

Supporting Information

Mussel-Inspired Anchoring of Polymer Loops that Provide Superior Surface Lubrication and Antifouling Properties

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Materials. Unless otherwise stated, ACS reagent grade chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. Tetrahydrofuran was collected from a dry solvent system and used immediately thereafter. Allyl glycidyl ether was purchased from TCI-America, Inc, degassed by freeze-pump-thaw, and distilled onto butylmagnesium chloride (Sigma-Aldrich) where it was stirred for 10 minutes at 0 °C, and distilled to a buret for use. Potassium naphthalenide was prepared from potassium metal and recrystallized naphthalene in dry THF and allowed to stir with a glass-coated stir-bar for 24 h at room temperature before use. Triethylsilane and tris(pentafluorophenyl)borane were purchased from Gelest. 2,2-dimethoxy-2-phenylacetophenone (99%), eugenol, ethane dithiol, ethylene oxide (99.5%+), and poly(ethylene oxide) were purchased from Sigma-Aldrich. Deuterated solvents for NMR were purchased from Cambridge Isotope Laboratories, Inc.

Instrumentation. ^1H and ^{13}C NMR spectra were recorded on Varian 600 or Bruker AC 500 spectrometers as indicated. Chemical shifts are reported in parts per million (ppm) and referenced to the solvent. The lamp used for irradiation of samples was a UVP Black Ray UV Bench Lamp XX-15L, which emits 365 nm light at 15W. Mass spectral data were collected on a Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer (FI-MS). Size exclusion chromatography (SEC) was performed on a Waters chromatograph with four Viscotek columns (two IMBHMW-3078, I-series mixed bed high molecular weight columns and two I-MBLMW-3078, I-series mixed bed low-molecular weight columns) for fractionation, a Waters 2414 differential refractometer and a 2996 photodiode array detector for detection of eluent, and chloroform with 0.1% tetraethylamine at room temperature was used as the mobile phase. Gas chromatography was carried out on a Shimadzu GC-2014 using a flame ionization detector and a Restek column (SHRXI-5MS) for separation.

Abbreviations. PEO- Poly(ethyleneoxide), DMPA- 2,2-dimethoxy-2-phenylacetophenone and TPFPB- Tris(pentafluorophenyl)borane, AGE- allyl glycidyl ether, EO- ethylene oxide.

Synthesis of triethylsilane-protected eugenol (3). The detailed synthesis was described in previous work¹. Briefly, the reaction between eugenol and triethylsilane (2.2 eq. to eugenol) was carried out for 6 hrs at room temperature using Tris(pentafluorophenyl)borane (0.002 eq. to eugenol) as a catalyst. The reaction mixture was filtered out through syringe filter which was filled with neutral alumina to remove Tris(pentafluorophenyl)borane with dichloromethane. Dichloromethane and unreacted triethylsilane were then removed under reduced pressure, to give the triethylsilane-protected eugenol (97-99%) in the form of yellowish liquid and the product was used in the next step without further purification.

Synthesis of thiolated triethylsilane-protected eugenol (5). (3) (38.0 g, 100.4 mmol, 1.0 equiv), ethane dithiol (75.7 g, 803.4 mmol, 8 equiv), and 2,2-dimethoxy-2-phenylacetophenone (514.8 mg, 2.01 mmol, 0.02 equiv) were added in a 250 mL round bottomed flask with stirring bar. The mixture was purged with dried argon for 30 minutes at room temperature and then exposed to the UV-lamp for 60 minutes. The excess ethane dithiol was evaporated under low pressure. (42.7 g, 99%); ¹H NMR (600MHz, CDCl₃): = 6.72 (d, 1H, Ar-*H*), 6.63 (s, 1H, Ar-*H*), 6.59 (d, 1H, Ar-*H*), 2.71 (m, 4H, -CH₂-CH₂-SH), 2.58 (t, 2H, Ar-CH₂-CH₂-CH₂-S-), 2.51 (t, 2H, Ar-CH₂-) 1.85 (m, 2H, Ar-CH₂-CH₂-CH₂-S-), 1.71 (t, 1H, -SH), 0.99 (t, 18H, -Si-CH₂-CH₃), 0.74 (q, 12H, -Si-CH₂-CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): = 146.52, 144.91, 134.35, 121.21, 120.79, 120.26, 36.15, 33.94, 31.20, 31.28, 24.72, 6.69, 6.67, 5.14, 5.09 ppm. Calcd: [M]⁺ (C₂₃H₄₄O₂S₂Si₂) *m/z* = 472.23; found FI-MS: [M+]
m/z = 472.23

