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One-Step Dip Coating of Zwitterionic Sulfobetaine Polymers on Hydrophobic and Hydrophilic Surfaces

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S Supporting Information

[AB](#page-5-0)STRACT: [Zwitterionic s](#page-5-0)ulfobetaine polymers with a catechol chain end (DOPA-PSB) were applied to a variety of hydrophobic polymer sheets and fibers. In addition, a silica surface was tested as a representative hydrophilic substrate. The polymer-coated surfaces showed significantly lower fouling levels than uncoated controls. Because of the anti-polyelectrolyte nature of sulfobetaine zwitterionic polymers, the effect of salt concentration on the coating solutions and the quality of the polymer coating against fouling are studied. The coating method involves only water-based solutions, which is

compatible with most surfaces and is environmentally friendly. To demonstrate the versatility of the reported method, we evaluated the fouling levels of the polymer coating on commonly used polymeric surfaces such as polypropylene (PP), polydimethylsiloxane (PDMS), polystyrene (PS), nylon, polyvinyl chloride (PVC), and poly(methyl methacrylate) (PMMA).

KEYWORDS: sulfobetaine, zwitterionic polymer, dip coating, DOPA binding, nonfouling, hydrophobic surfaces

■ INTRODUCTION

The need to prevent biofouling is ever growing and hence intensely studied.1−⁵ Neutral and hydrophilic polymers such as poly(ethylene glycol) (PEG)^{6,7} and zwitterionic polymers^{5,8} such as poly([2-](#page-5-0)[me](#page-6-0)thacryloyloxyethyl phosphorylcholine) (PPC),^{9,10} poly(sulfobetaine [me](#page-6-0)thacrylate) (PSB), and po[ly-](#page-6-0) $(carboxybetaine$ methacrylate) $(PCB)^{11}$ have been used as nonfou[ling](#page-6-0) materials. Zwitterionic polymers have a positively and a negatively charged group placed [o](#page-6-0)n the same repeating unit and have even stronger hydration than PEG. PEG binds to water through hydrogen bonding,¹² whereas zwitterionic polymers bind to water through electrostatically induced hydration.¹³ Zwitterionic polymers a[re](#page-6-0) shown to be ultra-low fouling $(< 5 \text{ ng/cm}^2)^{14}$ even when in contact with complex media suc[h](#page-6-0) as undiluted human plasma or serum.^{15,16}

Polymer attachmen[t to](#page-6-0) a surface is usually carried out either by "graft from" or by "graft to" techniques.^{17,18} "[Gra](#page-6-0)ft from" techniques involve growing the polymer chain from the surface whereas "graft to" techniques involve the att[achm](#page-6-0)ent of already made copolymers or polymer conjugates containing a surfaceadhesive group. Through "graft from" methods, it is easier to achieve a high grafting density. For example, a zwitterionic PSB polymer brush was grown from an atom transfer radical polymerization (ATRP) initiator attached by a thiol linkage to a gold surface and was found to be ultra-low fouling.^{15,19} However, "graft from" methods usually require pre-treatment of the surface to attach suitable initiator moieties and [the](#page-6-0) polymerization step needs to be carried out under an inert atmosphere, making this method unpractical for large and intricate shapes. On the other hand, "graft to" modification is convenient and simple to be implemented on surfaces. For example, a biomimetic catechol chain end PSB (DOPA-PSB) was attached via a "graft to" method on a functionalized gold surface.²⁰ The attachment of the chain-end functional polymer needs to be optimized to obtain a high grafting density.

