## Electronic Supporting Information for

# Mussel-Inspired Protein-Repelling Ambivalent Block Copolymers: Controlled Synthesis and Characterizations 

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Experiment S1. Synthesis of N -(3,4-dihydroxyphenethyl)methacrylamide (Dopamine methacrylamide) (DMA). A modified procedure has been adopted from Glass et al. to synthesize DMA monomer ${ }^{1}$. A two-neck round-bottom flask was charged with 20.2 g ( 52.9 mmol ) of $\mathrm{Na}_{2} \mathrm{~B}_{4} \mathrm{O}_{7} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ and 10.0 g of $\mathrm{Na}_{2} \mathrm{CO}_{3}$, and 575 mL of milli-Q water (18.2 M $\Omega . \mathrm{cm}$, Millipore). This basic aqueous solution was degassed in sonicator bath (Branson 2510 , $100 \mathrm{~W}, 42 \mathrm{KHz}$ ) for 1 h , applying light vacuum, following argon bubbling for another $2 \mathrm{~h} .5 .0 \mathrm{~g}(26.3 \mathrm{mmol})$ of dopamine hydrochloride (1, Scheme 2 in the manuscript) was added under argon atmosphere and continued stirring for 30 minutes. The flask was then cooled at $0^{\circ} \mathrm{C}$ before drop-wise addition of 8.0 mL ( 53.9 mmol ) of methacrylic anhydride with stirring. Another $10.0 \mathrm{~g} \mathrm{Na}_{2} \mathrm{CO}_{3}$ was added to maintain the pH of the solution above 9
during the reaction. After stirring for 12 h at room temperature, the solution was acidified to $\mathrm{pH} 1-2$ with 6 N HCl , and continued stirring for 1 h in an open vessel. The mixture was extracted five times with ethyl acetate, washed twice with 0.1 M HCl and dried over $\mathrm{MgSO}_{4}$. The solvent was removed in vacuum to yield crude greyish paste, which was further purified by flash silica gel column chromatography eluting with dichloromethane/methanol (9:1) mixture (white solid, $81 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( 250 MHz, DMSO- $d_{6}, \delta(\mathrm{ppm})$ ): $7.92(\mathrm{t}, 1 \mathrm{H},-\mathrm{NH}-$ $\mathrm{C}=\mathrm{O})$, 6.41-6.64 (m, $3 \mathrm{H}, \mathrm{Ph}), 5.61\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}_{2}=\mathrm{C}-\mathrm{CH}_{3}\right), 5.29\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}_{2}=\mathrm{C}-\mathrm{CH}_{3}\right), 3.21(\mathrm{q}$, $\left.2 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{NH}-\right), 2.55\left(\mathrm{t}, 2 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{NH}-\right), 1.84\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{2}=\mathrm{C}-\mathrm{CH}_{3}\right) .{ }^{13} \mathrm{C}$ NMR (400 MHz, DMSO- $\left.d_{6}, \delta(\mathrm{ppm})\right): 167.4$ (1C, -NH-C=O), 145.0 (1C, Ph-OH), 143.5 (1C, $\left.\mathrm{Ph}-\mathrm{OH}\right)$, $140.2\left(1 \mathrm{C}, \mathrm{CH}_{2}=\underline{\mathrm{C}}-\mathrm{CH}_{3}\right), 130.3\left(\mathrm{CH}_{2}-\mathrm{Ph}\right), 119.2\left(1 \mathrm{C}, \mathrm{CH}_{2}=\mathrm{C}-\mathrm{CH}_{3}\right), 118.8(1 \mathrm{C}, \mathrm{Ph}), 116.0$ (1C, Ph$), 115.4$ (1C, Ph$), 40.9\left(-\mathrm{CH}_{2}-\mathrm{NH}-\right), 34.8\left(\mathrm{Ph}-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\right), 18.7\left(1 \mathrm{C}, \mathrm{CH}_{2}=\mathrm{C}-\mathrm{CH}_{3}\right)$.


