Enhanced Stability of Low Fouling Zwitterionic Polymer Brushes in Seawater with Diblock Architecture

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Ⓢ Supporting Information

ABSTRACT: The successful implementation of zwitterionic polymeric brushes as antifouling materials for marine applications is conditioned by the stability of the polymer chain and the brush-anchoring segment in seawater. Here we demonstrate that robust, antifouling, hydrophilic polysulfobetaine-based brushes with diblock architecture can be fabricated by atom-transfer radical polymerization (ATRP) using initiator-modified surfaces. Sequential living-type polymerization of hydrophobic styrene or methyl methacrylate and commercially available hydrophilic sulfobetaine methacrylamide (SBMAm) monomer is employed. Stability enhancement is accomplished by protecting the siloxane anchoring bond of brushes on the substrate, grafted from silicon oxide surfaces. The degradation of unprotected PSBMAm brushes is clearly evident after a 3 month immersion challenge in sterilized artificial seawater. Ellipsometry and atomic force microscopy (AFM) measurements are used to follow changes in coating thickness and surface morphology. Comparative stability results indicate that surface-tethered poly(methyl methacrylate) and polystyrene hydrophobic blocks substantially improve the stability of zwitterionic brushes in an artificial marine environment. In addition, differences between the hydration of zwitterionic brushes in fresh and salt water are discussed to provide a better understanding of hydration and degradation processes with the benefit of improved design of polyzwitterionic coatings.
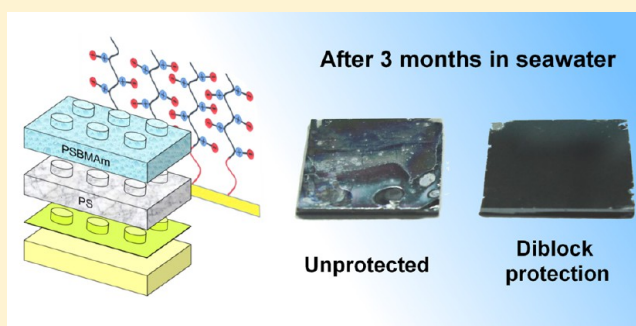
INTRODUCTION

Hydrophilic polymeric brushes, because of their unique properties, in particular, owing to their high degree of solvation in water, lend themselves well as environmentally benign antifouling coatings.[1,2] Recently, zwitterionic brushes have been reported to be promising candidates for ultralow marine biofouling surfaces.[1,3−7] Owing to their strong electrostatically induced hydration, zwitterionic molecules are considered to form a tightly bound and structured water layer in the vicinity of polymer chains, preventing initial nonspecific protein adsorption as well as the adhesion of various types of cells.[8]

Antifouling properties of hydrophilic zwitterionic polymers have been initially reported for biomedical applications and later explored as materials resisting marine fouling.[1,9−11] A popular example from this class of materials is polysulfobetaine-based polymer brushes usually prepared by the surface-initiated polymerizations of sulfobetaine methacrylate (SBMA)[4−6,10−22] or sulfobetaine methacrylamide (SBMAm)[23−25] monomers. Because of the commercial availability of these two monomers and, in particular, owing to well-established polymerization protocols of SBMA, several authors reported on nonfouling properties of surfaces grafted with polySBMA (PSBMA) or poly-SBMAm (PSBMAm). Substrates such as silicon,[10] glass,[6,9,11]

and gold[23,26] and different polymers such as polypropylene,[15] poly(ethylene terephthalate),[16] polystyrene,[12] and polyurethane[10,17] were investigated as supports. In all reported cases, surfaces covered with densely packed brushes were described.

Surface-initiated atom-transfer radical polymerization (SI-ATRP) is a robust and versatile grafting procedure with controlled character.[27,28] The "living" characteristics of ATRP allow one to prepare block-type polymer brushes via sequential polymerization.[29] As such, SI-ATRP became a routinely employed approach to the synthesis of polymer brushes from silicon oxide substrates modified with organosilane-terminated polymerization initiators.[28] PSBMA polymer brushes prepared by SI-ATRP from glass substrates have been reported to show antifouling activity against two major marine macrofoulers including marine algae[1] and barnacle cyprids.[9,11] This promising performance is, however, limited by the long-term stability of the brush-coated surface in seawater.