Alth[oug](#page-6-0)h existing "graft to" and "graft from" methods are often suitable for certain types of surfaces, there is no universal surface-adhesive group that is applicable to a variety of surfaces ranging from hydrophobic to hydrophilic. One such potential binding group for various surfaces is the amino acid, L-3,4 dihydroxyphenylalanine (DOPA). This amino acid residue is found on the mussel foot protein (mfp) ,^{21−23} which allows it to adhere to various surfaces under water. Although the binding mechanism is not fully understood, $22,23$ [it](#page-6-0) i[s b](#page-6-0)elieved to happen through the oxidation of a catechol to a quinone and other subsequent reactions. Similarly, [ano](#page-6-0)ther small molecule, dopamine, polymerizes itself to polydopamine, which can be used to coat many surfaces (hydrophobic and hydrophilic). The common chemical entity between DOPA, on the mfp, and dopamine is the catechol unit, which oxidizes to a quinone

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under slight alkaline conditions. In the case of dopamine, the quinone reacts with the free amines of other dopamine molecules, whereas in the case of mussel organisms and DOPA, it reacts with the amine groups of lysine residues on polypeptide chains.²¹ Catechol chain end hydrophilic polymers such as DOPA-PCB (DOPA-poly(carboxybetaine methacrylate)) and DOPA-[PEG](#page-6-0) (DOPA-poly(ethylene glycol)) are used for the modification of gold²⁴ and metal oxides such as silica²⁵ and titania.26,27 A low-molecular-weight DOPA-PSB zwitterionic polymer with only 1[5 r](#page-6-0)epeating units was studied on [a](#page-6-0) gold surfac[e fun](#page-6-0)ctionalized with different chemical groups.²⁰ It was found that the coating on amine-functionalized surfaces showed the least fouling against proteins because of [t](#page-6-0)he interaction of the quinone with amine groups. 23

Although PSB- and PCB-based zwitterionic polymers are attached to hydroxylated or amine-functio[na](#page-6-0)lized surfaces through "graft to" methods, a simple dip coating of zwitterionic polymers onto hydrophobic surfaces is challenging because of their higher solubility and stronger interactions with water. Hence, finding a universal yet simple method to attach zwitterionic polymers to hydrophobic surfaces in addition to hydrophilic surfaces is challenging. In this work, we have studied the possibility of achieving a universal coating method using catechol chain end sulfobetaine polymers for a variety of surfaces. The catechol chain end provides the anchoring point, whereas the zwitterionic polymer enhances the nonfouling behavior. This polymer coating was tested on a variety of surfaces such as hydrophilic metal oxides and hydrophobic polymeric sheets and fibers (PP, PS, PMMA, PVC, PDMS, and nylon).

EXPERIMENTAL SECTION

Materials. Dopamine.HCl, copper(I) bromide (CuBr), bromoisobutyryl bromide, N-(3-sulfopropyl)-N-(methacryloxyethyl)-N,N-dimethylammonium betaine (SBMA), 2,2′-bipyridine (BPY), 1-decanethiol, copper(II) bromide ($CuBr₂$), and albumin-fluorescein isothiocyanate conjugate (BSA-FITC) were purchased from Sigma-Aldrich. Tetrabutylammonium fluoride (TBAF) was purchased from Acros. 2-Amino-2-hydroxymethylpropane-1,3-diol (TRIS) and 1 N hydrochloric acid (HCl) was purchased from Fisher Scientific. High-impact polystyrene (PS), polyvinyl chloride (PVC), polypropylene (PP), and acrylate (PMMA) sheets were purchased from Tapplastics. PP, nylon, and PVC fibers were obtained from the U.S. Army Natick Soldier Research, Development and Engineering Center. Phosphate buffered saline (PBS) solution (0.01 M, pH 7.4) was made from PBS powder purchased from Sigma-Aldrich. Horeseradish peroxidase (HRP) conjugated goat anti-human IgG was purchased from Alpha Diagnostics. Milli-Q water (18.2 M Ω cm) was used to prepare water-based solutions. DOPA-Br (ATRP initiator synthesized from dopamine) was prepared as previously reported. 20

