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# Salt-Responsive Zwitterionic Polymer Brushes with Tunable Friction and Antifouling Properties

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Ⓢ *Supporting Information*

ABSTRACT: Development of smart, multifunction materials is challenging but important for many fundamental and industrial applications. Here, we synthesized and characterized zwitterionic poly(3-(1-(4-vinylbenzyl)-1*H*-imidazol-3-ium-3-yl)propane-1-sulfonate) (polyVBIPS) brushes as ion-responsive smart surfaces via the surface-initiated atom transfer radical polymerization. PolyVBIPS brushes were carefully characterized for their surface morphologies, compositions, wettability, and film thicknesses by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle, and ellipsometer, respectively. Salt-responsive, switching properties of polyVBIPS brushes on surface hydration, friction, and antifouling properties were further examined and compared both in water and in salt solutions with different salt concentrations and counterion types. Collective data showed that polyVBIPS brushes exhibited reversible surface wettability switching between in water and saturated NaCl solution. PolyVBIPS brushes in water induced the larger protein absorption, higher surface friction, and lower surface hydration than those in salt solutions, exhibiting "anti-polyelectrolyte effect" salt responsive behaviors. At appropriate ionic conditions, polyVBIPs brushes were able to switch to superlow fouling surfaces (<0.3 ng/cm² protein adsorption) and superlow friction surfaces ($u \sim 10^{-3}$). The relationship between brush structure and its salt-responsive performance was also discussed. This work provides new zwitterionic surface-responsive materials with controllable antifouling and friction capabilities for multifunctional applications.
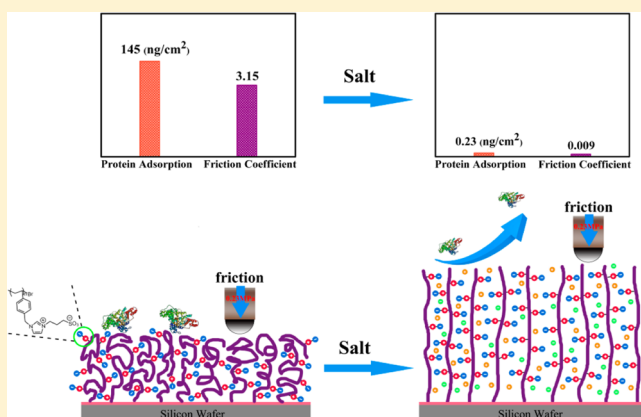
■ INTRODUCTION

Surface friction is the force resisting the relative motion of two bodies in contact, which is controlled by the atomic details at the sliding interface.[1−3] Especially, many biomedical applications, such as artificial joints (knees, hips, fingers)/eyes and BioMEMS/NEMS, require biological interfaces with superlow friction and biocompatible properties.[4−7] Natural synovial joints show the high efficiency of the lubrication with friction coefficients as low as $\sim 10^{-3}$, probably due to bottle-brush-like biolubricants such as phospholipids, hyaluronan (HA), lubricins, and glycoproteins in synovial fluids.[8−10] More interestingly, most of these biolubricants are biopolyelectrolytes that contain a large amount of sulfonic and carboxylic groups. Thus, the surfaces modified by "brush-like" synthetic polymers offer a simple and promising way to control surface frication.[11,12] As compared to neutral hydrophilic polymer brush layers, charged polyelectrolyte brush layers can act as very effective lubricants with much lower friction coefficients of $\sim 10^{-3}$ due to the high hydration of charged segments on polymer backbones and the exceptional resistance to mutual interpenetration displayed by the compressed yet swollen brushes.[13−15] Moreover, polyelectrolyte brushes often experience conformation changes from fully extended chains in water to collapsed chains in salt solutions, due to electrostatic screening effect. Such ion-responsive conformational transition (i.e., swelling−collapse transition) also depends on ion concentrations and types,[16−18] which offer a relatively easy way to tune surface friction from superior lubrication to ultrahigh friction.[19,20]

But, due to highly charged nature, polyelectrolyte brushes usually have poor biocompatibility because they inevitably induce significant adsorption of biomolecules (proteins, cells, and bacteria) on the surfaces, resulting in a typical biofouling problem.[21] The attached foulants in turn increase surface friction. Different from traditional polyelectrolytes, zwitterionic polymers, which have a positively and a negatively charged group placed on the same repeating unit, are reported to display antipolyelectrolyte behavior possessing greater solubility