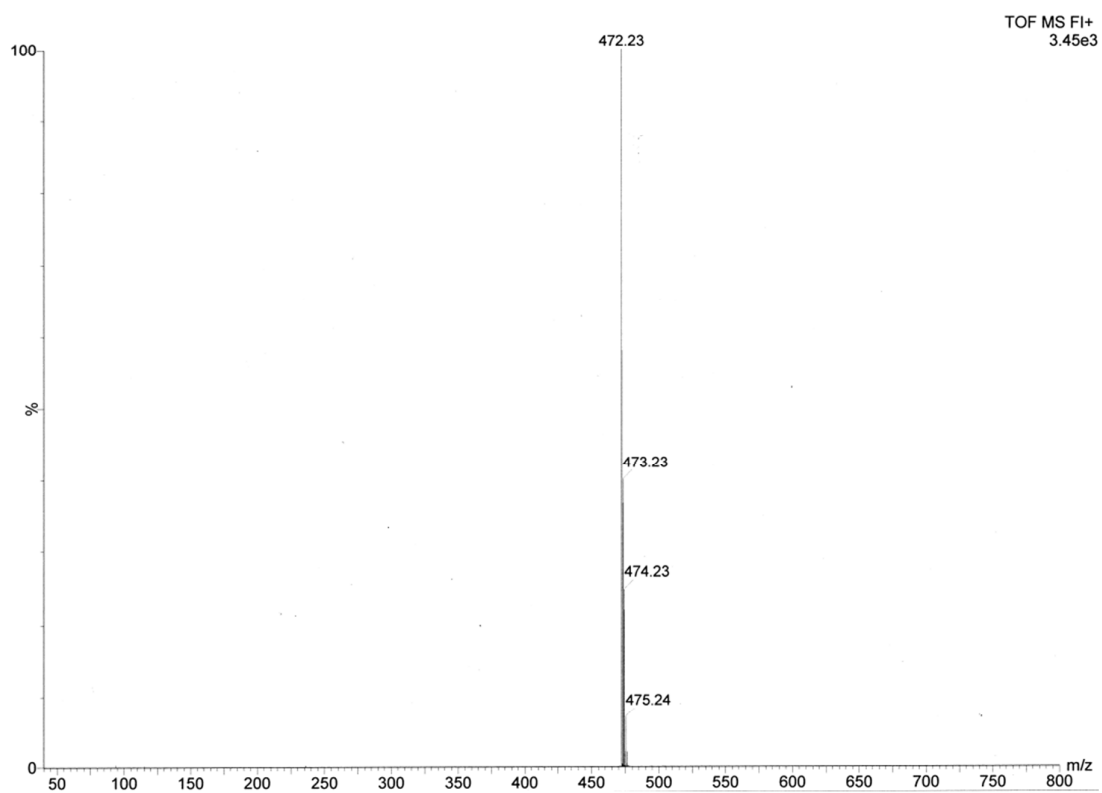


Figure S1. Mass spectrum of thiolated triethylsilane-protected eugenol (5).

Synthesis of poly[(ethylene oxide)-co-(allyl glycidyl ether)]-b-poly(ethylene oxide)-b-poly[(ethylene oxide)-co-(allyl glycidyl ether)] (9). The copolymerization of ethylene oxide and allyl glycidyl ether was carried out from a 20 kg/mol PEG-diol. The PEG-diol macroinitiator (30 g, 1 eq.) was dissolved in 200 mL of dry THF at 45 °C and titrated with potassium naphthalenide (0.3 M in THF) until a light green color persisted indicating complete deprotonation of the macroinitiator. Ethylene oxide (12.9 g, 196 eq.) and allyl glycidyl ether (2.06 g, 12 eq.) were added simultaneously, and the copolymerization was allowed to run for 20 hours at 45 °C. The polymerization was terminated with acidic methanol. The resulting polymer was precipitated in hexanes, filtered, and dried *in vacuo*. ¹H NMR (600MHz, CDCl₃): 5.95 (m, -O-CH=CH-CH₃), 5.87 (m, 1H, -O-CH₂-CH=CH₂), 5.24/5.14 (dd, 2H, -O-CH₂-CH=CH₂), 4.34 (q, O-CH=CH-CH₃), 3.98 (m, 2H, -O-CH₂-CH=CH₂), 3.84-3.47 (broad m, -O-CH₂-CH₂-O-, -O-CH₂-CH(CH₂-O-CH₂-CH=CH₂)-, and -O-CH₂-CH(CH₂-O-CH=CH-CH₃)-), 1.54 (d, -O-CH=CH-CH₃) ppm; ¹³C NMR (150MHz, CDCl₃): 146.04, 134.86, 116.85, 110.09, 100.92, 78.46, 72.33, 71.29, 70.61, 70.22, 69.81, 61.59, 9.27 ppm; GPC (Chloroform): M_n = 31500, M_w = 35900, PDI: 1.14