Indeed, the marine environment is challenging in terms of surface stability and corrosion. For instance, hydrophilic

poly(ethylene glycol) (PEG) and PEG derivatives, probably the most thoroughly studied nonfouling coating materials, which also inhibit the settlement of marine algae,[30−32] have limited use in marine applications as a result of the rapid oxidation of their backbone in the presence of oxygen and transition ion metals present in seawater.[33,34] Also in cases where polymeric brushes display sufficient hydrolytic stability in their main chain, an additional weak point may be associated with the anchoring element of the brush. This problem is particularly visible for hydrophilic brushes grown from silicon oxide substrates (silicon, glass, and quartz) and anchored to the surface by siloxane bonds (Si−O−Si).[35,36] In a hydrophilic environment, the hydrolytic stability of the siloxane bond is compromised because the water is drawn directly to the interface. In the presence of water, a hydrolysis equilibrium between siloxane and silanol (Si−OH) groups is established.[37−39] Although the equilibrium favors the formation of the siloxane groups, the activation energy for this process can be drastically

lowered at acidic and alkaline pH values.[38,40−43] Also, the generation of strong osmotic pressure at the glass/silane interface is presumed to promote the hydrolytic cleavage of siloxane as a consequence of the mechanochemical effect of tensile stress applied to the siloxane bond.[36,38] Recently, Paripovic et al. reported a strategy to enhance the stability of hydrophilic brushes in aqueous media grown from SiO$_x$ substrates.[35] These authors proposed the protection of anchoring points by introducing a short hydrophobic block between the siloxane layer and the hydrophilic polymer brush. The hydrophobic nature of the protecting block was supposed to prevent cleavage of the anchoring segment by limiting water penetration into the brush.

Kuang and Messersmith reported the good cell antifouling resistance of PSBMA brushes incubated in cell culture medium for up to 4 months.[10] However, stability data for grafted PSBMA from silicon oxide substrates have not been provided. To our knowledge, the long-term stability in seawater of polysulfobetaine-based polymeric brushes has not been systematically addressed.
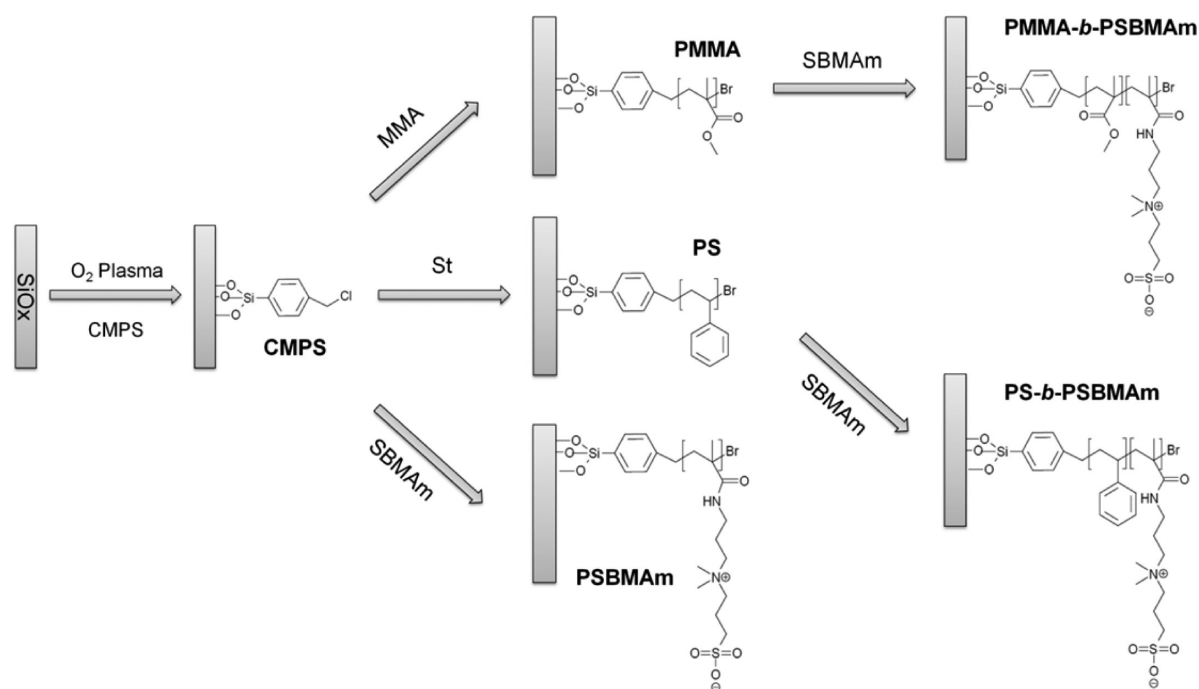
In this Article, we investigate diblock copolymer-type brushes composed of bottom hydrophobic segments and a polysulfobetaine top (bottom refers to the substrate, and top refers to the free interface), with the aim of studying a possible stability enhancement in seawater. For this purpose, two hydrophobic polymer blocks, PMMA (polymetyl methacrylate) and PS (polystyrene), placed between the anchoring layer including the siloxane bond and PSBMAm zwitterionic brush, are evaluated. For our study, SBMAm was chosen instead of SBMA because the amide groups, linking zwitterionic pendant group to the main chain, are more resistant to hydrolysis than are ester groups.[44,45] The effect of zwitterionic chain hydration in water and salt water is also discussed to provide a better understanding of the degradation mechanism.