#### Abstract

Experiment S2. Synthesis of $\mathbf{N}$-(2-(2,2-dimethylbenzo[d][1,3]dioxol-5yl)ethyl)methacrylamide ( $\underline{\text { Acetonide-protected dopamine methacrylamide) (ADMA). }}$ 250 mL of anhydrous toluene was dried over molecular sieves and transferred to a three-neck round-bottom flask, followed by bubbling with argon for 30 minutes. $10.0 \mathrm{~g}(45.2 \mathrm{mmol})$ of DMA (2b, Scheme 2 in the manuscript) and $430 \mathrm{mg}(2.26 \mathrm{mmol})$ of $p$-Toluenesulfonic acid ( $p-\mathrm{TsOH}$ ) as a catalyst was added under argon atmosphere. Dean-Stark apparatus was attached and solution was refluxed for 3 h . The flask was then cooled to $0^{\circ} \mathrm{C}$, and added 53.0 mL (432.5.0 mmol) of 2,2-dimethoxypropane. Soxhlet extractor, whose thimble was filled with 40.0 g of $\mathrm{CaCl}_{2}$ was attached and the flask was warmed to $40{ }^{\circ} \mathrm{C}$ for 2 h . The solution was then vigorously stirred in dark, under reflux (ca. $115{ }^{\circ} \mathrm{C}$ ) for another 4 h . The mixture was washed with water, brine and dried over $\mathrm{MgSO}_{4}$. The solvent was removed in vacuum to yield crude orange paste, which was further purified by flash silica gel column chromatography eluting with cyclohexane/ethyl acetate (5:5) mixture (white solid, $85 \%$


yield). ${ }^{1} \mathrm{H}$ NMR ( 250 MHz, DMSO- $d_{6}, \delta(\mathrm{ppm})$ ): $7.95(\mathrm{t}, 1 \mathrm{H},-\mathrm{NH}-\mathrm{C}=\mathrm{O})$, 6.57-6.73 (m, 3H, $\mathrm{Ph}), 5.60\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}_{2}=\mathrm{C}-\mathrm{CH}_{3}\right), 5.30\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH}_{2}=\mathrm{C}-\mathrm{CH}_{3}\right), 3.28\left(\mathrm{q}, 2 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{NH}-\right), 2.64$ ( $\left.\mathrm{t}, 2 \mathrm{H},-\mathrm{CH}_{2}-\mathrm{CH}_{2}-\mathrm{NH}-\right), 1.83\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{2}=\mathrm{C}-\mathrm{CH}_{3}\right), 1.61\left(\mathrm{~s}, 6 \mathrm{H},\left(\mathrm{CH}_{3}\right)_{2}-\mathrm{C}-\right) .{ }^{13} \mathrm{C}$ NMR (400
 $\left.\mathrm{O}\left(\mathrm{C}(\mathrm{Me})_{2}\right)\right), 140.0\left(1 \mathrm{C}, \mathrm{CH}_{2}=\underline{\mathrm{C}}-\mathrm{CH}_{3}\right)$, $132.8\left(\mathrm{CH}_{2}-\underline{\mathrm{Ph}}\right), 121.1\left(1 \mathrm{C}, \underline{\mathrm{C}}(\mathrm{Me})_{2}\right), 118.7(1 \mathrm{C}$, $\left.\underline{\mathrm{CH}}_{2}=\mathrm{C}_{-} \mathrm{CH}_{3}\right), 117.4(1 \mathrm{C}, \mathrm{Ph}), 108.7(1 \mathrm{C}, \mathrm{Ph}), 107.9(1 \mathrm{C}, \mathrm{Ph}), 40.7\left(-\mathrm{CH}_{2}-\mathrm{NH}-\right), 34.8(\mathrm{Ph}-$ $\left.\underline{\mathrm{CH}}_{2}-\mathrm{CH}_{2}-\right), 25.7\left(2 \mathrm{C},-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{2}\right), 18.5\left(1 \mathrm{C}, \mathrm{CH}_{2}=\mathrm{C}-\mathrm{CH}_{3}\right)$.