Scheme 1. (a) Synthesis of VBIPS Monomer and (b) Schematic SI-ATRP Process for Grafting PolyVBIPS onto a Silica Wafer Coated with Immobilized Initiators
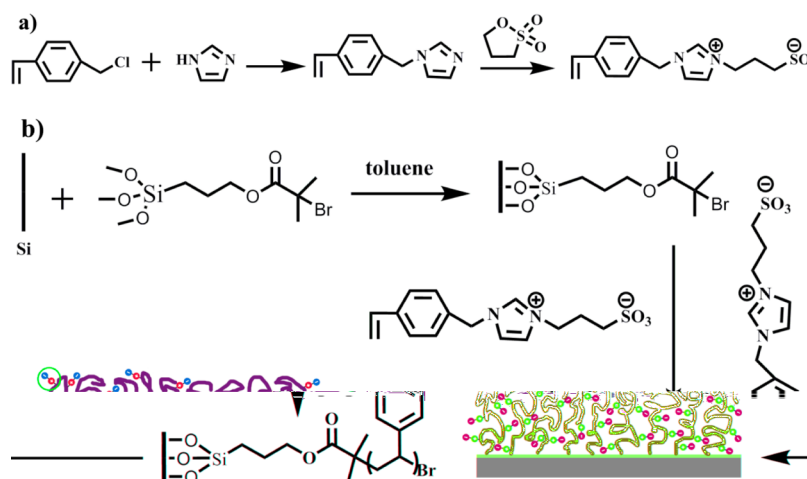
in salt water than in pure water. This antipolyelectrolyte behavior becomes even more pronounced for poly(sulfobetaine methacrylate) (polySBMA) because the inter- and intra-molecular charge interactions of polySBMA chains decrease greatly upon salt addition because of screening of the charged moieties.[22−24] Meanwhile, polySBMA brushes have demonstrated their superlow fouling ability to prevent nonspecific protein adsorption from undiluted blood plasma and serum[25] as well as to dramatically reduce bacterial attachment and biofilm formation.[26,27] On the other hand, due to the presence of strongly charged sulfobetaine groups, ion-responsive properties of polySBMA were compromised. Wei et al.[20] reported that the friction coefficients of polySBMA brushes were slightly increased from 0.006 to 0.01 when changing anions (Cl^{−}, ClO$_4$[−], PF$_6$[−], and bis(trifluoromethanesulfonimide) (TFSI[−])) in salt solutions. Thus, it is important, but challenging, to develop biocompatible, surface-responsive materials that have both controllable antifouling and friction capabilities.

In this work, we synthesized and characterized novel zwitterionic polymer brushes of poly(3-(1-(4-vinylbenzyl)-1H-imidazol-3-ium-3-yl)propane-1-sulfonate) (polyVBIPS) using surface-initiated atom transfer radical polymerization (SI-ATRP). Such brushes were carefully characterized for their surface morphologies, compositions, wettability, and film thicknesses by atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), contact angle, and ellipsometer, respectively. Surface-responsive properties of poly-VBIPS brushes were examined and compared both in water and in salt solutions with different salt concentrations and counterion types, followed by surface friction tests. Antifouling properties of polyVBIPS brushes were also rigorously tested by quantifying nonspecific protein adsorption from undiluted human blood plasma and serum using surface plasma resonance (SPR). Friction results showed that friction coefficients of polyVBIPS brushes can readily be continuously tuned from ultrahigh friction ($\mu \sim 10^0$) to superior lubrication ($\mu \sim 10^{-3}$) by changing salt concentrations and counterion types. Antifouling property of polyVBIPS brushes can also be tuned from a high protein absorption amount of ∼145 ng/cm^2 in PBS to almost zero protein adsorption (<0.3 ng/cm^2) in PBS solution with 1.0 M NaCl. This work demonstrates a new ion-responsive zwitterionic polymer brush as "smart" materials,

allowing to switch between absorption−desorption and friction−lubrication properties.

■ MATERIALS AND METHODS

Materials. 4-Vinylbenzyl chloride (90%), 1,3-propane sultone (98%), imidazole (99%), copper(I) bromide (CuBr) (98%), 2,2,2-trifluoroethanol, and phosphate buffer saline (PBS, pH 7.4, 0.15 M, 138 mM NaCl, 2.7 mM KCl) were purchased from Sigma-Aldrich Co. (Shanghai, China) and used as received. Tris[2-(dimethylamino)-ethyl]amine (Me6TREN, 99%) was purchased from J&K Chemical Ltd. (Beijing, China). ATRP initiator for gold surface, ω-mercapto-undecyl bromoisobutyrate, was kindly provided by Professor Shaoyi Jiang at the University of Washington. The initiator for grafting polymer brushes on silica wafer, 3-(2-bromoisobutyramido)propyl-(trimethoxy)silane, was purchased from Gelest, Inc. (Morrisville, PA). Water used in these experiments was purified by a Millipore water purification system with a maximum resistivity of 18.0 MΩ cm. All other reagents and solvents were commercially obtained at extra-pure grade and were used as received. SPR glass chips were coated with an adhesion-promoting titanium layer (2 nm in thickness) and a gold layer (48 nm) by electron beam evaporation under vacuum.