Synthesis of DOPA-PSB Polymer. DOPA-PSB polymer was synthesized as reported by Li G et al.²⁰ In a t[ypi](#page-6-0)cal reaction to get DOPA-PSB-100, 2g of SBMA monomer (7.1 mM) was polymerized with CuBr (0.0[71](#page-6-0) mM), $CuBr_2$ (0.0071 mM), BPY (0.15 mM) and DOPA-Br $(.071 \text{ mM})$ in a mixture of methanol and water $(1:4 \text{ v/v})$. The polymerization was carried out for 24 h. The polymer was purified by dialysis in Milli-Q water for 3 days and finally recovered by freeze drying. Catechol groups were deprotected by reaction of 1 mM catechol polymer with 5 mM TBAF in THF for 24 h. The polymer was repeatedly washed with THF and recovered by vacuum drying.

Gel Permeation Chromatogram Analysis (GPC). Aqueous gel permeation chromatography (GPC) (Waters 2695 Separations Module) fitted with a Waters 2414 refractive index detector and a Waters ultrahydrogel 250 column (7.8 mm \times 300 mm) was used for the detection of polymer molecular weight and molecular weight distribution. The buffer solution (0.05 M Tris buffer + 1.0 M NaCl)

was used as the eluent with a flow rate of 0.5 mL/min at 35 °C. All samples were filtered through 0.2 micrometer PTFE filters prior to the experiment. The system was calibrated with narrow molecular weight poly(ethylene oxide) polymer standards.

Dynamic Light Scattering Analysis (DLS). Dynamic light scattering measurements of the polymer solutions were performed using a Zetasizer NanoZS Instrument (Malvern Instruments, UK). Each measurement was repeated at least three times, and the average result was accepted as the final hydrodynamic diameter (D_h) . The measurements were performed with a thermostated cell temperature of 25 ± 0.1 °C and an equilibration time of 3 min. Polymer solutions were prepared in ultra-pure water.

Preparation of Self-Assembled Monolayer (SAM). Gold chips for SPR were cleaned by ultra violet radiation (UV) for 20 min. The cleaned gold chip was placed in a 0.05 mM ethanolic solution of 1 decanethiol for 24 h. Following incubation, the chip was rinsed with fresh ethanol and then dried with nitrogen.

Surface Plasmon Resonance (SPR) Experiment. A laboratory SPR sensor developed at the Institute of Photonics and Electronics, Prague, Czech Republic was used.¹⁴ This custom built SPR is based on the attenuated total reflection method and wavelength modulation. It is equipped with a temperature [co](#page-6-0)ntrol, four-channel flow-cell, and uses a peristaltic pump for delivering samples. Because the SPR sensitivity depends on the distance of the binding event from the SPR active surface, the sensor was made and calibrated using previously described methods.16,28 Gold-coated slides are utilized for the SPR sensor. To test coatings on silica surfaces, an additional 20 nm $SiO₂$ film is deposited o[n the](#page-6-0) gold-coated slides as reported previously.²⁵ A 1 nm shift in the resonant wavelength corresponds to a change in protein surface coverage of ~17.0 ng/cm².^{28,29} Details about al[l t](#page-6-0)he . SPR experiments and one representative SPR sensogram are provided in the Supporting Information (Figure [S1\)](#page-6-0). In a typical SPR experiment, the uncoated SPR chip was first mounted to the SPR sensor. Tris buffer (pH 8.5) solution was flown for 15 min to establish a flat ba[seline.](#page-5-0) [Polymer](#page-5-0) [coating](#page-5-0) [w](#page-5-0)as performed using a DOPA-PSB polymer solution (2 mg/mL) for 2 h followed by washing with Tris buffer for 15 min. The surface was then rinsed with copious amounts of PBS buffer (150 mM salt) for 2 h to completely remove any unbound polymer chains. Finally, a baseline was reestablished with Tris buffer to calculate the amount of the polymer bound to the surface. The non-specific protein adsorption of the polymer film was determined by flowing PBS for 10 min to establish a baseline, flowing a fibrinogen solution (in PBS 1 mg/mL) for 10 min, and flowing PBS buffer for 15 min to reestablish the baseline. Protein adsorption was quantified as the difference between buffer baselines and the difference in wavelength shift was converted to surface coverage. A flow rate of 50 μ L/min was used throughout the experiment.