## RAFT polymerization of ADA (3a).

Monomer conversion was calculated according to equation:

Monomer conversion (\%) $=\frac{[I]_{1.5}}{\left([I]_{1.5}+[I]_{1.6}\right)} \times 100$

Where $[I]_{1.5}$ - peak area of the signal assigned to acetonide protons in polymer (from 1.6 to $1.4 \mathrm{ppm})$.
$[I]_{1.6}-$ peak area of the signal assigned to acetonide protons in monomer (from 1.7 to $1.6 \mathrm{ppm})$.

Degree of polymerization was calculated according to equation:

$$
\mathrm{DP}=\frac{[I]_{6.6}}{[I]_{0.85}}
$$

Where $[I]_{6.6}$ - peak area of the signal assigned to aromatic protons in polymer (from 6.8 to 6.4 ppm).
$[I]_{0.85}$ - peak area of the signal assigned to $\omega$-end group of DMP at 0.85 ppm .

Number-average molar mass ( $\boldsymbol{M}_{\mathrm{n}, \mathrm{NMR}}$ ) was calculated as following:

$$
M_{\mathrm{n}, \mathrm{NMR}}=(\mathrm{DP} \times 247.29)+364.63
$$

Where 247.29 - molar mass of ADA monomer.
364.63 - molar mass of DMP (RAFT agent).


Fig. S1 ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathrm{P}(\mathrm{ADA})$ in DMSO- $d_{6}$ prepared from RAFT polymerization of ADA in DMF at $70^{\circ} \mathrm{C}$, with inset showing resonance for $\omega$-chain ends of RAFT agent. $*$ and \# in the spectrum corresponds to deuterated solvent and residual water, respectively.

Experiment S3. RAFT Polymerization of ADMA (3b, Scheme 2). A typical RAFT polymerization of ADMA, with a molar ratios of 75:1:0.75 ([ADMA]:[CTP]:[AIBN]) is described as follows: ADMA ( $0.5 \mathrm{~g}, 1.91 \mathrm{mmol}$ ), CTP ( $7.11 \mathrm{mg}, 0.025 \mathrm{mmol}$ ), AIBN ( 3.13
$\mathrm{mg}, 0.019 \mathrm{mmol})$ and DMF ( 2.0 g ) were taken in reaction tube equipped with magnetic stir bar. The reaction mixture was degassed by five freeze-pump-thaw cycles, filled with argon and placed in preheated oil bath at $60^{\circ} \mathrm{C}$. Approximately 0.1 mL of reaction mixture was taken out at regular time intervals to determine $M_{\mathrm{n}, \mathrm{SEC}}$ and $Đ$ by SEC. Monomer conversion and DP was calculated by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The polymerization reaction was stopped at predetermined time periods, quenching immediately in liquid nitrogen and exposing the solution to air. The polymer solution was dialysed with methanol, dried in vacuum at room temperature overnight, to obtain a pink powder.

Monomer conversion was calculated according to equation:

Monomer conversion $(\%)=\frac{[I]_{1.55}}{\left([I]_{1.55}+[I]_{1.61}\right)} \times 100$

Where $[I]_{1.55}$ - peak area of the signal assigned to acetonide protons in polymer (from 1.59 to $1.50 \mathrm{ppm})$.
$[I]_{1.61}-$ peak area of the signal assigned to acetonide protons in monomer (from 1.64 to 1.59 ppm$)$.

Degree of polymerization was calculated according to equation:

$$
\mathrm{DP}=\frac{5[I]_{6.6}}{3[I]_{7.4}}
$$

Where $[I]_{6.6}$ - peak area of the signal assigned to aromatic protons in polymer (from 6.8 to 6.4 ppm).
$[I]_{7.4}-$ peak area of the signal assigned to $\omega$-end group of CTP at 7.4 ppm .

