Supporting information for:

**Role of backbone chemistry and monomer sequence in amphiphilic oligopeptide- and oligopeptoid-functionalized PDMS- and PEO-based block copolymers for marine antifouling and fouling release coatings**

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**Synthesis**

\textit{Synthesis of PS-\textit{b}-P(DMS-co-VMS)-\textit{b}-PS triblock}

Siloxane block copolymers were synthesized as previously described (and as shown in Figure SI-1).\textsuperscript{1} A clean dry flask evacuated with nitrogen was filled with 50 mL of dried benzene. To this, 714 \textmu L of 1.4 M sec-butyl lithium in hexanes was added and stirred, followed by the addition of 7.7 mL (7 g) of dried and degassed styrene to initiate the polystyrene polymerization, and allowed to react for 24 hours to consume all monomer in the solution to produce a 7 kg mol\textsuperscript{-1} polystyrene block. \textit{Note that sec-butyl lithium is a pyrophoric and moisture sensitive material and should be handled with care}. A sample was taken after 24 hours for analysis by GPC. A 0.5 g mL\textsuperscript{-1}
solution of hexamethylcyclosiloxane (D3) in dried benzene was prepared to add to the polymerization. 98 mL of this solution (49 g of D3) was added to the polymerization to initiate the D3 polymerization. This was allowed to react for 24 hours until the solution was colorless. At this time, 20 mL of distilled THF was added to the reaction to accelerate the polymerization of the D3. After 2 hours, 1.42 g of 1,3,5-trivinyl-1,3,5-trimethylcyclosiloxane (V3) in THF was added to the polymerization via syringe pump over 48 hours and reacted at room temperature for an additional 2 days. A sample was taken from the polymerization for analysis by GPC and NMR. To couple the polymer and form a triblock, dichlorodimethylsilane was added to the polymerization. 40 µL of the coupling agent was added directly to the reaction and allowed to stir for 16 hours. An additional 22 µL of dichlorodimethylsilane in 2.5 mL of THF was added to the polymerization via syringe pump over 24 hours. The polymer was precipitated in 1 L of methanol, filtered and dried. The polymer was characterized by GPC to determine final molecular weight, and by NMR to determine vinyl content.

Figure SI-1: Anionic polymerization of PS-b-P(DMS-stat-VMS)-b-PS
Figure SI-2: GPC traces of PS-P(DMS/VMS)-PS triblock copolymer backbone.
Above: PS endblock precursor and uncoupled diblock (Cornell).
Below: Final triblock after diblock–diblock coupling (UCSB).

Figure SI-3: $^1$H-NMR spectrum of PS-P(DMS/VMS)-PS triblock copolymer backbone

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (kg/mol)</th>
<th>$\bar{D}$</th>
</tr>
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<tbody>
<tr>
<td>PS endblock</td>
<td>7.3$^a$</td>
<td>1.03</td>
</tr>
<tr>
<td>PS-P(DMS/VMS) uncoupled diblock</td>
<td>41.7$^a$</td>
<td>1.17</td>
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<tr>
<td>PS-P(DMS/VMS)-PS triblock</td>
<td>7.3-68.8-7.3</td>
<td>1.45</td>
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$^a$ versus polystyrene standards (Cornell)
Synthesis of PS-b-P(EO-co-AGE)-b-PS triblock

For comparison to the siloxane block copolymer produced, a PS-b-P(EO-co-AGE)-b-PS triblock was also synthesized. The block copolymer has two 7kDa PS blocks, and the PEO block is 70kDa with 2.5mol% AGE content to provide vinyl functional groups. The P(EO-co-AGE) midblock was synthesized as described previously. In short, ethylene glycol was used as an initiator for the anionic co-polymerization of ethylene oxide and allyl glycidyl ether in THF. The midblock was terminated with isopropyl alcohol to produce terminal alcohol groups. The molecular weight of the midblock was determined via GPC and vinyl content was determined by $^1$H-NMR. The chain-end hydroxyl groups were converted to initiator sites for further chain-extension of polystyrene by NMP. The following is an example reaction: P(EO/AGE) midblock (3 g, dried in vacuum overnight) was dissolved in 25 mL dry THF under an atmosphere of nitrogen. To this solution, 75 mg of sodium hydride was added, and the reaction was stirred for 8 hours. Note that sodium hydride is an extremely moisture sensitive material and should be handled with care and in small quantities. Next, 710 mg of N-tert-butyl-O-[1-[4-(chloromethyl)phenyl]ethyl]-N-(2-methyl-1-phenylpropyl)hydroxylamine (chloromethyl-TIPNO) was added, and the reaction was stirred at 50 °C for 24 hours. The reaction was quenched with methanol, then the macroinitiator was precipitated, filtered, and dried. The macroinitiator (1 g) was chain-extended by dissolving in 4 mL toluene and 314 µL styrene monomer (filtered through alumina to remove inhibitor). The polymerization was degassed with 5 freeze-pump-thaw cycles, and stirred at 120 °C for 25 hours. The resulting triblock was precipitated into diethyl ether, filtered, and dried, and then analyzed by NMR to determine polystyrene end block molecular weight (5 kg mol$^{-1}$ polystyrene block on each end).