Polymer Coating Protocol. The substrate was first cleaned with methanol and water and then dried with nitrogen. Polymer solution was prepared by dissolving DOPA-PSB in TRIS buffer (10 mM, pH 8.5) at a concentration of 2 mg/mL. The cleaned substrate was incubated in the polymer solution for at least 3 h to achieve surface coating. The substrate was then washed several times with PBS buffer solution (pH 7.4). Substrates were stored in PBS for further studies.

ATR-FTIR Spectra Characterization. The DOPA-PSB-100 coated PP fiber sample was rinsed and stored in PBS for 4 h. The sample was then stored in mQ water overnight and then dried under a vacuum at room temperature for 7 h. The sample was then used for ATR-FTIR characterization. The ATR-FTIR spectra were acquired using Harrick's GATR single-angle reflection accessory in conjugation with a Bruker Tensor spectrometer. Each spectrum was collected with a minimum of 50 scans at a resolution of 4 cm[−]¹ and an incident angle of 65°. Optimum contact between the germanium crystal and the sample surface were maintained throughout the measurements.

Standard Enzyme-Linked Immunosorbent Assay (ELISA) Method. Nonspecific protein adsorption binding to the surfaces is evaluated using HRP-conjugated anti-IgG adsorption.^{5,30} The samples were incubated with 1 μ g/mL anti-IgG for 1 h in 24-well plate. This was followed by five rinses with PBS buffer. Uncoate[d con](#page-6-0)trol surfaces and surfaces coated with DOPA-PSB-100 were all moved to new wells.

Next, 1 mL of 1 mg/mL OPD in 0.1 M citrate phosphate buffer (pH 5.5) containing 0.03 % hydrogen peroxide was then added. Enzyme activity was stopped by adding 1 mL of 1 N HCl after 15 min. Finally, the tangerine color of the solution (intensity is proportional to the amount of protein adsorption) was measured at 492 nm. For quantitative comparison, the uncoated bare surface fouling was normalized to 100%.

RESULTS AND DISCUSSION

Two PSB polymers, DOPA-PSB-20 and DOPA-PSB-100, with targeted degrees of polymerizations (DP) of 20 and 100 were prepared from the ATRP initiator DOPA-Br (Scheme 1). The molecular weights and polydispersity indices (PDI) of the synthesized polymers are given in Table 1.

Table 1. Gel Permeation Chromatogram (GPC) Characterization of Synthesized Polymers

polymer	targeted degree of polymerization	molecular weight	PDI
DOPA-PSB-20	20	8300	1.35
DOPA-PSB-100	100	35 100	1.38

DOPA-PSB was evaluated for nonspecific fibrinogen adsorption after attachment to model hydrophilic (silica) and hydrophobic (hydrocarbon SAM) surfaces using SPR. In this experiment, the surfaces were first exposed to the polymer solution and then cleaned with PBS solution until a constant base line was established. DOPA-PSB-100 was first tested on a piranha cleaned silica surface. The polymer coating on the silica surface showed undetectable fouling to fibrinogen (Figure 1A). This is due to the strong binding of the DOPA chain end of the polymer to metal oxides such as silica²⁵ and titania.^{23,26,27} Fibrinogen adsorption on an uncoated silica surface was [∼](#page-3-0)14 ng/cm². This fouling level is lower in co[mp](#page-6-0)arison to tha[t of an](#page-6-0) uncoated hydrophobic surface because of charge repulsion as

both silica and fibrinogen are negatively charged in the tested pH range.