Synthesis of VBIPS Monomer. VBIPS monomer was synthesized and purified using a previously published method (Scheme 1a).[28,29] Sodium hydrogen carbonate (10.5 g, 124.8 mmol) dissolved in 200 mL of a binary mixture of water/acetone (v/v = 1:1) was added into a 500 mL three-neck round-bottomed flask equipped with a reflux condenser, a thermometer, and a magnetic stirring bar. Imidazole (27.22 g, 0.398 mol) and hydroquinone (0.1 g, 0.908 mmol) were added, and the mixture was agitated for ∼30 min under ambient temperature. 4-Vinylbenzyl chloride (15.22 g, 99.6 mmol) was added to the flask in a dropwise manner, and the solution was heated to 50 °C and maintained at this temperature for 20 h to complete the reaction. Upon reaction completion, the solution was cooled to room temperature and filtered to remove salt. Acetone in the filtrate was removed through distillation, and the remaining solution was diluted in 500 mL of ether and washed with 50 mL of deionized water for six times to remove unreacted imidazole. The product was back-extracted from the solution by adding 100 mL of 2 M aqueous hydrochloric acid solution. An opaque heterogeneous solution was obtained when 200 mL of 4 M aqueous sodium hydroxide solution was added to the hydrochloric acid solution. The product was recovered with 50 mL of ether for three times and dried with anhydrous magnesium sulfate. A transparent oily liquid sample was obtained when ether was distilled. The transparent oily liquid (8 g, 43.475 mmol) was dissolved in 180 mL of dry acetonitrile, and the solution was then added with hydroquinone (0.02 g, 0.182 mmol) and 1,3-propane sultone (5.312 g, 43.47 mmol). The reaction was carried out at 50 °C under stirring for
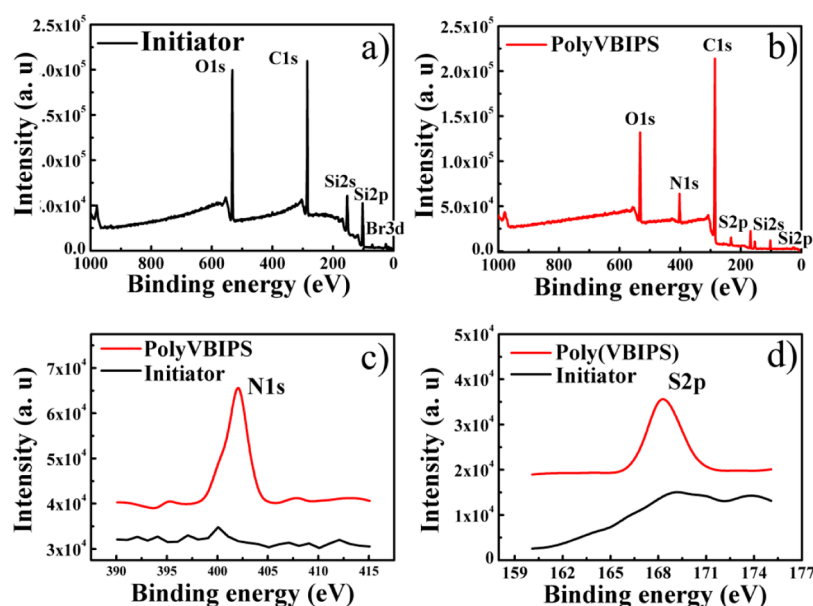
Figure 1. XPS survey spectra for the silicon surfaces grafted with (a) initiators and (b) polyVBIPS brushes. (c) N_{1s} and (d) S_{2p} high-resolution survey scans.

48 h. A white precipitate produced from the ring-opening reaction was recovered through filtration. The precipitate was then dried in a vacuum oven at 40 °C and stored at 2−4 °C. The H NMR spectrum (in D_2O) was used for structure certification.

Preparation of Polymer Brushes via SI-ATRP Method. A single crystal silicon wafer (20 mm × 20 mm) was placed into a fresh piranha solution (H_2SO_4:H_2O_2 = 3:1) at 120 °C for ∼0.5 h. The wafer was then repeatedly washed with deionized water and dried using a nitrogen stream. The wafer was subsequently treated with plasma (CORONA Lab. CTP-2000, Nanjing, China) for ∼2 min to enhance hydrophilicity. The cleaned silica wafer was immediately immersed into 1 mM dehydrate toluene solution containing 3-(trimethoxy-silylpropyl)-2-bromo-2-methylpropionate for 12 h at room temperature. The initiator-grafted surface was sequentially washed with toluene, ethanol, and water and then dried under a stream of nitrogen. Zwitterionic polymer brushes were synthesized through SI-ATRP. The VBIPS monomer (1.96 mmol) and Me6TREN (0.14 mmol) were dissolved in water (2.5 mL), and the mixture was degassed by flowing a stream of nitrogen for 20 min. 2,2,2-Trifluoroethanol was also degassed in the same manner. A 15.7 mg portion of CuBr (0.11 mmol) and silica wafer with the initiator-coated SAM surface were placed in a reaction tube. The tube was immediately evacuated and backfilled with nitrogen for three times to remove oxygen. The degassed 2,2,2-trifluoroethanol (2.5 mL) and water solution containing the monomer and ligand were added using a syringe to the reaction tube under nitrogen protection. The tube was then subjected to two evacuation−nitrogen purging cycles and kept at room temperature for the SI-ATRP reaction. After the prespecified reaction time, the solution was exposed to air to terminate the reaction. The silica wafer was collected, washed with 2,2,2-trifluoroethanol and saturated NaCl solution, and dried through nitrogen blowing.

SPR chips were cleaned, and the initiator on these chips was immobilized using a previously reported method.[30] Upon formation of the initiator monolayer, the ATRP procedure for grafting polymer brushes was the same to that used for polymer brushes on silica wafer.

Polymer Thickness by Ellipsometry. The film thickness of polymer brushes was measured by ellipsometric measurements performed on a an α-SE ellipsometer (J.A. Woollam Co., Lincoln, NE) with a He−Ne laser (λ) 632.8 nm) and a fixed angle of incidence of 70°. Bare silicon wafer was used to determine the thickness of SiO_2 layer.

Surface Composition by XPS. X-ray photoelectron spectroscopy (XPS) measurements were performed using an Axis Ultra DLD

spectrometer (Kratos Analytical). The instrument is equipped with a monochromatized aluminum X-ray source powered at 15 kV and 3 mA that delivers an X-ray beam of 300×700 μm^2. The takeoff angle was 45° with respect to the surface normal, making the X-ray-to-electron angle 90°.