Number-average molar mass ( $\boldsymbol{M}_{\mathrm{n}, \mathrm{NMR}}$ ) was calculated as following:

$$
M_{\mathrm{n}, \mathrm{NMR}}=(\mathrm{DP} \times 261.67)+279.38
$$

Where 261.67 - molar mass of ADMA monomer.

$$
279.38 \text { - molar mass of CTP (RAFT agent). }
$$

Experiment S4. RAFT polymerization of PEGA: RAFT polymerization of PEGA, with a molar ratios of 35:1:0.1 ([PEGA]:[DMP]:[AIBN]) is described as follows: PEGA $(2.00 \mathrm{~g}, 4.17 \mathrm{mmol})$, DMP $(43.4 \mathrm{mg}, 0.12 \mathrm{mmol})$, $\operatorname{AIBN}(1.95 \mathrm{mg}, 0.01 \mathrm{mmol})$ and DMF $(4.0 \mathrm{~g})$ were taken in reaction tube equipped with magnetic stir bar. The reaction mixture was degassed by five freeze-pump-thaw cycles, filled with argon and placed in preheated oil bath at $60^{\circ} \mathrm{C}$. Approximately 0.1 mL of reaction mixture was taken out at regular time intervals to determine $M_{\mathrm{n} \text {, SEC }}$ and $\doteq$ by SEC. Monomer conversion and DP was calculated by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The polymerization reaction was stopped at predetermined time periods, quenching immediately in liquid nitrogen and exposing the solution to air. The polymer solution was dialysed with methanol, dried in vacuum at room temperature overnight, to obtain a yellow coloured viscous liquid.

Monomer conversion was calculated according to equation:

Monomer conversion $(\%)=\frac{[I]_{4.15}}{\left([I]_{4.15}+[I]_{4.3}\right)} \times 100$

Where $[I]_{4.15}$ - peak area of the signal assigned to oxymethylene groups in polymer (from 4.25 to 4.00 ppm$)$.
$[I]_{4.3}$ - peak area of the signal assigned to oxymethylene groups in monomer (from 4.35 to 4.25 ppm$)$.

Degree of polymerization was calculated according to equation:

$$
\mathrm{DP}=\frac{3[I]_{4.15}}{2[I]_{0.85}}
$$

Where $[I]_{0.85}$ - peak area of the signal assigned to $\omega$-end group of DMP at 0.85 ppm .

Number-average molar mass ( $\boldsymbol{M}_{\mathrm{n}, \mathrm{NMR}}$ ) was calculated as following:

$$
M_{\mathrm{n}, \mathrm{NMR}}=(\mathrm{DP} \times 480)+364.63
$$

Where 480 - molar mass of PEGA monomer.

$$
364.63 \text { - molar mass of DMP (RAFT agent). }
$$

Experiment S5. RAFT polymerization of PEGMA: RAFT polymerization of PEGMA, with a molar ratios of 75:1:0.1 ([PEGMA]:[CTP]:[AIBN]) is described as follows: PEGMA ( $1.00 \mathrm{~g}, 2.11 \mathrm{mmol}$ ), CTP ( $7.84 \mathrm{mg}, 0.028 \mathrm{mmol}$ ), AIBN ( $0.46 \mathrm{mg}, 0.0028 \mathrm{mmol}$ ) and DMF ( 3.0 g ) were taken in reaction tube equipped with magnetic stir bar. The reaction mixture was degassed by five freeze-pump-thaw cycles, filled with argon and placed in preheated oil bath at $70{ }^{\circ} \mathrm{C}$. Approximately 0.1 mL of reaction mixture was taken out at regular time intervals to determine $M_{\mathrm{n}, \text { SEC }}$ and $Đ$ by SEC. Monomer conversion and DP was calculated by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The polymerization reaction was stopped at predetermined time periods, quenching immediately in liquid nitrogen and exposing the solution to air. The polymer solution was dialysed with methanol, dried in vacuum at room temperature overnight, to obtain a pink coloured viscous liquid.

Monomer conversion was calculated according to equation:

Monomer conversion $(\%)=\frac{[I]_{4.0}}{\left([I]_{4.0}+[I]_{4.25}\right)} \times 100$

Where $[I]_{4.0}$ - peak area of the signal assigned to oxymethylene groups in polymer (from 4.20 to 3.9 ppm ).
$[I]_{4.25}$ - peak area of the signal assigned to oxymethylene groups in monomer (from 4.35 to 4.2 ppm$)$.