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<thead>
<tr>
<th>Sample</th>
<th>$M_n$ (kg/mol)</th>
<th>$D$</th>
</tr>
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<tbody>
<tr>
<td>P(EO/AGE) macroinitiator</td>
<td>48.4$^a$</td>
<td>1.35</td>
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<tr>
<td>PS-P(EO/AGE)-PS triblock</td>
<td>3.2-48.4-3.2$^b$</td>
<td>1.46</td>
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$^a$ determined via GPC versus PEO standards (UCSB)
$^b$ determined via $^1$H NMR

Figure SI-4: GPC traces of PS-P(EO/AGE)-PS triblock copolymer backbone
Figure SI-5: $^1$H-NMR spectrum of PS-P(EO/AGE)-PS triblock copolymer backbone

Synthesis of non-natural amino acids for oligopeptides

Oligopeptides were synthesized from two synthetic non-natural amino acids, one with a triethylene glycol side group and the other with a fluorinated side group (Figure SI-2). The fluorinated amino acid was synthesized by first reacting 20 g (75.8 mmol) of 3,3,4,4,5,5,6,6,6-nonafluoro 1-hexanol with 9.24 g (80.6 mmol) of methanesulfonyl chloride in 150 mL of THF for 18 hours under nitrogen to form a mesylate. The reaction was then passed through a plug of silica gel to remove excess methanesulfonyl chloride and formed salts, and the solvent was removed by rotary evaporation.

Serine-Fmoc (10 g, 30.6 mmol) was dissolved in 150 mL of acetonitrile with 12 mL of DIEA (68.8 mmol). To this, 11 g of the mesylate (32 mmol) was added, and the reaction was refluxed under nitrogen for 24 hours. After cooling, the reaction was quenched with DI water (300 mL) and then extracted with ethyl acetate and dried with sodium sulfate. Solvent was removed by rotary evaporation to yield the fluorinated amino acid.

The oligo-PEO-functionalized amino acid was synthesized in a very similar way, by first forming a mesylate by reacting 20 g of diethylene glycol monomethyl ether (168 mmol) with 21.1 g of methanesulfonyl chloride (185 mmol) in 200 mL of THF under nitrogen for 18 hours. The reaction was then passed through a plug of silica gel to remove excess methanesulfonyl chloride and formed salts, and the solvent was removed by rotary evaporation.

Serine-Fmoc (10 g, 30.6 mmol) was dissolved in 150 mL of acetonitrile with 12 mL of DIEA (68.8 mmol). To this, 6.3 g of the mesylate (32 mmol) was added, and the reaction was refluxed under nitrogen for 24 hours. After cooling, the reaction was quenched with DI water (300 mL) and then extracted with ethyl acetate and dried with sodium sulfate. Solvent was removed by rotary evaporation to yield the PEG functionalized amino acid.

Synthesis of oligopeptides

The synthesis of the oligopeptides via solid phase peptide synthesis was carried out using published procedures. Two sequences were made, one with three fluorinated amino acids followed by three triethylene glycol amino acids and the other alternating fluorinated amino acid then triethylene glycol amino acid three total times. These will be respectively referred to as block peptide and alternating peptide. S-trityl-3-mercaptopropionic acid (5 eq.), O-(benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium hexafluorophosphate (HBTU) (5 eq.), and DIEA (5 eq.) was used to cap each oligopeptide at the N-terminus to provide a thiol which could be used to perform thiolene “click” chemistry to attach to the polymer backbone. Cleavage from the resin was performed in a 1:1 solution of dichloromethane and TFA for 20 minutes. To prevent disulfide bonds from forming, 1.5 equivalents of triethyl silane were added as a reducing agent. The resin was rinsed multiple times with methanol, dichloromethane, and toluene, and all rinses were collected and dried on a rotary evaporator before being dried in a vacuum oven.
**Synthesis of oligopeptoids**