Synthesis of silane-protected catechol functionalized P(EO-AGE)-b-P(EO)-b-P(EO-AGE) (10). P(EO-AGE)-b-P(EO)-b-P(EO-AGE) (3.0 g, 0.1 mmol, 1.0 equiv), 5 (4.18 g, 8.84 mmol, 8 equiv. per alkene), and 2,2-dimethoxy-2-phenylacetophenone (14.2 mg, 0.055 mmol, 0.05 equiv. per alkene) were added in a 100 mL round bottomed flask with stirring bar. Dichloromethane (5 mL) was added as a solvent and the mixture was purged with dried argon for 30 minutes at room temperature and then exposed to the UV-lamp for 60 minutes. The reaction mixture was precipitated twice in n-Hexane and the resulting white powder was dried under low pressure. (3.4 g, 96 %); ¹H NMR (600MHz, CDCl₃): = 6.70 (d, 1H, Ar-H), 6.61 (s, 1H, Ar-H), 6.58 (d, 1H, Ar-H), 3.63 (m, -O-CH₂-CH₂-O-), 2.68 (m, 4H, -S-CH₂-CH₂-

S-), 2.58 (m, 4H, $-CH_2-S-CH_2-CH_2-S-CH_2-$), 2.51 (t, 2H, Ar- CH_2-), 1.82 (m, 4H, Ar- $CH_2-CH_2-CH_2-S-CH_2-CH_2-S-CH_2-CH_2-$), 0.97 (t, 18H, $-Si-CH_2-CH_3$), 0.73 (q, 12H, $-Si-CH_2-CH_3$) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): = 146.46, 144.84, 134.41, 121.17, 120.76, 120.22, 70.54, 61.67, 33.95, 32.09, 31.42, 31.15, 29.73, 28.81, 6.68, 6.66, 5.11, 5.05 ppm. ; GPC (Chloroform): M_n = 33500, M_w = 40500, PDI: 1.21

Synthesis of amine functionalized P(EO-AGE)-b-P(EO)-b-P(EO-AGE) (11). P(EO-AGE)-b-P(EO)-b-P(EO-AGE) (1.5 g, 0.05 mmol, 1.0 equiv), cysteamine hydrochloride (0.5 g, 4.42 mmol, 8 equiv. per alkene), and 2,2-dimethoxy-2-phenylacetophenone (514.8 mg, 2.01 mmol, 0.02 equiv) were added in a 20 mL round bottomed flask with stirring bar. Methanol (5 mL) was added as a solvent and the mixture was purged with dried argon for 20 minutes at room temperature and then exposed to the UV-lamp for 60 minutes. The reaction mixture was dialyzed in Milli-Q water and then lyophilized to dry. (1.4 g, 90 %); 1H NMR (600MHz, $CDCl_3$): = 3.75 (m, $-O-CH_2-CH_2-O-$), 3.27 (t, 2H, $-S-CH_2-CH_2-NH_2$), 2.91 (t, 2H, $-S-CH_2-CH_2-NH_2$), 2.71 (t, 2H, $-O-CH_2-CH_2-CH_2-S-$), 1.93 (q, 2H, $-O-CH_2-CH_2-CH_2-S-$) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): = 77.47, 71.68, 69.55, 68.59, 60.33, 38.30, 28.38, 28.13, 27.28 ppm. ; GPC (Water): M_n = 31500, M_w = 36200, PDI: 1.15

Friction test.

1) Substrate preparation.