Surface Morphology and Roughness by AFM. Surface morphology and roughness measurements were conducted on a Veeco multimode III AFM (Veeco Instruments Inc., USA) in tapping mode. An AFM tip with a radius of ∼10 nm and a cantilever spring constant of 50 N/m was employed and driven at a frequency of 170−180 kHz. All the measurements are carried out in ambient conditions.

Contact Angle Measurement. Water or salt solution contact angles on polyVBIPS-grafted surfaces were recorded with OCA 15EC video-based optical contact angle measuring system (Eastern-Dataphy Instruments Co., Ltd., Beijing), equipped with a sessile drop shape analysis system and a video camera. A 5 μL droplet of water or salt solution was placed on the surface by a microsyringe for the static contact angle measurement. The data presented were averaged by five independent measurements on different positions.

Nonspecific Protein Adsorption by SPR. Protein adsorption was determined using a custom-built SPR sensor through wavelength interrogation. A peristaltic pump (Ismatec) was utilized to deliver liquid sample to four independent channels of the flow cell. After rinsing water, the SPR chip was air-dried and attached to the base of the prism. A baseline signal was established by flowing PBS buffer at a rate of 0.05 mL/min through the sensor until the baseline was stabilized. Undiluted blood serum and blood plasma were flowed through independent channels for 10 min, followed by PBS buffer solution for 10 min. Then 1 M NaCl solution was flowed for another 10 min to remove unbound or loosely bound proteins followed by PBS buffer solution for 10 min. The amount of adsorbed proteins on the surface was quantified by determining the changes in wavelength between the baselines before and after protein injection. A 1.0 nm SPR wavelength shift at 750 nm represents approximately ∼15 ng/cm^2 adsorbed proteins.

Friction Coefficient Measured through Macroscopic Friction Test. The lubrication performance of polyVBIPS brushes in different environment conditions was evaluated using the method reported by Wei et al.[20] A conventional pin-on-disk tribometer was used to determine friction coefficients. Measurements were conducted on a Universal Micro tribometer (UMT-2, CETR), with an elastomeric poly(dimethylsiloxane) (PDMS) hemisphere with a diameter of 6 mm as a pin against polyVBIPS brushes. The distance of a sliding cycle,

sliding velocity, and loading of PDMS hemisphere exerted on polyVBIPS brushes were set as 10 mm, 2×10^{-3} m/s, and 0.5 N (Hertzian contact pressure = 0.23 MPa), respectively. Each friction coefficient was obtained from three independent measurements on different positions. Each measurement included 20 sliding cycles, and 60 data points were used to obtain average value and standard deviation.

RESULTS AND DISCUSSION

Surface Characterization of PolyVBIPS Brushes. PolyVBIPS brush was prepared through the "graft-from" SI-ATRP method (Scheme 1b). To demonstrate the success of surface grafting by polyVBIPS brush, XPS was performed to analyze and compare the surface compositions of initiator-coating and polymer brush-coating surfaces (Figure 1). Surface grafting of initiators resulted in the appearance of a Br_{3d} peak at 70.3 eV and a C_{1s} peak at 285 eV (Figure 1a), indicating the successful grafting of initiators on a silicon surface. The associated signals for the silicon appeared at 153 and 103 eV for Si_{2s} and Si_{2p}, respectively. Upon polymerization, two new peaks of N_{1s} at 401 eV and S_{2p} at 168 eV were observed (Figure 1b), while the Br_{3d} peak disappeared. Further high-resolution survey scans for N_{1s} at 168.1 eV (Figure 1c) and S_{2p} at 401.9 eV (Figure 1d) corresponded to the positively charged nitrogen in imidazolium and sulfonate, respectively.[31,32] This indicates that the subsequent transformation of surface Br groups to zwitterionic groups in polyVBIPS brush was successful.

To control the film thickness of polymer brushes, Figure 2 shows the dependence of film thickness of polyVBIPS brushes
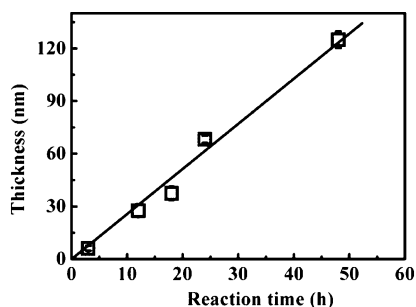
Figure 2. Film thickness of polyVBIPS brushes as a function of reaction time.