The synthesis of oligopeptoids was carried out adapted from published procedures on a Prelude synthesizer (Protein Technologies, Inc.). Using Rink amide MBHA resin at 0.2 mmol g\(^{-1}\) loading, the resin was deprotected using a solution of 20% (v/v) 4-methylpiperidine in DMF, agitating for 20 minutes by bubbling with nitrogen, and then washing with DMF. All DMF washes consisted of the addition of 2 mL DMF followed by 1 minute of agitation (repeated 5 times). An acylation reaction was then performed on the free amine chain end by addition of 1.0 mL of 0.6 M bromoacetic acid in DMF, followed by 0.15 mL of N,N-diisopropylcarbodiimide (DIC) solution (59% v/v in DMF). The mixture was agitated for 20 minutes at room temperature, drained, and washed with DMF. Nucleophilic displacement of the bromide chain end with either 2-[2-(methoxyethyl)ethoxy]ethanamine (room temperature) or 1H,1H-perfluoropentylamine (stirred in a vial at 50°C) for 60 minutes. The monomer solution was drained from the resin, and the resin washed with DMF. The acylation and displacement steps were repeated until the desired sequence and length were achieved. All polypeptoids were functionalized with a thiol endgroup on the resin using a mixture of 0.4 M S-trityl-3-mercaptopropionic acid and 0.4 M hydroxybenzotriazole (HOBt) in DMF (2 mL per 50µmol peptoid) for 30 minutes, followed by washing with DMF. Peptoid chains were cleaved from the resin by addition of 4 mL of a trifluoroacetic acid (TFA) cleavage cocktail (95% TFA, 2.5% water, 2.5% triisopropylsilane) for 10 minutes, which was then evaporated on a rotary evaporator equipped with an ethanol/dry ice cold finger. This simultaneously cleaved the oligopeptoids from the resin and deprotected the thiol functionality. Following cleavage, peptoids were dissolved in appropriate acetonitrile/water mixtures and lyophilized. The peptoid materials were redissolved in 50:50 acetonitrile/water and washed with hexanes before a second lyophilization to yield the isolated product.
Thiol–ene “click” of representative SABC

**Figure SI-7:** Representative $^1$H-NMR of blocky peptoid clicked onto the PS-P(DMS/VMS)-PS backbone.

Coating morphology

**Figure SI-8:** A) AFM phase image of SEBS underlayer, demonstrating sphere morphology. Image size is 1 µm. B) Optical micrograph of spray-coated surface. Scale bar represents 100 µm.
These micrographs demonstrate that the spherical microphase morphology dominates the structure. The PS-\textit{b-}((PEO-\textit{co-}AGE)-\textit{b-})PS and PS-b-P(DMS-\textit{co-}VMS)-b-PS triblocks were designed to match this geometry to create strong physical crosslinks between glassy spheres and prevent delamination of the top layer in water. Due to the eventual application of these coatings to ship hulls, spray coating the functional layer is a requirement of the application. As one might expect, spray coating results in a film that is very rough, as shown via optical microscopy (scale bar represents 100 µm), and tens of microns thick. Samples were stable in water for prolonged times, suggesting a strong physical bond at the SEBS–functional polymer interface. XPS spectra discussed within the manuscript indicate that the surface chemistry is also dominated by the peptoid or peptide top coat and is stable over the timescale of this experiment.

Tapping-mode AFM measurements were made using a Veeco MultiMode Scanning Probe Microscope. Phase-contrast images were collected over 1 µm × 1 µm regions, revealing hard PS blocks (shown as light circles) in a matrix of soft PEB blocks (shown as dark). Images were collected using Nanosensors long cantilevers at 1.00 Hz. Optical micrographs were taken with an Olympus BX51 microscope equipped with an Olympus DP73 digital camera.
Figure SI-9: Summary of high resolution C1s X-ray photoelectron spectroscopy for all coatings after equilibrating in Millipore deionized water. Spectra are given in counts per second in arbitrary units, normalized to a similar scale.
**Ulva linza bioassays**

**Figure SI-10:** A) The density of attached spores after 45 minute settlement. Each point is the mean of 90 counts on 3 replicate slides. Bars show 95% confidence limits. B) Percent removal of 7 day old sporelings due to an impact pressure of 70 kPa. Each point is the mean removal of biomass from 6 replicate slides measured using a fluorescence plate reader. Bars show standard error of the mean derived from arc-sin transformed data.

**Navicula incerta bioassays**

**Figure SI-11:** A) The density of attached diatoms before and after exposure to a shear stress of 33 Pa. Each point is the mean from 45 counts on 3 replicate slides. Bars show 95% confidence limits. B) Percent removal of diatoms from coatings due to a shear stress of 33 Pa. Each point is the mean from 45 counts on 3 replicate slides. Bars show 95% confidence limits derived from arc-sine transformed data.
References