To explore the possibility of grafting DOPA-PSB onto a hydrophobic surface, we used a C10 hydrocarbon SAM on a gold chip. Hydrophobic SAMs display high fouling to proteins.³¹ The bare C10 SAM surface fouls heavily (350 ng/ cm²) with fibrinogen. Although DOPA-PSB-20 is reducing the fouling [lev](#page-6-0)el to some extent, the surface still exhibits high protein binding (65 ng/cm²). This is similar to the result obtained by Li et al. with a low-molecular-weight DOPA-PSB-15.²⁰ Because DOPA-PSB-20 did not effectively make the surface nonfouling, a higher-molecular-weight polymer DOPA-PS[B-](#page-6-0)100 was tested. There is no measurable fouling noted for the DOPA-PSB-100 coating (Figure 1B). This is an indication that DOPA-PSB-20 was not able to achieve full surface coverage, which is necessary [fo](#page-3-0)r low fouling. 32 The binding of DOPA-PSB to the hydrophobic surface could be occurring through hydrophobic interactions as repo[rte](#page-6-0)d recently for mussel foot proteins.³³ In addition, dopamine is known to oxidize and cross-link under alkaline conditions, $34,35$ which may contribute to surface [bin](#page-6-0)ding. Substitution of gold thiols on the surface by DOPA-PSB is unlikely based on e[arlier](#page-6-0) studies of DOPA-PSB on self-assembled monolayers.²⁰ On the basis of the SPR experiments, DOPA-PSB-100 can coat hydrophilic as well as hydrophobic surfaces, allowing [th](#page-6-0)e resistance of nonspecific protein adsorption. Because the DOPA-PSB-100 coating provides nonfouling to hydrophobic surfaces, we focused on the modification of hydrophobic substrates with DOPA-PSB-100 polymer.

During the coating process, it was noted that the polymer solutions appeared cloudy. Zwitterionic polymers, especially PSB, are reported to display antipolyelectrolyte behavior possessing greater solubility in salt water than in pure water.36−³⁸ This is due to the inter- and intramolecular charge interactions of PSB chains, which decrease upon salt addition becau[se](#page-6-0) [eo](#page-6-0)f screening of the charged moieties.^{38,39} The same

Figure 1. (A) SPR fouling experiment of DOPA-PSB-100 coating on a silica surface. (B) SPR fouling experiment on a C10 hydrophobic SAM using DOPA-PSB-100 and DOPA-PSB-20 polymers. A 1 nm shift in the resonant wavelength corresponds to a change in protein surface coverage of ∼17.0 ng/cm². The uncoated hydrophobic C10 SAM displayed fouling of about 350 ng/cm² and the uncoated silica surface showed a fouling of about 14 $ng/cm²$ to fibrinogen.

effect could also be brought about by increasing temperature (see Figure S2 in the Supporting Information). In this work, we studied the effect of salt on the solution behavior of DOPA-PSB, and how this in turn affected the nonfouling behavior of the resulting coatin[g.](#page-5-0) [DOPA-PSB](#page-5-0) [polyme](#page-5-0)r was found to aggregate in solution containing no or little salt using dynamic light scattering (DLS) (Figure 2). When the salt concentration

Figure 2. Change in hydrodynamic diameter (nm) of DOPA-PSB-100 polymer with change in sodium chloride salt (NaCl) concentration. The inset diagrams $((A)$ no salt, (B) low salt, and (C) high salt contents) show possible intermolecular interactions between polymer chains. The line is drawn to guide the viewer's eye.

is low, the solution is turbid because of the intermolecular interactions between different polymer chains. In fact, when the salt concentration is around 10−20 mM, the aggregate size is larger than in pure water. This is attributed to the swelling of the inter-molecularly associated chains. At higher salt concentrations (∼45 mM), the hydrodynamic diameter is around 10 nm, indicating that the polymer aggregate is disassociated with individual chains. The theta concentration of sodium chloride (the minimum concentration required for complete solubility) was shown to be around 75 mM for sulfobetaine-based zwitterionic polymer brushes^{40,41} tethered to a surface. This value is slightly higher than what we have found (45 mM) as shown in Figure 2 for the free poly[mer](#page-6-0) in solution.