as a function of ATRP reaction time. It can be seen that the film thickness of polyVBIPS brushes increased linearly and gradually to ~6.1, 27.6, 37.5, 68.2, and 124.9 nm in 3, 12, 18, 24, and 48 h, respectively. This demonstrates that the presence of living polymerization enables to well control the growth of polymer brushes. The microscopic morphology of polyVBIPS brushes with different film thicknesses were visualized and measured by the tapping-mode AFM (Figure 3). PolyVBIPS brushes with ~6.1 nm thickness were largely covered by many small, isolated clusters, resulting in a root-mean-square (rms) roughness value of 1.2 nm. When polymer film thickness increased to ~28 and ~68 nm, polymer brushes became denser and the surfaces appeared as a macroscopically homogeneous flat thin film with segregated domains, as indicated by the lower rms roughness values of 1.0 and 0.7 nm. Beyond 48 h of polymerization, as polymer film thickness was increased to ~124.9 nm, several hole-like domains were observed, leading to a higher rms roughness value of 1.8 nm. Thus, polymer brushes prepared by in the time range of 12−24 h enable to yield more uniform and
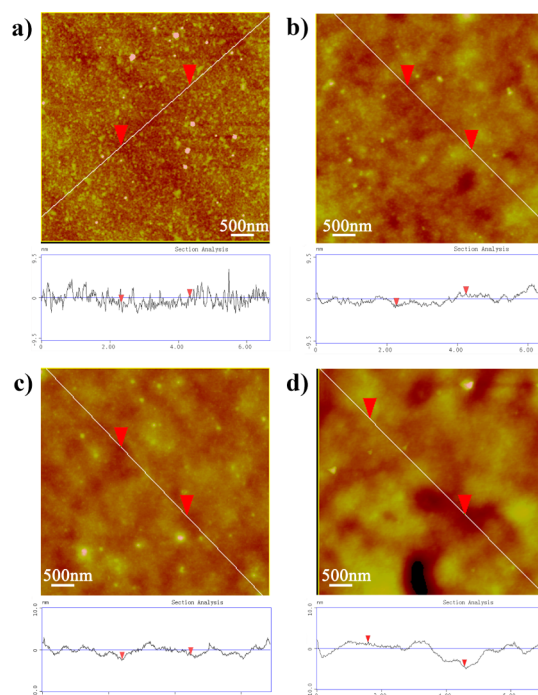
Figure 3. Tapping-mode AFM for pVBIPS brushes with film thicknesses of (a) 6.1, (b) 27.6, (c) 68.2, and (d) 124.9 nm.

smoother surfaces, and they will be used for later tests of friction and protein adsorption.

Surface Hydration and Wettability Switching of PolyVBIPS Brushes. Surface hydration is a critical factor for friction force at the interface.[33] To evaluate the surface hydration of polyVBIPS brushes and surface response to salts, we measured the dynamic changes of contact angles (i.e., wettability switching) on polyVBIPS brushes of varied film thicknesses from 6.1 to 124.9 nm in both water and saturated NaCl solution (Figure 4). Overall, regardless of film thickness and solvent type, contact angles always decreased as time. In water solution, when water was dropped and spread on polymer brushes, it needs approximately 2 min for both water and polymers to reach an equilibrium state, probably due to the hydrophobic yet swelling in water properties of the polymer. Differently, polymer brushes in salt solution showed the smaller contact angles, the shorter time to reach the equilibrium, and the larger contact angle drops during spreading process than those corresponding polymer brushes of the same film thickness in water, indicating the higher hydration of polymer brushes in salt solution. In Figure S1, we further performed a side-by-side comparison of the equilibrate contact angles of polymer brushes in water and NaCl solutions as a function of film thickness. It can be seen clearly that at all film thicknesses tested polymer brushes showed wettability switching behaviors between water and salt solutions, as evidenced by contact angle changes. Specifically, for the thin polymer brush of ~6.1 nm thickness, the difference of contact angles between salt solution and water solutions is minor and only about 5°. As the film thicknesses increased, the differences became much more pronounced, i.e., ~15° at 37 nm, ~21° at 68 nm, and ~24° at 124.9 nm.

Because of the salt-responsive nature of polymer brushes, surface wettability of polyVBIPS brushes is expected to depend on salt concentrations and types. To validate this assumption, we examined the effects of NaCl concentrations (from 0.05 to
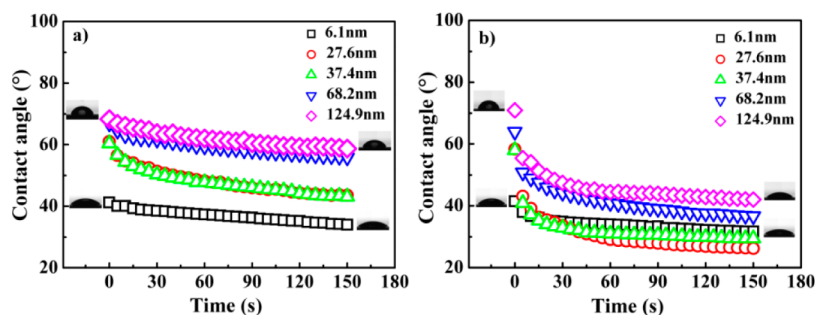
Figure 4. Dynamic contact angles of polyVBIPS brushes of different thickness as a function of time in (a) water and (b) saturated NaCl solution.
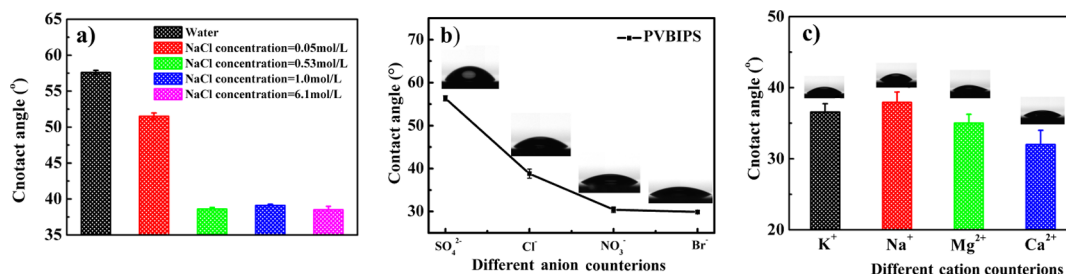

Figure 5. Contact angles of (a) NaCl solutions with different concentrations, (b) salt solutions (1.0 M) containing different anions of SO_4^{2-}, Cl^-, NO_3^-, and Br^-, and (c) salt solutions (1.0 M) containing different cations of Na^+, K^+, Mg^{2+}, and Ca^{2+} on polyVBIPS brushes of ~68 nm thickness.