Degree of polymerization was calculated according to equation:

$$
\mathrm{DP}=\frac{5[I]_{4.0}}{2[I]_{7.4}}
$$

Where $[I]_{7.4}$ - peak area of the signal assigned to $\omega$-end group of CTP at 7.4 ppm .

Number-average molar mass ( $\boldsymbol{M}_{\mathrm{n}, \mathrm{NMR}}$ ) was calculated as following:

$$
M_{\mathrm{n}, \mathrm{NMR}}=(\mathrm{DP} \times 475)+279.38
$$

Where 475-molar mass of PEGMA monomer.
279.38 - molar mass of CTP (RAFT agent).

RAFT Chain end-groups determination by UV-vis spectroscopy: Four different concentrations of 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DMP) were prepared in DMSO and their absorption values were measured at 310 nm . From these absorption values, the molar absorptivity $(\varepsilon)$ of the trithiocarbonate moiety of DMP at $25^{\circ} \mathrm{C}$ in DMSO was calculated as $14370 \mathrm{~L} \mathrm{~mol}^{-1} \mathrm{~cm}^{-1}$ (Beer-Lambert law). With the experimental
values of mass ( $m$, in g ) and volume ( $V$, in $\mathrm{cm}^{3}$ ), the number-average molar mass ( $M_{\mathrm{n}, \mathrm{UV} \text {-vis }}$ ) and $\%$ chain end-groups retention were calculated from the following equations.

$$
M_{\mathrm{n}, \mathrm{UV}-\mathrm{vis}}=\frac{(m \times l \times \varepsilon)}{(A \times V)}
$$

Where $A$ is the absorption and $l$ is the path length of the cell $(\mathrm{cm})$.
$\%$ chain end-groups retention $=\frac{M_{\mathrm{n}, \mathrm{UV}}-\text { vis }}{M_{\mathrm{n}, \mathrm{NMR}}} \times 100$


Fig. S2 Calculation of molar absorptivity of trithiocarbonate moiety of DMP (Beer-Lambert law) by UV-visible spectroscopy.

## Experiment S6. Synthesis of P(ADA-b-PEGA) Block copolymer using P(ADA) as

 macro-CTA: A typical block copolymerization procedure with a molar ratios of 35:1:0.1 ([PEGA]:[P(ADA)]:[AIBN]) is described as follows: PEGA (1.00 g, 2.08 mmol ), PDMA (macro-CTA, $\left.M_{\mathrm{n}, \mathrm{SEC}}=5600 \mathrm{~g} \mathrm{~mol}^{-1}, ~ Đ=1.07,333 \mathrm{mg}, 0.06 \mathrm{mmol}\right), \operatorname{AIBN}(1.0 \mathrm{mg}, 0.006$ mmol ) and DMF ( 4.0 g ) were taken in reaction tube equipped with magnetic stir bar. The reaction mixture was degassed by five freeze-pump-thaw cycles, filled with argon and placedin preheated oil bath at $60^{\circ} \mathrm{C}$. The polymerization reaction was stopped at predetermined time period, quenching immediately in liquid nitrogen and exposing the solution to air. The polymer solution was dialysed with methanol, dried in vacuum at room temperature overnight, to obtain a yellow coloured viscous liquid.