On the basis of these results, it is crucial to study the effect of salt concentration on the polymer coating and the nonfouling behavior. A hydrocarbon self-assembled monolayer (C10 SAM) attached onto a gold surface was chosen as a hydrophobic model. The polymer solution DOPA-PSB-100 was flown over the surface in three different salt concentrations (0, 10, and 100 mM). Zwitterionic polymers are known to exhibit the antipolyelectrolyte effect and it is evident from the photographs (insets Figure 3A) that the solutions are turbid when there is no or little salt in the polymer solution.

In this work[, w](#page-4-0)e evaluate three quantities: (i) the amount of polymer associating with the surface (Figure 3A), (ii) the amount of polymer remaining on the surface after coating (Figure 3A), and (iii) the fouling level of fibri[no](#page-4-0)gen (Figure 3B). All values are calculated with respect to a constant base line con[ta](#page-4-0)ining only buffer. PBS washing between steps was [p](#page-4-0)erformed until the base line became stable. It is interesting to note that when the salt concentration is 10 mM, the amount of polymer near the surface is higher than when there is no salt (0 mM). As discussed before this solution showed bigger particle sizes in DLS experiments among the polymer solutions tested (Figure 2). The cloudiness of the solution might bring more polymers closer to the surface. Intentional clouding of solutions before coating by adjusting solvent composition²⁴ or by adjusting temperature and salt concentrations 32 has been used to achieve higher grafting densities on surfaces. [H](#page-6-0)owever, it does not mean that all polymers brought close[r a](#page-6-0)re strongly bound to the surface. The free unbound polymers are removed from the surface by using a PBS wash. The fully dissolved polymer (clear solution) in 100 mM salt had the lowest association with the surface. The amount of polymer washed off from the surface during PBS rinsing is proportional to the amount of polymer, which initially associates with the surface. However, the important result is that the amount of polymer remaining on the surface after PBS washing is nearly identical for all the coatings. This illustrates that the mode of polymer attachment to the surface is the same regardless of the salt

Figure 3. Effect of salt concentration on the coating and the resultant fouling from SPR experiments. (A) Polymer solution behavior with different salt concentrations and (B) their corresponding fibrinogen fouling. Photographs of the polymer solutions are shown in the insets. A 1 nm shift in the resonant wavelength corresponds to a change in protein surface coverage of ∼17.0 ng/cm² . The raw SPR sensogram is shown in Figure S1 in the Supporting Information.

concentration because of catechol surface binding. All the [DOPA-PSB](#page-5-0) [coatings](#page-5-0) assembled using different salt concentrations showed ultra-low fouling to fibrinogen. This demonstrates that the polymer binds to the surface strongly via catechol groups and covers the entire surface and thus makes it inert to fibrinogen. In comparison, uncoated hydrophobic surfaces showed very high fibrinogen adsorption.

To demonstrate the use of DOPA-PSB on commonly used hydrophobic surfaces, a PP sheet was coated in three different salt concentrations as mentioned earlier. This is to confirm that the attachment of the zwitterionic polymer follows the same trend on a hydrophobic surface in comparison to a hydrophobic SAM. The results are given in Figure 4. The PP surfaces

Figure 4. HRP conjugated IgG fouling levels on PP surface coated with DOPA-PSB-100 at different salt concentrations measured by ELISA technique.

coated with DOPA-PSB-100 at different salt concentrations showed low fouling compared to the uncoated control. The polymer-coated surfaces display fouling around 10% of the control surface. This test confirmed that the fouling level of the DOPA-PSB zwitterionic polymer coating on a PP surface is independent of the salt concentration of the solution.