Atomically smooth mica surfaces were freshly cleaved under a laminar flow hood and immediately deposited on another large freshly cleaved mica backing sheet for storage. In this way, the mica interface in adhesive contact with the backing sheet is kept free from dust contamination while the other interface can be coated with silver. The thickness of the mica

sheets was 2.5-3.5 μm . The thickness of the silver coating was kept constant (55 nm) and deposited by Joule effect vapor deposition. Silvered mica sheets were glued, silvered side down, on silica cylindrical disks (2 cm curvature) using a hard epoxy glue (EPON 1004F[®] from Exxon Chemicals).

2) Adsorption of triblock polymers on mica surfaces.

After mounting the surface in the Surface Forces Apparatus, the apparatus was purged with dry nitrogen for 1h in order to eliminate adsorbed water on the mica and to decrease the humidity of the surrounding atmosphere. After measuring the thickness of the mica surfaces by bringing them into adhesive contact, the surfaces were separated and a droplet of polymer solution of 100 $\mu\text{g/mL}$ (pH = 3) was introduced between them. The bottom part of the apparatus was then filled with the same buffer solution as the polymer solution in order to maintain saturated conditions and avoid evaporation of the polymer droplet solution during the adsorption process. After 1 h of adsorption, the polymer solution was removed and surfaces were abundantly rinsed with buffer solution at pH 3.

3) Measuring interaction forces using the Surface Forces Apparatus.

The Surface Force Apparatus model 2000 (SFA 2000)² was used in this study for accurate force-distance measurements. The upper surface was installed on recently developed 3D sensor-actuator device that allows for displacement in the normal and lateral direction to be controlled with nm resolution as well as to simultaneously measure dynamic interaction forces in 3 dimensions (normal and lateral forces).

During a typical experiment, the separation distance between the two surfaces is measured using optical interferometry³: a white light beam is shined through the surfaces and the interference fringes generated from the reflections of the light beam between the two silvered

mica sheets are analyzed in a spectrometer equipped with a digital camera (Hamamatsu Orca 03G, USA). The separation distance D between the surfaces is calculated (to $\pm 1 \text{ \AA}$) from the wavelength of the interference fringes (also called fringes of equal chromatic order, FECO)³. The normal interaction force function $F(D)$ between the polymer coated surfaces as a function of the separation distance D was obtained by measuring the deflection of the double cantilever spring supporting the lower surface⁴⁻⁶. The real contact area – with a resolution of $1 \text{ }\mu\text{m}$ – can be extracted from the analysis of the FECO fringes⁷. Any localized defects, such as an initial sign of wear during shearing, can be precisely visualized, quantitatively measured, and monitored using the FECO technique as a function of time and normal force (or pressure).

NEXAFS Test.

Iron oxide (Fe_2O_3) and titanium oxide (TiO_2) were used as the substrates as alternatives for mica, a kind of Si/Fe/Ti/O composite. The substrates were coated as follows. The tri-block copolymer was dissolved as 1 mg/ml in 0.1 M acetic acid (*aq*). The solution was stirred for 1 hour to de-protect silyl groups, filtered by $0.2 \text{ }\mu\text{m}$ syringe filter. The both substrates were immersed in the solution for 48 hr, then vigorously washed with distilled water, and dried in vacuum-oven overnight. The NEXAFS experiments were performed at the 2A undulator beamline at the Pohang Accelerator Laboratory (PAL) in Korea. The total energy resolution is about 100 meV with a beam size of $0.5 \text{ mm} \times 0.2 \text{ mm}$. A linearly polarized X-ray beam was irradiated on the sample at 30° and 90° of the two different incidence angles (θ) between surface normal and light polarization (E-vector). The all data was simultaneously collected in the total electron yield (TEY) and the partial electron yield (PEY) modes by recording the current to ground. Then the data were normalized to the beam current using a grid located upstream of the beamline. The experimental environment was maintained at room

temperature and a base pressure of $\sim 10^{-10}$ Torr. Both TEY and PEY mode NEXAFS techniques have been known as surface-sensitive tools. It is worth noting that PEY mode acquires more surface-sensitive electron signal (~ 1 nm of electron escape depth) than TEY mode (more than 10 nm of electron escape depth)^{8,9}.

To investigate the bonding conformation of catechol groups onto metal oxide and identify the loop conformation of PEO-based polymers chains, NEXAFS spectra from tri-block copolymer on TiO₂ and Fe₂O₃ substrates were measured (Figure S2). In all NEXAFS spectra, single peak at around 284.9 eV and several peaks in the range of 286.2 to 299.7 eV were assigned to the π^* orbital and the several σ^* orbitals, respectively. The spectra was fitted using a nonlinear least-squares routine with Gaussian functions for the π^* resonant features, a Gaussian broadened step function for the edge jump, and asymmetrically broadened Gaussian functions for the σ^* resonant features as reported earlier¹⁰.