Experiment S7. Synthesis of P(ADMA $\boldsymbol{n}_{\boldsymbol{n}}$-b-PEGMA $\boldsymbol{m}_{\boldsymbol{m}}$ ) Block Copolymers: A typical block copolymerization procedure with a molar ratios of 75:1:0.1 ([PEGMA]:[P(ADMA)]:[AIBN]) is described as follows: PEGMA ( $1.00 \mathrm{~g}, 2.10 \mathrm{mmol}$ ), $\mathrm{P}(\mathrm{ADMA})$ (macro-CTA, $\left.M_{\mathrm{n}, \mathrm{SEC}}=4000 \mathrm{~g} \mathrm{~mol}^{-1}, ~ D=1.16\right)$, AIBN $(0.46 \mathrm{mg}, 0.0028 \mathrm{mmol})$ and DMF ( 10.0 g ) were taken in reaction tube equipped with magnetic stir bar. The reaction mixture was degassed by five freeze-pump-thaw cycles, filled with argon and placed in preheated oil bath at $60^{\circ} \mathrm{C}$. The polymerization reaction was stopped at predetermined time period, quenching immediately in liquid nitrogen and exposing the solution to air. The polymer solution was dialysed with methanol, dried in vacuum at room temperature overnight, to obtain a pink coloured viscous liquid. Two families of $\mathrm{P}_{\left(\mathrm{ADMA}_{n}-b-\mathrm{PEGMA}_{m}\right)}$ block copolymers using $\mathrm{P}(\mathrm{ADMA})$ macro-CTA of two different molar masses, which intern consisting of block copolymers with different DP with respect to PEGMA block (using different [PEGMA]/[P(ADMA)] ratios), employing same $\mathrm{P}(\mathrm{ADMA})$ macro-CTA, were synthesized, and their molecular characteristics are summarized in Table 1.

Experiment S8. Oxidation of $\mathbf{P}\left(\mathbf{P E G A}_{\boldsymbol{m}}-\boldsymbol{b}-\mathbf{D A}_{\boldsymbol{n}}\right) .10 \mathrm{mg}$ of $\mathrm{P}\left(\mathrm{PEGA}_{\boldsymbol{m}}-b-\mathrm{DA}_{n}\right)$ dissolved in 10 mL of distilled water, and a $\mathrm{NaOH}(0.1 \mathrm{M})$ is added slowly in order to raise the pH above 10 . This oxidation step lasts at least one night under air and is followed by UVvis spectroscopy.


Fig. S3 UV-vis spectra of $\mathrm{P}\left(\mathrm{PEGA}_{29}-b-\mathrm{DA}_{17}\right)$ in methanol, and corresponding oxidized $\mathrm{P}\left(\mathrm{PEGA}_{29}-b-\mathrm{DQA}_{17}\right)$ in water.


Fig. S4 ${ }^{1} \mathrm{H}$ NMR spectrum of DMA (2b) monomer in DMSO- $d_{6} . *$ and $\#$ in the spectrum corresponds to deuterated solvent and residual water, respectively.


Fig. S5 ${ }^{1} \mathrm{H}$ NMR spectrum of ADMA ( $\mathbf{3 b}$ ) monomer in DMSO- $d_{6}$. * and \# in the spectrum corresponds to deuterated solvent and residual water, respectively.


Fig. S6 ${ }^{13} \mathrm{C}$ NMR spectrum of DA (2a) monomer in DMSO- $d_{6}$.


Fig. S7 ${ }^{13} \mathrm{C}$ NMR spectrum of ADA (3a) monomer in DMSO- $d_{6}$.


Fig. S8 ${ }^{13} \mathrm{C}$ NMR spectrum of DMA (2b) monomer in DMSO- $d_{6}$.


Fig. S9 ${ }^{13} \mathrm{C}$ NMR spectrum of ADMA (3b) monomer in DMSO- $d_{6}$.


Fig. S10 The number-average molar mass of $\mathrm{P}(A D A)$, obtained from the RAFT polymerization of ADA with different [monomer]/[CTA] ratios in DMF at $70{ }^{\circ} \mathrm{C}$ (PS calibration).


Fig. S11 Semilogarithmic plot with $\doteq$ values against polymerization time, and (B) the corresponding $M_{\mathrm{n}}$ versus monomer conversion plot for the RAFT polymerization of ADMA, with a molar ratios of 50:1:0.4 ([ADMA]:[CDP]:[ACHN]) in DMF at $80^{\circ} \mathrm{C}$ (PS calibration).


Fig. S12 RI-SEC traces as a function of elution time, obtained from the RAFT polymerization of ADMA, with a molar ratios of 50:1:0.4 ([ADMA]:[CDP]:[ACHN]) in DMF at $80^{\circ} \mathrm{C}$.


Fig. S13 Semilogarithmic plot with $Đ$ values against polymerization time for the RAFT polymerization of ADMA, with a molar ratios of 75:1:0.75 ([ADMA]:[CTP]:[AIBN]) in DMF at $60^{\circ} \mathrm{C}$ (PS calibration).


