders. 0.50% w/w copolymer solutions were prepared in HPLC-grade DMF containing 10 mM LiBr and DMSO (1.0 % v/v) was used as a flow rate marker. GPC studies were conducted at 60 °C using a flow rate of 1.0 mL min$^{-1}$. The GPC set-up comprised an Agilent 1260 Infinity series degasser and pump, a Agilent PL-gel guard column, two Agilent PL-gel Mixed-C columns and a refractive index detector. Sixteen near-monodisperse poly(methyl methacrylate) standards ranging from $M_p$ = 645 g mol$^{-1}$ to 2,480,000 g mol$^{-1}$ were used for calibration.

## Transmission Electron Microscopy

Copper/palladium grids were surface-coated in-house to produce a thin film of amorphous carbon and then plasma glow-discharged for 20 seconds to give a hydrophilic surface. A 10 µL droplet of the freshly-prepared 0.1% w/v aqueous copolymer dispersion was placed on the hydrophilic grid for 15 seconds, blotted to remove excess sample and then negatively stained with uranyl formate solution (0.75% w/v; 10 µL) for a further 15 seconds. Excess stain was removed by blotting and each grid was carefully dried with a vacuum house. TEM studies were performed using a FEI Tecnai Spirit 2 microscope equipped with an Orius SC1000B camera operating at 80 kV.

## $^1$H NMR Spectroscopy

All NMR spectra were recorded in either $CD_3OD$ or $D_2O$ at 298 K using a 400 MHz Bruker AV3-HD spectrometer. Sixty-four scans were averaged per spectrum. All chemical shifts are reported in ppm (δ).

## Ellipsometry

Dry ellipsometry measurements were performed on bare silicon wafers or worm-coated silicon wafers in air and at room temperature using a J. A. Woollam M2000 V ellipsometer at a fixed angle of incidence of 70° to the sample surface normal. Measurements were conducted from λ = 370 – 1000 nm and obtained ellipsometry parameters Ψ and Δ were fitted to a three layer model consisting of a silicon substrate, a native oxide layer and Cauchy layer (equation S1). Data analysis and modelling were performed using CompleteEase software (provided by the ellipsometer manufacturer) which fits values of Ψ and Δ calculated from this three-layer model to the experimentally measured values.

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} \qquad \text{S1}$$

## Dynamic Light Scattering

All DLS measurements were recorded at a copolymer concentration of 0.1% w/w and at 20 °C using a Malvern Instruments Zetasizer Nano-SZ instrument equipped with a 4 mW, 633 nm He−Ne laser and an avalanche photodiode. Scattered light was detected at 173°. Aqueous electrophoresis measurements were conducted in the presence of 1 mM KCl. The dispersion pH was adjusted as required with either 1 M or 0.1 M HCl or KOH. Three mobility measurements (comprising 20 runs each) were averaged to obtain mean zeta potentials, which were calculated using the Henry equation by applying the Smoluchowski approximation.

## Laser Doppler Electrophoresis (Surface Zeta Potential) Measurements

Surface zeta potentials were calculated for both bare and worm-coated silicon wafers *via* laser Doppler electrophoresis measurements using a Malvern Surface Zeta Potential ZEN1020 cell. Clean or worm-coated silicon wafers (4 mm x 5 mm) were attached to the sample holder using ethyl cyanoacrylate ‘superglue’ (Gorilla Super Glue, Gorilla Glue Europe A/S) and the wafer-loaded sample holder was placed into a Malvern ZEN 1020 dip cell. The Zetasizer was set to detect forward-scattered light at an angle of 13° with the attenuator adjusted to position eleven (100% laser transmission). The voltage was selected to be automatic (typically 10 V was selected). The dip cell was placed in a cuvette containing 1.0 mL of 0.0025 % w/w $PGMA_{58}$-$PBzMA_{500}$ spherical nanoparticles in the presence of 1 mM KCl at 25 °C. This nanoparticle concentration was selected to give an optimal derived count rate of ≈ 500 kcps when the attenuator was set to 11.[4] The instrument was set up to perform five slow-field reversal measurements at four distances from the sample surface (125 μm, 250 μm, 375 μm and 500 μm), with each measurement comprising 15 sub-runs and 1 min between measurements. Lastly, three fast-field reversal measurements were performed at a distance of 1000 μm from the sample surface to calculate the electrophoretic mobility of the tracer nanoparticles. In this case, each measurement consisted of 100 sub-runs with an interval of 20 s between each measurement. Zeta potentials were calculated using the Henry equation using the Smoluchowski approximation.

$$\zeta_{surface} = -intercept + \zeta_{Ep} \qquad \text{S2}$$

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