The average tilted angle (α) of aromatic moieties could be obtained by quantitative analysis of the angular dependence of the NEXAFS resonance intensities¹¹. The π^* peak relative intensity (I_{90}/I_{30}) was calculated considering I_{90} and I_{30} as the intensity values of the π^* peak at 90° and 30° of incidence angle, respectively. The tilted angle of catechol moieties was obtained from the function I_{90}/I_{30} versus $\cos^2\theta$ ^{10,11}. The tilted angles of the catechol moieties on TiO₂ and Fe₂O₃ were investigated using TEY mode because the loop thickness was expected to be ~ 60 nm. Consequently, catechol moieties on TiO₂ and Fe₂O₃ exhibited relatively standing-up orientation with $\sim 64^\circ$ and $\sim 68^\circ$ of the tilted angle, respectively, which were lower than $\sim 85^\circ$ of dopamine tilted angle on TiO₂ probably due to polymer chain strain¹². The preferred orientation of them suggested that the lateral blocks were bound onto substrates not by sulfur or oxygen binding but by coordinative bonds.

The relative concentration of catechol moieties depending on depth was investigated by comparing both PEY and TEY spectra with different surface sensitivity^{8,9}. In the spectrum of

TiO₂ substrate, the peak intensity of π^* resonance from PEY mode was quite lower than that of σ^* C-O at around 288.5 in PEY mode, and also 3.5 fold lower than the π^* intensity from the TEY mode at the same incidence angle, 90° (Figure A)⁹. Likewise, the NEXAFS spectra from Fe₂O₃ substrate exhibited the similar tendency (Figure B). The results indicated that the catechol groups were more dominantly distributed in relatively deeper area than in the uppermost several nm. Thus, the lateral blocks of PEO chains were rarely exposed onto the coated surfaces, which supported the loop structure.

When catechol moieties in the triblock are partially oxidized at pH 6.5, the intensity of the π^* peak from the PEY mode was compatible with the π^* intensity from the TEY mode at the same incidence angle, 90° (Figure S3). This observation suggests that the catechol groups were randomly distributed in the partially oxidized triblock copolymer coating.

In conclusion, the loop conformation of tri-block copolymers on mica, a Si/Fe/Ti/O composite, was identified by NEXAFS data. The rare distribution of catechol moieties in the uppermost several nm supported that the lateral blocks were not exposed onto the coated surfaces. The preference of catechol groups for the standing-up orientation onto the substrate suggested that the lateral blocks were bound onto the surface not by just sulfur or oxygen binding but by coordinative bonding, known as a strong interaction.

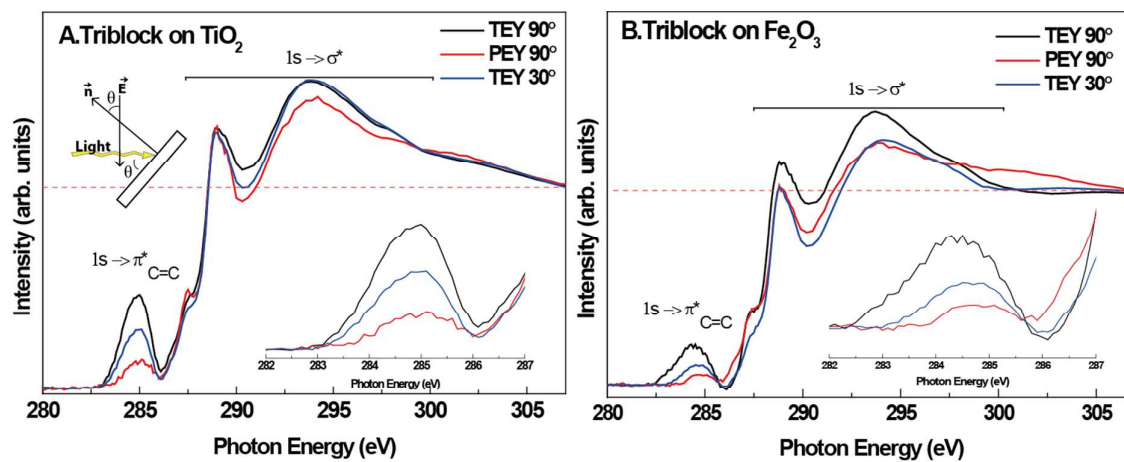


Figure S2. NEXAFS spectra of the tri-block copolymer on both TiO_2 (A) and Fe_2O_3 (B) substrates: TEY mode spectra at 90° and 30° of two different incidence angles and PEY mode spectra at 90° of incidence angle.