Fig. S14 $M_{n}$ versus monomer conversion plot for the RAFT polymerization of ADMA, with a molar ratios of 75:1:0.75 ([ADMA]:[CTP]:[AIBN]) in DMF at $60^{\circ} \mathrm{C}$ (PS calibration).


Fig. S15 RI-SEC traces as a function of elution time, obtained from the RAFT polymerization of ADMA, with a molar ratios of 75:1:0.75 ([ADMA]:[CTP]:[AIBN]) in DMF at $60^{\circ} \mathrm{C}$.


Fig. S16 Semilogarithmic plots with $D$ values against polymerization time for the RAFT polymerization of (A) PEGA, with a molar ratios of 35:1:0.1 ([PEGA]:[DMP]:[AIBN]) at 60 ${ }^{\circ} \mathrm{C}$, and (B) PEGMA, with a molar ratios of 75:1:0.1 ([PEGMA]:[CTP]:[AIBN]) at $70{ }^{\circ} \mathrm{C}$, in DMF (PMMA calibration).


Fig. S17 $M_{\mathrm{n}}$ versus monomer conversion plots for the RAFT polymerization of (A) PEGA, with a molar ratios of 35:1:0.1 ([PEGA]:[DMP]:[AIBN]) at $60^{\circ} \mathrm{C}$, and (B) PEGMA, with a molar ratios of 75:1:0.1 ([PEGMA]:[CTP]:[AIBN]) at $70^{\circ} \mathrm{C}$, in DMF (PMMA calibration).


Fig. S18 RI-SEC traces as a function of elution time, obtained from the RAFT polymerization of (A) PEGA, with a molar ratios of 35:1:0.1 ([PEGA]:[DMP]:[AIBN]) at 60 ${ }^{\circ} \mathrm{C}$, and (B) PEGMA, with a molar ratios of 75:1:0.1 ([PEGMA]:[CTP]:[AIBN]) at $70{ }^{\circ} \mathrm{C}$, in DMF.


Fig. S19 RI-SEC traces as a function of elution time, obtained from the RAFT polymerization of PEGA, with a molar ratios of 35:1:0.1 ([PEGA]:[P(ADA)]:[AIBN]) in DMF at $60^{\circ} \mathrm{C}$.




$\begin{array}{lllllllllll}9.5 & 8.5 & 7.5 & 6.5 & 5.5 & \begin{array}{c}4.5 \\ (\mathrm{ppm})\end{array} & 3.5 & 2.5 & 1.5 & 0.5 & -0.5\end{array}$
(ppm)

Fig. S20 ${ }^{1} \mathrm{H}$ NMR spectrum of (A) P(DMA $9-b$-PEGMA ${ }_{17}$ ), and (B) expanded region of A (4$3.1 \mathrm{ppm})$ in $\mathrm{DMSO}-d_{6} . *$ in the spectrum corresponds to deuterated solvent.


Fig. S21 ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathrm{P}\left(\right.$ ADMA $_{9}-b-$ PEGMA $\left._{17}\right)$ in DMSO- $d_{6} . *$ in the spectrum corresponds to deuterated solvent.



Fig. S22 ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathrm{P}(\mathrm{ADMA})_{9}$ in $\mathrm{DMSO}-d_{6} . *$ and \# in the spectrum corresponds to deuterated solvent and residual water, respectively.


Fig. S23 ${ }^{1} \mathrm{H}$ NMR spectra of $\mathrm{P}\left(\mathrm{PEGA}_{29}-b-\mathrm{DA}_{17}\right)$ in DMSO- $d_{6}(1$, bottom $)$, and $\mathrm{D}_{2} \mathrm{O}(2$, top). ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathrm{P}\left(\mathrm{PEGA}_{29}-b-\mathrm{ADA}_{17}\right)$ in $\mathrm{D}_{2} \mathrm{O}$ was similar to that of $\mathrm{P}\left(\mathrm{PEGA}_{29}-b-\mathrm{DA}_{17}\right)$.