To evaluate the effectiveness of this simple coating method on porous materials, we tested polymeric nylon, PP, and PVC

fibers. Because these materials are porous, a fluorescentlylabeled protein, BSA-FITC, was used to determine nonspecific protein adsorption. The fouling levels are compared between uncoated and DOPA-PSB coated surfaces by exposing them to the same excitation light intensity and exposure time. The fluorescent images (Figure 5) indicate that the bare fiber controls show high protein fouling, whereas the zwitterionic polymer coated fibers display nonfouling properties.⁴²

Figure 5. Fluorescent microscopy images of BSA-FITC exposed (A) bare nylon fiber, (B) PP fiber, (C) PVC fiber, (D) DOPA-PSB-100 coated nylon fiber, (E) PP fiber, and (F) PVC fiber.

The PP fibers before and after modification with DOPA-PSB-100 were analyzed with X-ray photoelectron spectroscopy (XPS) to evaluate the surface characteristics. The PP surface modified with SB polymer showed the presence of characteristic atoms from the polymer chain. Nitrogen and sulfur peaks from DOPA-PSB polymer chains were found at 400 eV (N 1s), 170 eV (S 1s), and 230 eV (S 2p), whereas the bare PP showed no signals for sulfur and nitrogen (Figure 6). This indicates that

Figure 6. XPS survey scan of (A) unmodified PP fiber control and (B) DOPA-PSB-100-coated PP fiber.

the DOPA-PSB-100 polymer chains are attached to the PP surface. The XPS analysis on control and DOPA-PSB coated PP fiber show that the DOPA-PSB-100 polymer covers the PP fiber surface almost completely based on the theoretical value (Table 2) for the SB polymer. 43 This was also compared with

Table 2. Elemental Percentag[e](#page-7-0) Calculated From XPS for PP Fiber and DOPA-PSB-100 Coated Fiber Compared with the Theoretical Value for PSB

surface	C	λ	N	
РP	96.63	3.37		
PP-DOPA-PSB-100	63.82	25.37	5.712	5.087
PSB (theoretical)	61.1	27.7	5.6	5.6

attenuated total reflectance fourier transform infrared spectroscopy ATR-FTIR (see Figure S3 in the Supporting Information). On the basis of these results, it is evident that DOPA-PSB-100 attaches to PP surfaces.

Finally, the polymer was tested on a variety of different commercially used polymeric surfaces, including PMMA, PVC, PS, PDMS, and PP. The surfaces were coated with DOPA-PSB-100 zwitterionic polymer and then tested for protein fouling via ELISA. The results are summarized in Figure 7. All coated surfaces showed significantly lower fouling relative to their respective control, which is normalized to 100% fouling. PVC, PDMS, PMMA, and PP showed fouling levels close to 10% with respect to their corresponding controls. Polystyrene showed fouling around 20%. This experiment clearly demonstrates the potential of DOPA-PSB-100 as a simple and versatile polymer, which could be used for the coating of many different surfaces at the same time to reduce fouling.

■ CONCLUSIONS

A zwitterionic sulfobetaine-based polymer with a biomimetic catechol chain end was found to reduce fouling levels significantly on many different surfaces such as hydrophilic silica and a number of hydrophobic substrates. The coating of DOPA-PSB polymer was extended to the surfaces of polymers

Figure 7. HRP-conjugated IgG fouling measured by ELISA on a variety of commercially used polymeric sheets such as PMMA, PVC, PS, PDMS, and PP.

such as PP, PDMS, nylon, PVC, and PS either on flat sheets or fibrous structures. Among two DOPA-PSB polymers of different molecular weights tested on hydrophobic surfaces, the polymer with the higher molecular weight was found to have better nonfouling than the low-molecular-weight polymer because of increased surface coverage. It is found that DOPA-PSB can be dissolved completely at a salt concentration of 45 mM or higher. However, the nonfouling behavior is independent of salt concentration despite the difference in solubility.

■ ASSOCIATED CONTENT

6 Supporting Information

Details about SPR experiments, SPR sensogram, DLS studies, ATR-FTIR characterization of uncoated control PP surface and PP surface coated with DOPA-PSB-100. This material is available free of charge via the internet at http://pubs.acs.org.

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Notes

The auth[ors declare no](mailto:sjiang@uw.edu) competing financial interest.

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