



Sulfobetaine-based polymer brushes in marine environment: Is there an effect of the polymerizable group on the antifouling performance?



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ABSTRACT

Three different zwitterionic polymer brush coatings for marine biofouling control were prepared by surface-initiated atom transfer radical polymerization (ATRP) of sulfobetaine-based monomers including methacrylamide (SBMAm), vinylbenzene (SBVB) and vinylimidazolium (SBVI). None of these brush systems have been assessed regarding marine antifouling performance. Antifouling tests performed indicate that surfaces featuring these three brush systems substantially reduce the adhesion of the marine microalgae, *Amphora coffeaeformis*, and the settlement of cyprid larvae of the barnacle, *Amphibalanus amphitrite*, in a similar way, displaying comparable performance. Thus, it appears that the chemical structure of the polymerizable group has no substantial influence on marine antifouling performance.

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1. Introduction

Polyzwitterionic brushes such as phosphobetaines, carboxybetaines and sulfobetaines have been reported as promising candidates for environmentally benign, ultralow fouling, marine coatings [1–8]. Considered as non-toxic and non-leaching coatings, polyzwitterionic sulfobetaine-based brushes have been explored to prevent (a) initial nonspecific protein adsorption [4,9–11] as well as (b) adhesion of various types of cells and marine organisms

[1,12–14]. The dipolar nature of the sulfobetaine repeating units in combination with the polymeric brush structure, is considered to be responsible for the formation of a tightly bound and structured water layer, to which the suppression of non-specific protein adsorption is attributed [15].

Atom transfer radical polymerization (ATRP) is a robust and versatile technique, which allows the uniform growth of polymeric chains and fabrication of complex polymeric architectures [16–19]. ATRP can be initiated in solution or from a surface featuring surface-anchored initiators [20]. Owing to the high control over polymerization and the “living” character of the reaction, surface initiated ATRP (SI-ATRP) is frequently used for the preparation of various types of polymeric brushes [16]. Accessibility of the commercial sulfobetaine methacrylate (SBMA) monomer, and facile polymerization of methacrylates by ATRP [18] favoured research on SBMA brushes [21–24]. However, sulfobetaine monomers containing other polymerizable functional groups, such as methacrylamides or styrenes, have attracted substantially lower interest. The SI-ATRP of sulfobetaine methacrylamide, SBMAm, have been employed to prepare polymer brushes from gold [25], silicon [26] and polymer surfaces [27]. Liu et al. reported the SI-ATRP of sulfobetaine vinylbenzene (SBVB), initiated from

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cellulose membranes [28] and polyurethane substrates [29]. SI-ATRP of sulfobetaine vinylimidazolium (SBVI), was carried out to prepare coated chips for Surface Plasmon Resonance (SPR) [30]. Data on the growth of poly(sulfobetaine vinylbenzene) (PSBVB) and poly(sulfobetaine vinylimidazolium) (PSBVI) brushes (thickness versus polymerization time), optimized process conditions and fabrication of block copolymers have not been reported.

Surfaces grafted with PSBMAM, PSBVB and PSBVI have been reported to present improved resistance to nonspecific protein adsorption and platelet adhesion in physiological medium [25,29,31,32]. In view of the antifouling properties of PSBMA brush systems in biomedical applications, which correlates well with resistance against settlement of marine organisms [1], it is of interest to explore other brushes featuring sulfobetaine groups, but different structures for the polymerizable group. This would allow one to better assess brush chemical structure–antifouling correlations.

The distinctive wetting characteristics of PSBMA brushes have been associated with the effect of the extremely high dipole moment of their zwitterionic groups and with the brush conformation [21,22]. Although the sulfonate and quaternary ammonium groups in SBMAM, SBVB and SBVI molecules, which are also separated by the three methylene units, have a similar structure (and thus a similar dipole moment), the polymerizable units linking the zwitterionic groups into a main chain show distinct differences (see Fig. 1). Thus the question arises, whether indeed marine antifouling performance would show variations with the chemical structure. By systematically varying the structure of the polymerizable unit that connects the zwitterionic group with the backbone and preparing and characterizing the resulting brush systems we presume to obtain insights into possible variations of marine antifouling performance of the corresponding brushes. We also anticipate an improvement of hydrolytic stability when moving from methacrylic to styrene and imidazole based linkers [33,34], which would be advantageous for marine antifouling applications. Additionally, enhanced hydration of polyzwitterionic brushes may compromise the stability of polymer brush system [26].

In this work, controlled surface initiated polymerization leading to polymer brush fabrication is discussed in details for three different sulfobetaine-based monomers with three different polymerizable groups. Methacrylamide, vinylbenzene and vinylimidazolium derivatives were polymerized from a surface grafted ATRP initiator to prepare uniform polymer brushes. The fabricated polymeric structures were subsequently compared as antifouling films for marine application in assays against adhesion of microalgae and barnacle cyprid settlement.