5.4 M) on the surface wettability of polyVBIPS brushes of ~68 nm. In Figure 5a, contact angles of polymer brushes in water were always larger than those of polymer brushes in NaCl solutions at all concentrations tested. At a low concentration of NaCl of 0.05 M, polymer brushes only yielded a small decrease of contact angles by ~6°. However, as the NaCl concentrations increased to 0.53 M or above, contact angles of polymer brushes were largely decreased to ~37°, almost independent of NaCl concentrations. This indicates that polyVBIPS brushes achieve the saturated surface hydration at or above the threshold values of NaCl solution (≥0.53 M). Interestingly, this threshold value of NaCl (0.53 M) is very close to that of salt concentration in marine environment. Figure 5b examines the effect of different counterions (i.e., SO_4^{2-}, Cl^-, NO_3^-, and Br^-) on the surface hydration of polyVBIPS brushes by contact angle measurement. In this test, all salt concentrations of different counterions were fixed at 1.0 M. Salt solution with SO_4^{2-} showed the highest contact angle of ~56° similar to that in water, while salt solutions with Cl^-, NO_3^-, and Br^- displayed much lower contact angles of ~38°, 31°, and 30°, respectively. Particularly, introduction of NO_3^- and Br^- ions in solutions induces the higher surface hydration of polyVBIPS brushes. In parallel to anion counterions, different cations including monovalent cations (Na^+ and K^+) and divalent cations (Mg^{2+} and Ca^{2+}) were also used to test the effect of the cations on the surface hydration of polyVBIPS brushes. To this end, Figure 5c shows the contact angles of polyVBIPS brushes of ~68 nm in 1.0 M KCl, NaCl, $MgCl_2$, and $CaCl_2$ solutions. Overall, the cation-induced contact angle changes were minor and ranged from ~38° to ~32°. Specifically, for monovalent cations, KCl solution (~36.5°) exhibited a slightly lower contact angle than NaCl solution (~38°). This indicates that polyVBIPS binds K^+ more strongly than Na^+, in agreement with previous simulation and experiment results.[24,34] As compared to monovalent cations, $MgCl_2$ and $CaCl_2$ further decreased contact angles to ~35° and ~32°, respectively. These results are consistent with the sum frequency generation (SFG) vibrational spectroscopy

results as reported by Leng et al.;[24] i.e., sulfobetaine polymer binds divalent cations more strongly than monovalent cations.

These results showed that an intrinsic wettability of polyVBIPS brushes, with "anti-polyelectrolyte effect" salt responsive behavior. The presence of benzene groups in polyVBIPS offers molecular hydrophobicity, inducing high contact angle in water. When salts are introduced in solution, the counterions adsorb and penetrate into polymer brushes, destroy the electrostatic inter/intrachain dipole−dipole interaction, and thus induce the more extended chain conformations of polyVBIPS brushes in salt solutions. More importantly, polyVBIPS brushes show the reversible wettability switching in response to the changes of salt concentrations and counterion types (Figure 6). Similar wettability switching behaviors were also observed in other zwitterionic polymers such as polySBMA.[22,35]
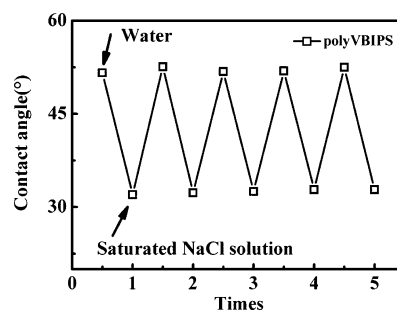

Figure 6. Reversible surface wettability switching for polyVBIPS brushes between in water and in saturated NaCl solution.

Relationship between Lubrication Performance and Surface Wettability. On the basis of the reversible and tunable wettability switching behavior of polyVBIPS brushes, we further investigated the lubrication and frication behaviors of polyVBIPS brushes as smart surfaces with salt stimuli-responsive properties. In situ friction tests (Figure S2) were

performed on polyVBIPS brushes using elastomeric PDMS hemispheres of a diameter of 6 mm as a pin against the tested polymer surface. Figure 7 compares the friction coefficients of
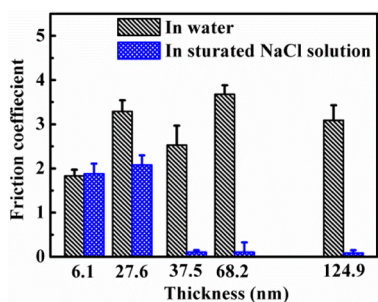

Figure 7. Comparison of friction coefficients of polyVBIPS brushes of different thicknesses between in water and in saturated solution.