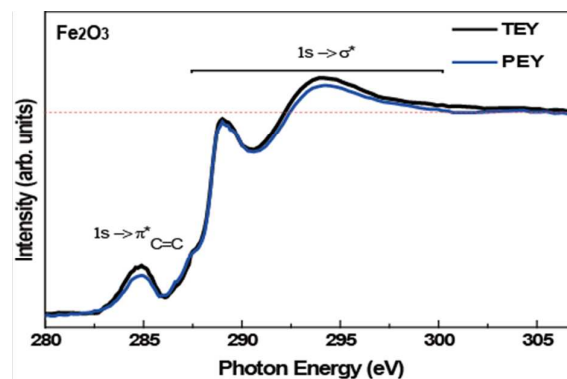


Figure S3. TEY and PEY modes NEXAFS data for triblock copolymer layer that is coated on Fe_2O_3 surface at pH ~ 6.5 (0.1 M acetate buffer).

Anti-fouling Test

Glass disks (R = 12 mm, Thickness = 1 mm) were placed in glass dishes and incubated with 1 mg/mL of PEO, catechol-functionalized triblock copolymer (**10**) without irons, and **10** with FeCl₃ in TFA, respectively for 24 hours. Unbound polymers and solvents were washed away by 2 times incubations the sample coated surfaces in PBS (Hyclone) for 2 hours and sonication for 30 seconds. The polymer coating on glass disks were confirmed by SEM images after polymer deposition. Uncoated glass disks were used as controls. Antifouling properties of the catechol-functionalized triblock copolymer against mammalian cells (MC-3T3) and marine red alga (*Porphyra suborbiculata*) were tested. The mouse pre-osteoblast cell line, MC3T3-E1 (Riken, Japan), was maintained in minimal essential medium- α (MEM- α ; Hyclone) with 10% (v/v) fetal bovine serum (FBS; Hyclone) and 1% penicillin/streptomycin (Hyclone) at 37°C in a humidified atmosphere of 5% CO₂ and 95% air. The subconfluent cells were detached by 0.25% trypsin-EDTA (Hyclone), and the viable cells were counted by trypan blue assay with hemocytometer. 5×10^4 of the cell (> 95% viable) in MEM- α with 10% FBS were placed on each sample coated glass disks which placed in a 24-well plate to test anti-fouling activity. For a quantitative measurement of cell number, Cell Counting Kit-8 (CCK-8; Dojindo Laboratories, Japan) solution, which contains 2-(2-methoxy-4-nitrophenyl)-3-(4-nitrophenyl)-5-(2,4-disulfophenyl)-2H-tetrazolium (WST-8) producing a highly water-soluble formazan dye (yellow) upon reduction in the presence of an electron carrier from the viable cells. 1 ~ 3 days after cell seeding, 250 μ l of CCK-8 were added to the wells to allow the formation of formazan crystals for 3 hours at 37 °C. Finally, absorbance was measured at 450 nm using a microplate reader (Bio-Rad). For fluorescence microscopy, the cells were fixed with 4% (v/v) paraformaldehyde, and permeabilized with 0.1% (v/v) Triton X-100. For nucleus staining, fixed cells were washed with PBS, and immersed in 0.001% (w/v) 4',6-diamidino-2-phenylindole (DAPI). The fixed cells were

washed again with PBS, and incubated 0.001% (w/v) Fluorescein isothiocyanate (FITC) conjugated phalloidin containing PBS for 20 min to stain actin filaments of the cells. Finally, cells were fixed with Lisbeth's embedding medium (30 mM Tris-Cl, pH 9.5, 70% glycerol, 50 mg/ml *N*-propyl gallate), and examined by fluorescence microscopy. Monospores of *Porphyra suborbiculata* Kjellman were collected from the intertidal zone of the rocky shore at Cheongsapo, Busan, S. Korea. Axenic isolation and culturing of the monospores were performed by following previous studies. Approximately 200 spores in Provasoli's enriched seawater (PES) medium were placed on each sample coated glass disks which placed in a 24-well plate to test anti-fouling activity at 20 °C. 1 ~ 7 days after spore seeding, attached spores or attached alive cells hatching from the spore attached on the surfaces were scraped, and the number of spores were counted under a microscope.

