# **Supporting Information**

# **Mussel-inspired Antifouling Coatings bearing Polymer Loops**

Lin Li,<sup>a</sup> Bin Yan,<sup>a</sup> Ling Zhang,<sup>a</sup> Yu Tian<sup>b</sup> and Hongbo Zeng <sup>a,\*</sup>

<sup>a</sup> Chemical and Materials Engineering, University of Alberta, Edmonton, AB, Canada T6G 2V4

<sup>b</sup> State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China;

\*Corresponding author: E-mail address: Hongbo.Zeng@ualberta.ca; Tel.:+1 780 492 1044

**Table of Contents** 

- 1. Materials, polymer synthesis and characterization
- 2. Experimental setups and methods
- 3. Supplementary SFA and QCM-D results

### 1 Materials, polymer synthesis and characterization

#### 1.1 Materials

*N,N*-Dimethylacrylamide (DMA) was purchased from Sigma-Aldrich and passed through a short column of basic Aluminum oxide. Macro-RAFT agents RAFT-PEG<sub>90</sub>-RAFT (**2**) and PEG<sub>45</sub>-RAFT(**3**) were synthesized by attaching the chain transfer agent (S)-1-dodecyl-(S')- $(\alpha, \alpha'$ -dimethyl- $\alpha''$ -acetic acid) trithiocarbonate (**1**) to ends of PEG precursors following a reported procedure.<sup>1</sup> *N*-(3,4-Dihydroxyphenylethyl)acrylamide (**4**) was synthesized according to a modified procedure reported.<sup>2</sup> All the other chemicals were purchased from Aldrich and used as received.

#### 1.2 Synthesis of ABA Triblock Copolymer PDN-PEG-PDN (5) with PEG<sub>90</sub> as B block

Macro-RAFT agent RAFT-PEG<sub>90</sub>-RAFT (0.2365 g, 0.05 mmol), *N*-(3,4-Dihydroxyphenylethyl)acrylamide (0.0828 g, 0.4 mmol), DMA (0.1782 g, 1.8 mmol) and azobisisobutyronitrile (AIBN) (0.0041 g, 0.025 mmol) were dissolved in 1 ml dioxane. After purging N<sub>2</sub> for 15 min, the whole system was stirred at 78 °C for 1 h. The final reaction mixture was dissolved in a small amount of dichloromethane and precipitated twice in ethyl ether. The resulting polymer was collected by filtration and dried in vacuum as a white solid of 0.3933 g. The composition of the resulting polymer was characterized by <sup>1</sup>H NMR and was determined as Poly{DMA<sub>15</sub>-*co*-[*N*-(3,4-dihydroxyphenethyl)acrylamide]<sub>2</sub>}-*b*-PEG<sub>90</sub>-*b*-Poly{DMA<sub>15</sub>-*co*-[*N*-(3,4dihydroxyphenethyl)-acrylamide]<sub>2</sub>}(denoted as PDN-PEG-PDN).





Fig. S1 Synthesis route and raw NMR data for PDN-PEG-PDN

# **1.3** Synthesis of AB diblock Copolymer PDN-PEG (6) with PEG<sub>45</sub> as B block

Similar procedures as those described above were used to prepare diblock copolymer PDN-PEG. A typical example was shown as follows: PEG<sub>45</sub>-RAFT (0.2365 g, 0.1 mmol), *N*-(3,4-Dihydroxyphenylethyl)acrylamide (0.0828 g, 0.4 mmol), DMA (0.1782 g, 1.8 mmol) and AIBN (0.0041 g, 0.025 mmol) were dissolved in 1 ml dioxane. The whole system was purged with N<sub>2</sub> for 15 min and then stirred at 78 °C for 1 h. The resulting polymer was precipitated twice with ethyl ether and vacuum-dried to obtain a white solid of 0.2786 g. The composition of the resulting polymer was characterized by <sup>1</sup>H NMR and was determined as Poly{DMA<sub>15</sub>-*co*-[*N*-(3,4-dihydroxyphenethyl)acrylamide]<sub>2</sub>}-*b*-PEG<sub>45</sub> (denoted as PDN-PEG).





Fig. S2 Synthesis route and raw NMR data for PDN-PEG



Fig. S3 GPC trace of PDN-PEG-PDN (black curve) and PDN-PEG (red curve).