Table 1. Reaction Systems Used and Brush Dry Thickness of Samples Covered with Polymer Brushes Prepared for Long-Term Stability Testing

	reaction system[a]			thickness (nm)[b]	
sample	catalyst	solvent	T (°C)	first block	diblock copolymer
PS	CuBr; PMDETA	anisole	90	40	
PMMA	CuBr; Bipy	water/MeOH (1:4)	28	31	
PSBMAm	CuBr; Bipy	water/MeOH (4:1)	60	11	
PS-b-PSBMAm	CuBr; Bipy	water/MeOH (4:1)	60	19	28
PMMA-b-PSBMAm	CuBr; Bipy	water/MeOH (4:1)	60	20	28

[a]Reaction time of 24 h. [b]Determined by ellipsometry.

Scheme 1. Synthesis of PS-b-PSBMAm and PMMA-b-PSBMAm Copolymer Brushes on SiO$_x$ Surfaces via Surface-Initiated ATRP

Figure 2. Evolution of polymer graft thickness on a silicon substrate: step I, PS-graft polymer; step II, PS-*b*-PSBMAm graft copolymer. The error bars correspond to standard deviations of at least three independent experiments.
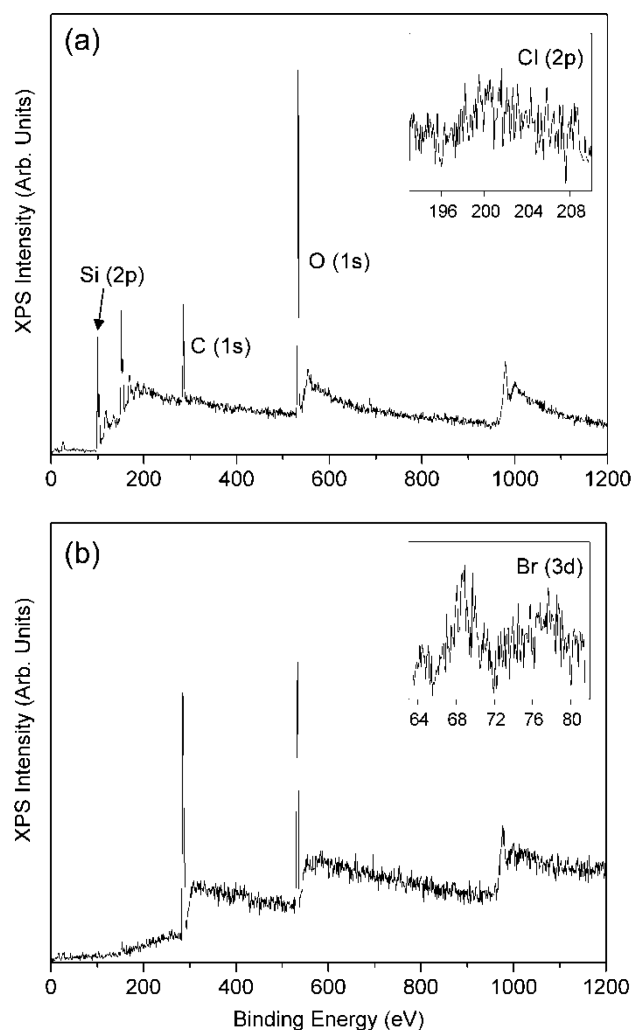
Figure 1. XPS survey spectra for (a) the CMPS ATRP initiator layer and (b) a 20-nm-thick PMMA layer grown from the initiator surface. (Insets) High-resolution spectra of the regions associated with peaks from chlorine and bromine.