polyVBIPS brushes of different thicknesses in both water and saturated NaCl solutions. In water, all polyVBIPS brushes of different thicknesses showed high friction coefficients of 1.9–3.7. For the lubrication of hydrophilic polymer brushes, both surface hydration and surface topography have large effects on friction coefficient.[36,37] When the grafted polyVBIPS film is thin (∼7 nm), polyVBIPS film is more hydrophilic than other thicker polyVBIPS films (Figure 4a), thus resulting in a relatively low friction coefficient of ∼2. As film thickness increases, both surface topography and wettability of polyVBIPS brushes will change to different extents. The complex interplay between these two factors causes small fluctuation of friction coefficients between 2.7 and 3.7. When polyVBIPS brushes were immersed in saturated NaCl solutions, the brushes clearly showed the thickness-dependent friction/lubrication switching behaviors. At the lowest film thickness of 6.1 nm, polyVBIPS brushes displayed almost identical friction coefficients of ∼1.9 in water and saturated NaCl solution. As film thickness increased to 27.6 nm, friction coefficients in water and saturated NaCl solution were ∼3.2 and ∼2, respectively, indicating a moderate salt-responsive friction switching behavior. However, when the film thicknesses were increased to ∼37 nm or above, friction coefficients were significantly reduced from 2.7 to 3.7 in water to ∼0.05 in saturated salt solution, clearly demonstrating a salt-responsive friction/lubrication switching behavior. Friction results are consistent with contact angle results, suggesting a positive relationship between surface hydration and lubrication performance.

To explore the potential of friction/lubrication switching ability, we measured friction coefficients of polyVBIPS brushes in NaCl solutions of difference concentrations and in different salt solutions containing different counterions (i.e., SO_4^{2-}, Cl^-, NO_3^-, and Br^-). PolyVBIPS brushes of ∼68 nm thickness were used for all friction tests. Figure 8a shows the changes of friction coefficients in response to NaCl solutions of different concentrations. It can be seen that friction coefficients were monotonously decreased with salt concentrations, i.e., ∼3.7 in water and ∼2, ∼0.75, ∼0.6, and ∼0.07 in 0.05, 0.53, 1.0, and 5.4 M NaCl solutions, respectively. Along similar lines, Figure 8b shows the friction coefficients of polymer brushes in salt solutions of different counterions. The friction coefficients in salt solutions containing SO_4^{2-}, Cl^-, NO_3^-, and Br^- were ∼3.1, ∼ 0.6, ∼0.017, and ∼0.008, respectively. The SO_4^{2-} ionic effect was different from other anions, likely due to its bivalent
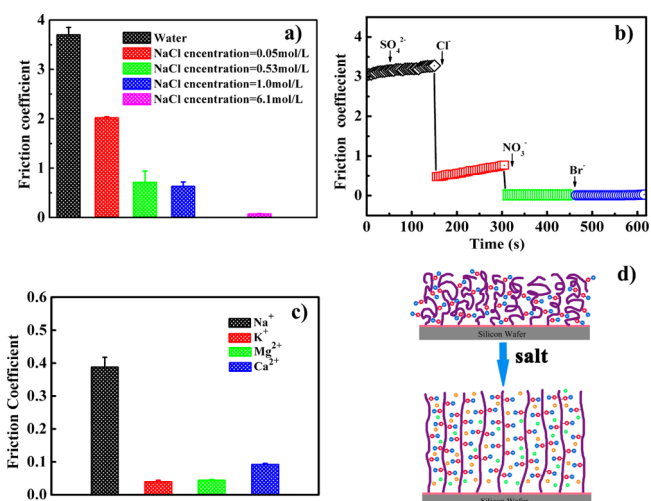

Figure 8. Changes of fiction coefficients of polyVBIPS brushes of ∼68 nm thickness in response to (a) NaCl solutions with different concentrations, (b) salt solutions (1.0 M) with different anions of SO_4^{2-}, Cl^-, NO_3^-, and Br^-, and (c) salt solutions (1.0 M) with different cations of Na^+, K^+, Mg^{2+}, and Ca^{2+}. (d) Schematic of chain conformation from a collapse state to an extended state induced by salt solutions.

property. A similar SO_4^{2-} effect was also observed on polySBMA surface, as reported by Wang et al.,[22] which found that when SO_4^{2-} concentration was above a threshold value of 1.0 M, SO_4^{2-} anions would compete for water molecules, decreasing the amount of water coupling with polySBMA chains. It is worth noting that the use of Br^- as counterions induces an extremely low friction coefficient of ∼10⁻³, which is comparable to that of natural synovial joints. The changes of friction coefficients in response to counterions showed a similar trend to that of contact angles, where NaBr solution showed the lowest contact angle, while Na_2SO_4 showed the highest contact angle. Combining friction and contact angle results, we conclude that polyVBIPS-grafted surface can be continuously tuned from ultrahigh friction ($\mu \sim 10^0$) to moderate lubrication ($\mu \sim 10^{-2}$) and further to superior lubrication ($\mu \sim 10^{-3}$) by different salt concentrations and salt types. The influence of different cations on friction coefficient of polyVBIPS brushes was also evaluated. In Figure 8c, using the same ion concentrations of 1.0 M and the same polyVBIPS brushes of ∼68 nm, friction coefficients of polyVBIPS brushes in different cation solutions were in a decreased order of $Na^+ > Ca^{2+} > K^+ \approx Mg^{2+}$. Especially Na^+ induced much higher friction coefficients than other cations, while the variation of friction coefficients in K^+, Ca^{2+}, and Mg^{2+} was minor. This result indicates that Na^+ ions bind to polyVBIPS more weakly than other cations. Different ionic-binding ability to polyVBIPS will induce counterions to adsorb and penetrate into polymer brushes and destroy the electrostatic inter/intrachain dipole–dipole interaction, and the reduced chain–chain interactions will, in turn, promote polymer–water interactions at the interface, which results in different friction coefficients and contact angles.[22] It is also possible that combined polymer–polymer and polymer–water interactions cause the conformational change of polymers from a collapse conformation to a more extended conformation (Figure 8d), which requires for a further study in details.

