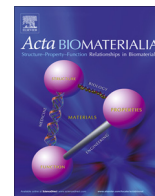




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Salt-responsive polyzwitterionic materials for surface regeneration between switchable fouling and antifouling properties [☆]

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ABSTRACT

Development of smart regenerative surface is a highly challenging but important task for many scientific and industrial applications. Specifically, very limited research efforts were made for surface regeneration between bio-adhesion and antifouling properties, because bioadhesion and antifouling are the two highly desirable but completely opposite properties of materials. Herein, we developed salt-responsive polymer brushes of poly(3-(1-(4-vinylbenzyl)-1H-imidazol-3-ium-3-yl) propane-1-sulfonate) (polyVBIPS), which can be switched reversibly and repeatedly between protein capture/release and surface wettability in a controllable manner. PolyVBIPS brush has demonstrated its switching ability to resist both protein adsorption from 100% blood plasma/serum and bacterial attachment in multiple cycles. PolyVBIPS brush also exhibits reversible surface wettability from $\sim 40^\circ$ to 25° between in PBS and in 1 M NaCl solutions in multiple cycles. Overall, the salt-responsive behaviors of polyVBIPS brushes can be interpreted by the “anti-polyelectrolyte effect”, i.e. polyVBIPS brushes adopt a collapsed chain conformation at low ionic strengths to achieve surface adhesive, but an extended chain conformation at high ionic strength to realize antifouling properties. We expect that polyVBIPS will provide a simple, robust, and promising system for the fabrication of smart surfaces with biocompatible, reliable, and regenerative properties.

Statement of Significance

Unlike many materials with “one-time switching” capability for surface regeneration, we developed a new regenerative surface of zwitterionic polymer brush, which exhibits a reversible salt-induced switching property between a biomolecule-adhesive state and a biomolecule repellent state in complex media for multiple cycles. PolyVBIPS is easily synthesized and can be straightforward coated on the surface, which provides a simple, robust, and promising system for the fabrication of smart surfaces with biocompatible, reliable, regenerative properties.

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1. Introduction

Real-time control of biomolecule–surface interactions at polymer interface is of great interest in many scientific and industrial

applications, such as biosensor, drug delivery, and regenerative medicine [1–5]. Biomolecule adhesion and prevention at interfaces are two highly desirable but completely opposite properties of materials. Some applications (e.g. tissue engineering scaffolds) require the materials to have strong bio-adhesion properties for promoting protein adsorption and cell attachment/growth/proliferation [6–10], while other applications (e.g. medical implants) need the materials to have antifouling properties against biomolecule adhesion [11–18]. Conventional wisdom prevents these two distinct properties from co-existing within a single material. Thus,

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it is highly desirable but challenging to develop a single material that can switch reversibly and easily between bio-adhesion and antifouling properties, so that the surface can be regenerated back-and-forth between two distinct states.

Many stimuli-responsive materials exhibit a surface regeneration function by dynamically controlling their interfacial properties in response to changes of light, temperature, and pH [19–24]. However, very limited research efforts were made for surface regeneration between bio-adhesion and antifouling properties. There are some successes, such as temperature-responsive poly(*N*-isopropylacrylamide) (pNIPAM) and pH-dependent tertiary amine incorporated-carboxylate materials switching between bioadhesion and antifouling properties [25–27]. However, these “bioadhesion-antifouling” regenerative surfaces usually possess “one-time-switching” capability for surface regeneration. A few could achieve multiple surface regenerations over several regeneration cycles. These regenerative surfaces were often tested with single protein solutions. It is far more challenging to develop “bio adhesion-antifouling” regenerative surfaces, which can function well in complex media such as undiluted blood serum and plasma containing hundreds of proteins. Moreover, bioadhesion-antifouling surfaces usually do not work well to retain their same/similar nonfouling capacity after multiple cycles of protein loadings as the original surface, because the adsorbed proteins in previous cycles cannot be completely or largely removed from the surfaces. Consequently, protein accumulation on the surfaces would cause loss of surface regeneration. Zwitterionic polymers have been well demonstrated as excellent antifouling materials to resist protein/cell/bacterial attachment due to the strong surface hydration layer via electrostatic interaction or hydrogen bonding [28]. Many polyzwitterions, such as carboxy betaines, phosphobetaines, and sulfobetaines, are acrylamide-based or acrylate-based materials that often contain ester groups, which are potentially unstable upon hydrolysis.

Herein, we overcome these challenges to develop salt-responsive polymer brushes of poly(3-(1-(4-vinylbenzyl)-1H-imidazol-3-ium-3-yl) propane-1-sulfonate) (polyVBIPS) capable of switching reversibly and repeatedly between two conformational states to achieve capture and release of proteins from undiluted blood plasma and serum and bacteria in a controllable manner. The zwitterionic nature of polyVBIPS shows anti-polyelectrolyte behavior, i.e. polyVBIPS brushes adopt a collapsed chain conformation at low ionic strengths to achieve surface adhesive properties, but an extended chain conformation at high ionic strength to realize antifouling properties, respectively. The presence of hydrophobic imidazole group not only prevents polyVBIPS from hydrolysis, but also provides unique solubility characteristics where polyVBIPS only swells in water, but soluble in brine solution. Combining these unique characteristics of polyVBIPS, we present proof-of-concept experiments to demonstrate the use of this smart material in capture and release of proteins and bacteria in a multiple, reversible manner.