Fig. S24 The size distribution determined by DLS and corresponding TEM image (inset, scale bars 100 nm ) of (A) $\mathrm{P}\left(\mathrm{DMA}_{9}-b-\mathrm{PEGMA}_{17}\right)$, and (B) $\mathrm{P}\left(\mathrm{DMA}_{15}-b-\mathrm{PEGMA}_{32}\right)$ block copolymer micelles, prepared from $1.0 \mathrm{mg} \mathrm{mL}^{-1}$ aqueous solution.


Fig. $\mathbf{S 2 5}$ (A) Frequency shift ( $\Delta f$ ), (B) dissipation shift ( $\Delta D$ ), and (C) $\Delta D /(\Delta f / 7)$ data plots induced by immobilization of $\mathrm{P}\left(\mathrm{PEGA}_{29}-b-\mathrm{DA}_{17}\right)$ onto gold surface. $\Delta D$ and $\Delta f$ are measured simultaneously at different overtones ( $n=5,7,9,11$ ), and $\Delta f_{n}$ normalized by their overtone numbers.


Fig. $\mathbf{S 2 6}$ (A) Frequency shift ( $\Delta f$ ), (B) dissipation shift ( $\Delta D$ ), and (C) $\Delta D /(\Delta f / 7)$ data plots induced by the adsorption of $1 \%$ BSA onto gold surface. $\Delta D$ and $\Delta f$ are measured simultaneously at different overtones ( $n=5,7,9,11$ ), and $\Delta f_{n}$ normalized by their overtone numbers.


Fig. S27 Immobilization of block copolymers from their aqueous solution onto gold surfaces. Error bars correspond to the range within which $\chi^{2}$ does not increase by more than two-fold from the value obtained for the best fit.


Fig. S28 Raw $\Delta f$ data plots as a function of time for polymer immobilization, and subsequent BSA adsorption experiments on gold surface. Time-axis has been normalized (0-100), and $\Delta f$ responses have been translated along the time-axis by +10 , and +20 min, respectively for $\mathrm{B}=$ $\mathrm{P}\left(\mathrm{PEGA}_{29}-b-\mathrm{DA}_{53}\right)$, and $\mathrm{C}=\mathrm{P}\left(\mathrm{PEGA}_{29}-b-\mathrm{DA}_{17}\right)$ for clarity purposes.


Fig. S29 Raw $\Delta f$ data plots as a function of time for BSA adsorption on bare and polymer deposited gold surfaces. Time-axis has been normalized ( $0-100$ ), and $\Delta f$ responses have been translated along the time-axis by +15 , and +25 min respectively for bare steel surface, and $\mathrm{P}(\mathrm{DA})$ deposited gold surface, for clarity purposes.


Fig. $\mathbf{S 3 0}$ (A) Frequency shift ( $\Delta f$ ), (B) dissipation shift ( $\Delta D$ ), and (C) $\Delta D /(\Delta f / 7)$ data plots data plots induced by deposition of $\mathrm{P}(\mathrm{DA})$ from methanol solution $(1 \mathrm{mg} / \mathrm{mL})$ onto gold surface. $\Delta D$ and $\Delta f$ are measured simultaneously at different overtones ( $n=5,7,9,11$ ), and $\Delta f_{n}$ normalized by their overtone numbers.


Fig. S31 Raw $\Delta f$ data plots as a function of time for polymer immobilization, and subsequent BSA adsorption on stainless steel surfaces. For clarity purposes, time-axis has been normalized ( $0-100$ ), and $\Delta f$ responses have been translated along the time-axis by +85 min , for $\mathrm{P}\left(\mathrm{PEGA}_{29}-b-\mathrm{DA}_{17}\right)$.


Fig. S32 Adsorption of BSA on bare and polymer immobilized stainless steel surfaces. Percentage was calculated by dividing the protein adsorbed amount on the respective modified surfaces by the amount on bare surface (as derived from QCM-D measurements). Error bars correspond to the range within which $\chi^{2}$ does not increase by more than two-fold from the value obtained for the best fit.

## Reference

1 H. Lee and P. B. Messersmith, Nature, 2007, 448, 338-341.