Salt-Induced Surface Resistance to Nonspecific Protein Adsorption. Considering the fact that polyVBIPS

brushes possess high surface hydration and low friction in salt solutions that are critical for antifouling surfaces, polyVBIPS brushes may have additional antifouling properties under appropriate salt-stimuli conditions. To test our hypothesis, we prepared polyVBIPS brushes of ~27 nm thickness via the SI-ATRP method and evaluated their surface resistance to nonspecific protein adsorption from undiluted human blood serum and plasma using an in-house SPR sensor. Film thickness of 27 nm was selected because our previous studies have demonstrated that film thickness of 20−30 nm seems to be a safe range to achieve effective antifouling performance for polyHEMA brushes,[38] polyHPMA brushes,[38] and polyHEAA brushes.[39,40] Undiluted blood plasma and serum were used to challenge our polymer brushes, since they offer the most rigorous tests for antifouling performance as compared to single protein solutions.[41,42] To evaluate how the surface switching between water and NaCl solution affect protein adsorption, Figure 9 shows the protein adsorption from undiluted blood
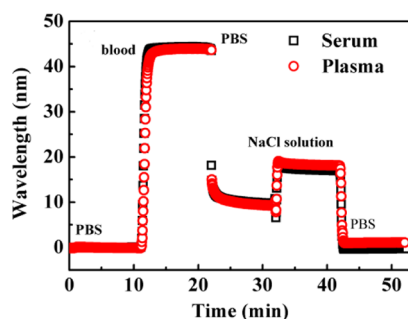

Figure 9. Protein adsorption on polyVBIPS brushes from undiluted human blood plasma and serum by SPR. 1 nm SPR wavelength shift is approximately equal to ~15 ng/cm^2 adsorbed proteins.

plasma and serum on polyVBIPS brushes and protein desorption upon salt solution addition by SPR sensor measurement. First, upon establishment of a baseline by PBS buffer, undiluted protein solutions flowed through the SPR channels, and immediately a huge amount of proteins, as high as ~660 ng/cm^2, was adsorbed on polymer brushes. Then, replacing the blood plasma and serum solution with PBS buffer enabled to remove most of loosely absorbed proteins, but polymer brushes still retained ~140 and ~145 ng/cm^2 for plasma and serum proteins, respectively. Based on ultralow fouling criteria of (<5 ng/cm^2 adsorbed proteins on the surface), polymer brushes in water are fouling surfaces that cannot effectively resist protein adsorption. Interestingly, when flowing the 1.0 M NaCl through the channels, the absorbed proteins that cannot be removed by regular PBS buffer were almost completely washed out, resulting in much lower protein absorption of ~18 and ~0.23 ng/cm^2 for blood plasma and serum, respectively. The enhanced antifouling performance could be attributed to cooperative effects of enhanced surface hydration and electrostatic screening upon introduction of NaCl solution; both effects cause protein release from the surface. Thus, polyVBIPS brushes can be used as salt-responsive materials for protein capture and release applications.

CONCLUSIONS

In this work, we synthesized and characterized zwitterionic, ionic-responsive polyVBIPS brushes via the SI-ATRP method.

PolyVBIPS brushes exhibited "anti-polyelectrolyte effect" salt responsive and switching behaviors between in water and salt solutions. Surface properties and salt-responsive behaviors were systemically investigated by XPS, AFM, SPR, contact angle, and macroscopic friction test, and the ion-responsive behaviors are attributed to the conformational change of polymer chains (i.e., swelling-to-collapse transition) depending on film thicknesses, salt concentrations, and counterion types. Specifically, poly-VBIPS brushes exhibited reversible surface wettability switching between in water and saturated NaCl solution. Salt solutions led to the lower contact angles on polyVBIPS brushes than water solution, indicating the higher surface hydration of polyVBIPS brushes in salt solutions. By changing salt concentrations and counterion types, polyVBIPS brushes can be continuously tuned from ultrahigh friction ($\mu \sim 10^{0}$) to moderate lubrication ($\mu \sim 10^{-2}$) and further to superior lubrication ($\mu \sim 10^{-3}$). Similarly, polymer brushes also exhibited salt-induced surface resistance to nonspecific protein adsorption from undiluted human blood serum and plasma at a ultralow fouling level (<0.3 ng/cm^2). These salt-responsive surface switching behaviors between surface friction and lubrication and between protein adsorption and resistance are likely attributed to cooperative effects of enhanced surface hydration and electrostatic screening. This work presented new zwitterionic, ionic-responsive polymer brushes that can be used as smart surfaces for the applications switching between protein capture/release and surface friction/lubrication.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b02119.

Figures S1 and S2 (PDF)

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Notes

The authors declare no competing financial interest.

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