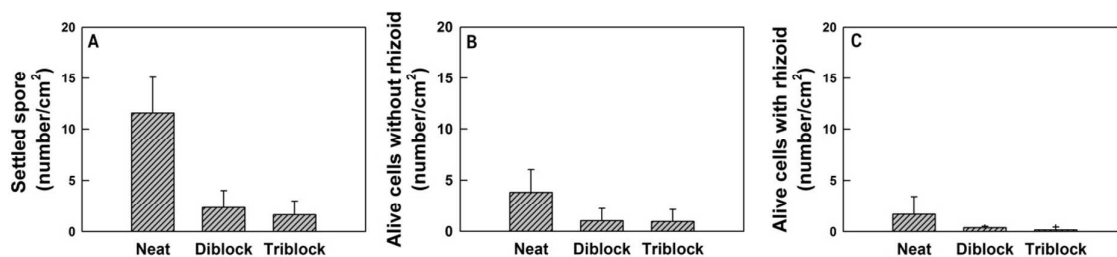


Figure S4. Comparison of the *Porphyra suborbiculata* (A) spore settlement 1 day after seeding, (B) attached alive cells without rhizoid hatching from the spore 7 day after seeding, and (C) attached alive cells with rhizoid hatching from the spore 7 day after seeding on bare glass (Neat), catechol-functionalized diblock copolymer (Diblock), and catechol-functionalized triblock copolymer (Triblock). Each value and error bar represents the mean of quintuplicate samples and its standard deviation.

Interaction force profiles

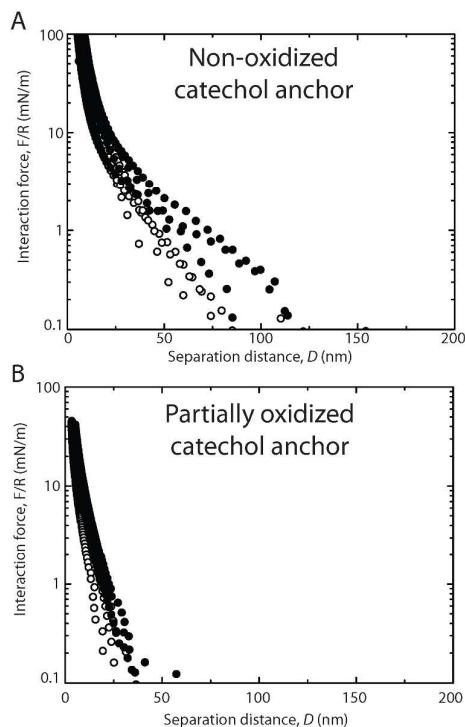


Figure S5 Interaction force profiles between mica surface bearing non-oxidized (A) or partially oxidized (B) PEG triblock polymer

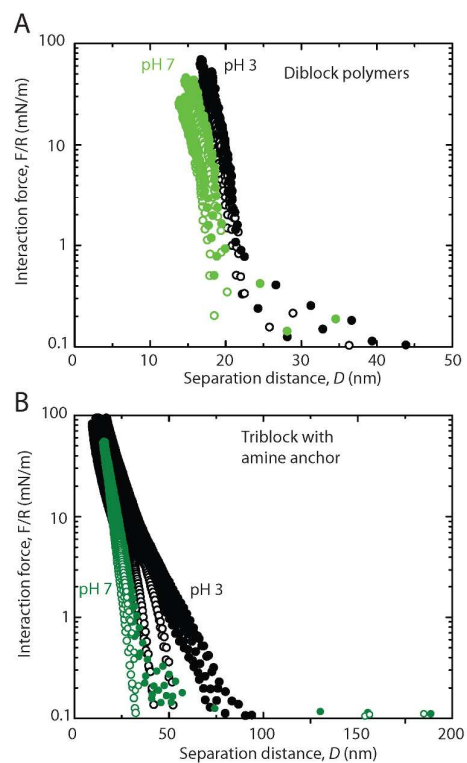


Figure S6: Interaction force profiles between mica surface bearing non-oxidized diblock polymers (A) or amine functionalized polymer triblocks (B). These forces profiles were measured prior to the friction test shown in the manuscript

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