2. Materials and methods

2.1. Materials

Sodium chloride (GR), diethyl ether (GR), acetonitrile (GR), sodium sulfate (anhydrous, GR) were purchased from EMD chemicals. Sodium hydroxide (>97.0%), sodium bicarbonate (>99.7%), sodium bromide (>99%), potassium chloride (>99.0%), copper (I) bromide (CuBr, 99.999%), acetone (99.9%), ethanol (absolute 200), phosphate buffered saline (PBS, 0.01 M, pH = 7.4, 0.138 M NaCl, 0.0027 M KCl), 4-vinylbenzyl chloride (90%), 1,3-propanesultone (98%), imidazole (99%), and hydroquinone (99%) were bought from Sigma-Aldrich Inc. (Milwaukee, WI). Tris [2-(dimethylamino)

ethyl]amine (Me6TREN), 2,2,2-trifluoroethanol, silica gel (0.036–0.071 mesh) were bought from Alfa Aesar Inc. (Ward Hill, MA). Pooled human blood plasma and serum were bought from BioChemed Service (Winchester, VA). Water was purified by a Millipore water purification system with a resistivity of 18.2 MΩ cm. The ATRP initiator ω-mercaptopundecyl bromoisobutyrate were synthesized by the reaction of bromoisobutryl bromide and 11-mercaptop-1-undecanol as previously reported [29]. The deuterated solvent D₂O for NMR was purchased from Cambridge Isotope Laboratories.

2.2. Synthesis of VBIPS monomer

VBIPS monomer was synthesized using the same two-step reaction as reported in previous works (Scheme 1a) [30,31]. Sodium bicarbonate (10.5 g, 0.125 mol) was first dissolved in a mixture of water/acetone (v/v = 1:1, 200 mL), then added to a three-neck round-bottomed flask equipped with a reflux condenser and a thermometer. Imidazole (27.22 g, 0.398 mol) and a small trace of hydroquinone were added to the flask under a gentle stir for ~30 min. 4-Vinylbenzyl chloride (15.22 g, 0.1 mol) was added to the flask by drops. The reaction mixture was heated to 50 °C and kept stirring for 20 h. Once the reaction was completed, the solution was cooled down to room temperature and filtered to remove any salt. After solvent evaporation, the remaining mixture was diluted with diethyl ether (500 mL) and washed with deionized water (50 mL) six times to remove unreacted imidazole. The product was back-extracted by an aqueous hydrochloric acid solution (2 M, 100 mL). An opaque heterogeneous solution was obtained when sodium hydroxide solution (4 M, 200 mL) was added. The product was recovered with ether (50 mL) three times, followed by drying over anhydrous magnesium sulfate. A transparent oily liquid sample was obtained when ether was evaporated. The transparent oily liquid (8 g, 0.043 mol) was dissolved in dry acetonitrile (180 mL), followed by the addition of hydroquinone (0.02 g, 0.182 mmol) and 1,3-propanesultone (5.312 g, 43.47 mmol). The reaction mixture was kept stirring at 50 °C for 48 h. A white precipitate from the ring-opening reaction was recovered by filtration. The precipitate was then dried in vacuum at 40 °C and stored at 2–4 °C. ¹H NMR confirms the successful synthesis of VBIPS monomer (Fig. 1). ¹H NMR (300 MHz, D₂O): (ppm), 6.07–6.25 (m, 2H), 5.66–5.72(ddd, 1H), 3.53–3.65(m, 6H), 3.38–3.42(m, 2H) and 8.76 (s, 1H) N-CH = N; 7.28–7.48 (m, 6H) CH_{aromatic} and CH_{imidazole}; 6.66–6.75 (dd, 1H) CH_{olefine}; 5.82 and 5.25 (d, 2H) CH_{cis} and _{trans}; 5.28 (s, 2H) CH_{2benzyl}; 4.26 (t, 2H) –N-CH₂; 2.82 (t, 2 H) S-CH₂; 2.2–2.3 (m, 2 H) C-CH₂-C.

2.3. Surface initiated atom transfer radical polymerization (SI-ATRP) of polyVBIPS brushes

The polyVBIPS brush was synthesized by the same SI-ATRP method as reported previously [13,14]. Briefly, SPR chip was prepared by coating a titanium adhesion layer (2 nm) and a gold layer (48 nm) on a microscope glass slide using an electron beam evaporator. The SPR chip was washed by ethanol and water, dried in air, and cleaned by 20 min UV/ozone. First, a self-assembled monolayer (SAM) of initiators was immobilized on the SPR chip by simply soaking the clean SPR chip into 1 mM ethanol solution of ω-mercaptopundecyl bromoisobutyrate (initiator) at room temperature overnight. The chip was then washed with ethanol and dried in air before SI-ATRP. Scheme 1b shows a general SI-ATRP process for grafting polyVBIPS onto an initiator-coated gold surface. First, VBIPS monomers (1.22 g), ligand Me6TREN (26μL), and solvent mixture of trifluoroethanol (5 mL), and water (5 mL) were sequentially added to a reaction tube, followed by oxygen removal by inputting nitrogen for 30 min. Then, the SPR chip coated with

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