## 2 Experimental setup and methods

#### 2.1 Surface preparation

The polymer films for surface force measurement were prepared by drop coating method on mica surface. Several drops of polymer solution (1 mg/ml in acetate buffer, pH 5.0) were placed on the mica surface in a water vapor saturated petri dish. After 30 minutes of adsorption the surface was rinsed with a capacious amount of acetate buffer and deionized (DI) water for

several times and dried in vacuum. The same procedure was applied for the preparation of BSA film on mica. Several drops of 5 wt% BSA in phosphate buffer saline (PBS, pH 7.4) were placed onto the mica surface. After 30 minutes of adsorption the surface was rinsed with DI water and dried in vacuum.

Dry film thickness of the polymer film was measured in situ using multiple beam interferometry employing fringes of equal chromatic order (FECO) coupled with the surface forces apparatus (SFA). The polymer film thickness was also confirmed by drop-coating a film on silicon wafer cleaned with ethanol and UV/ozone using a Sopra GESP-5 spectroscopic ellipsometer (France).

#### 2.2 Surface force measurements in aqueous solution using SFA

In this study the interactions between prepared surfaces were measured in NaCl solution using an SFA. Two back-silvered mica sheets of the same thickness (1-5  $\mu$ m) were separately glued onto two cylindrical silica disks (radius R = 2 cm). After drop-coated with the synthetic polymers, the two prepared surfaces were mounted in the SFA chamber in a crossed-cylinder conformation, of which the interactions was locally equivalent to a sphere of radius R interacting with a flat surface or two spheres of radius 2R when the surface separation D was much smaller than R ( $D \ll R$ ). In this study, the interaction forces between two polymer-bearing surfaces and between a polymer-bearing surface and a protein-bearing surface were measured in NaCl solution. For each fixed experimental condition, the surface force measurements were repeated for at least three different positions of each pair of surfaces with at least two pairs of surfaces to ensure the reproducibility.

#### 2.3 AFM imaging

Surface morphology of the mica surface coated with polymers or BSA were characterized using an AFM (MFP-3D, Asylum, Santa Barbara, CA). The sample surfaces were imaged using tapping mode in air. For each AFM imaging, at least three samples were imaged at different (>3) positions of each sample and typical images were presented.

#### 2.4 Protein adsorption tests using QCM-D

Antifouling properties of the polymer surfaces were examined using a QCM-D (Q-sense E4, Sweden). A typical procedure for a QCM-D measurement is shown as follows. Before the

experiment, silica sensors were placed in a UV/Ozone cleaning chamber (UV/Ozone ProCleaner, BioForce Nanosciences Inc, Iowa, USA) for 10 minutes followed by an immersion in 2% sodium dodecyl sulphate (SDS) for 20 minutes. After rinsed with DI water and dried with nitrogen, the sensors were placed in the UV/Ozone chamber for another 10 minutes. Then the cleaned silica sensors were drop coated with different polymers (1 mg/ml in acetate buffer, pH 5.0) and mounted into the QCM-D chamber. The system was firstly run in a PBS buffer to attain a stable baseline, then the sensor was exposed to BSA solution (5 wt% in PBS buffer, pH 7.4) introduced at a flow rate of 50  $\mu$ L/min before rinsed with pure PBS buffer. The shifts in resonance frequency and the changes in energy dissipation, corresponding to the 3rd, 5th and 7thovertones, were recorded and fitted to the Voigt viscoelastic model in the QTools software to obtain the mass of adsorbed proteins. All the experiments were performed at 25°C and repeated for at least three times.

### **3** Supplementary SFA and QCM-D results



**Fig. S4** Force-distance profiles between two thick PDN-PEG-PDN films prepared by spincoating using relatively high concentration of polymer solution (2.5mg/ml in toluene and DCM).



**Fig. S5** Changes in frequency and dissipation during the adsorption of BSA protein on silica sensors coated with different polymers using a QCM-D.



**Fig. S6.** Force-distance profiles between two PDN-PEG-PDN films in (a) 0.001M, (b) 0.01M and (c) 0.1M NaCl solutions

## References

- 1. Y. He and T. P. Lodge, *Macromolecules*, 2008, **41**, 167.
- 2. J. Nishida, M. Kobayashi and A. Takahara, ACS Macro Lett., 2013, 2, 112.