2. Experimental

2.1. Materials

Copper(I) bromide (Cu(I)Br, 99.999%), 2,2'-bipyridyl (BiPy), pentamethyldiethylenetriamine (PMDETA) (99%), 1-vinylimidazole (>99%), 1,3-propanesultone (98%), and [3-(methacryloylamino)propyl]dimethyl-(3-sulfopropyl)ammonium hydroxide inner salt (SBMAM) (96%) were purchased from Sigma–Aldrich and were used without further purification. *N,N*-dimethylvinylbenzylamine was purchased from ACROS and sodium bromide from AR, Merck. (*p*-Chloromethyl)phenyl-trichlorosilane (CMPS, 95%), was purchased from Gelest, stored inside a nitrogen filled glove box and used as received. All other chemicals were reagent grade and were used without further purification. Deionized (DI) water (18 M Ω cm) and ultrapure nitrogen were used throughout. Silicon wafers with the thickness of 0.56 mm were purchased from Lotech Scientific Supply Pte. Ltd. (Singapore) and cut into 2 cm \times 2 cm pieces.

2.2. Measurements

The thicknesses of SAMs and polymeric films were measured with a Variable Angle Spectroscopic Ellipsometer (WVASE32) (J.A. Woollam Co., Inc.). Polymeric film samples on silicon were scanned with a light source wavelength ranging from 400 to 800 nm at 60, 65 and 70° angle of incidence, respectively. Experimental data was fitted against a three layer model encompassing Si/SiO₂/Cauchy layers, using the VASE software with atmosphere compensation. Refractive index (630 nm) values of 1.46, 1.53 and 1.50 were calculated for PSBMAM, PSBVB and PSBVI, respectively, assuming isotropic and homogeneous brush structures. Four different points on each sample were measured, and the average values were reported in this paper. Static water contact angle (CA) measurements were performed in a Ramé–Hart CA goniometer. The sessile drop method was used with a 3 μ L droplet and at least 4 different drops were measured for each surface. Infrared spectra were acquired using an FT-IR spectrometer (Bruker, Vertex 80v) and a liquid-nitrogen-cooled MCT detector operating at 4 cm⁻¹ spectral resolution across the 700–4000 cm⁻¹ range. The spectrometer was purged with nitrogen before applying vacuum. Silicon substrates were measured in the transmission mode and at least 2000 scans were recorded for each sample. X-ray photoelectron spectroscopy (XPS) was performed with a VG ESCALAB 250i-XL spectrometer using an Al K α X-ray source (1486.6 eV photons). Emitted photoelectrons were detected by a multichannel detector at a takeoff angle of 90° relative to the surface. XPS data processing, including peak assignment and peak fitting (fitting algorithm Simplex), was done using the software package Thermo Avantage, version 4.12 (Thermo Fisher Scientific). A NanoWizard II instrument (JPK Instruments AG, Berlin, Germany) equipped with a NanoWizard head and controller was used in tapping mode for dry AFM measurements. For AFM measurements silicon probes with aluminium reflection coating (Budgetsensors, Tap300Al-G) were used. The nominal spring constant of the cantilever was 40 N/m.

2.3. ATRP-initiator layer fabrication

Silicon wafers were exposed to oxygen plasma for 5 min at 250 W using a microwave plasma chamber (Triple P, Duratek) in order to activate the surface. Subsequently, CMPS ATRP-initiator was deposited from gas phase and exposed to 120 °C for 3 min [35]. The organo-modified silicon wafers were stored in a nitrogen filled glove box.

2.4. Monomer synthesis

Following the nomenclature frequently used for sulfobetaine monomers, *N,N*-dimethyl-*N*-(*p*-vinylbenzyl)-*N*-(3-sulfopropyl) ammonium and 4-(3-vinyl-1-imidazolium)-1-propanesulfonate are referred in this work as sulfobetaine vinylbenzene (SBVB) and sulfobetaine vinylimidazolium (SBVI), respectively. SBVB and SBVI monomers were synthesized via quaternization of the tertiary amine precursor with sultone (Fig. 1). The monomer SBVB was synthesized using a modification of the earlier reported protocols [36,28]. In a 250 mL flask, 2.44 g (20 mmol) of 1,3-propanesultone dissolved in 100 mL of dry acetonitrile was added to 3.22 g (20 mmol) of *N,N*-dimethylvinylbenzylamine in acetonitrile through the addition funnel drop wise under argon at room temperature. The reaction mixture was then heated at 50 °C for 48 h. The white precipitate obtained was washed with acetonitrile, and vacuum dried to yield a crude product in 81.2% yield. It was recrystallized from ethanol to yield fine white needles which were highly hygroscopic [28]. ¹H NMR (400 MHz, NaCl/D₂O, δ , ppm): 7.5–7.6 (m, 4H, aromatic CH), 6.7–6.8 (dd, 1H, olefin CH), 5.95 (d, 2H, *cis* and *trans* CH), 4.4 (s, 2H, benzyl CH₂), 3.43 (t, 2H,

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