■ EXPERIMENTAL SECTION

Materials. Copper(I) bromide (99.999%), 2,2′-bipyridyl (Bipy), pentamethyldietylenetriamine (PMDETA, 99%), and [3-(methacryloylamino)propyl]dimethyl-(3-sulfopropyl)ammonium hydroxide inner salt (SBMAm, 96%) were purchased from Sigma-Aldrich and were used without further purification. (*p*-Chloromethyl)phenyl-trichlorosilane (CMPS, 95%) was purchased from Gelest, stored inside a nitrogen-filled glovebox, and used as received. Styrene (St, ≥99%) and methyl methacrylate (MMA, ≥99%) obtained from Sigma-Aldrich were purified by passing through a short basic alumina column, before use, to remove the inhibitor. All other chemicals were reagent grade and were used without further purification. Deionized water (18 MΩ cm) and ultrapure nitrogen were used throughout. Silicon wafers with a thickness of 0.56 mm were purchased from Latech Scientific Supply Pte. Ltd. (Singapore) and cut into 2 cm × 2 cm pieces.

ATRP-Initiator Layer Fabrication. Silicon wafers were exposed to oxygen plasma for 5 min at 250 W in order to activate the surface with a large number of hydroxyl groups. Subsequently, CMPS ATRP initiator was deposited and exposed to 120 °C for 3 min.[46] The organo-modified silicon wafers were stored in a nitrogen-filled glovebox.

Formation of Polymer and Block Copolymer Brushes. For the synthesis of polystyrene brushes, 5 mL of styrene (45 mmol) and 5 mL of anisole were mixed and purged with nitrogen for at least 30 min. Subsequently, CuBr (128.9 mg, 0.9 mmol) was added to an
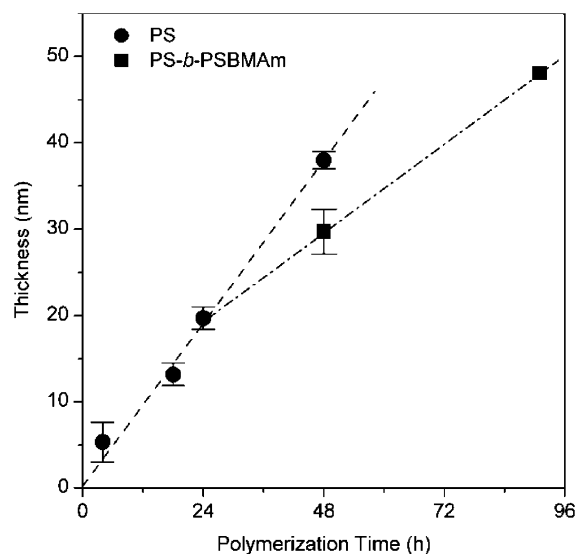
oven dried Schlenk flask and deoxygenated by four consecutive vacuum nitrogen refill cycles. The degassed solution containing the monomer was transferred by cannula to a Schlenk flask when immersed in liquid nitrogen and was further degassed by three freeze−pump−thaw cycles. The ligand, PMDETA (207.2 μL, 1.0 mmol), was then added and the resulting mixture was stirred. After homogenization, the reaction mixture was transferred by cannula to a customized reactor containing ATRP initiator-modified silicon substrates, which were placed in the reactor inside a nitrogen-filled glovebox. The reactor was placed in an oil bath at 90 °C, and the reaction was allowed to proceed for the specific reaction time. Subsequently monomer solution was withdrawn from the reactor without exposing the substrate to the oxygen atmosphere. Substrates were taken out of the reactor and repeatedly washed with *N*-methylpyrrolidone, dichloromethane, and toluene and dried under a stream of argon.

Following a similar procedure, SI-ATRP of MMA (5 mL, 47 mmol) was carried out at an [MMA]/[CuBr]/[Bipy] molar feed ratio of 60:1:2 in a 1:4 water/methanol mixture at 28 °C with 50% v/v monomer concentration in solvent. A halogen exchange procedure, using a CuBr catalyst, was selected to improve the initiation efficiency of MMA ATRP from the benzyl chloride-grafted initiator.[47] For the SI-ATRP of SBMAm (1 g, 3.4 mmol), the molar feed ratio [SBMAm]/[CuBr]/[Bipy] was 50:1:2 in a 4:1 water/methanol mixture at 60 °C with 15% w/v monomer concentration in solvent. For both cases, substrates were repeatedly washed with warm water and methanol and finally rinsed with water and dried under a stream of argon.

Block copolymers of PSBMAm were prepared by SI-ATRP using silicon substrates modified with a PS or PMMA macroinitiator. A molar feed ratio of [SBMAm]/[CuBr]/[Bipy] 50:1:2 was used, and the reaction was carried out in a 4:1 water/methanol mixture at 60 °C. After being cleaned with warm water and methanol, substrates were stored in a drybox.

Seawater Long-Term Stability Experiments. Artificial seawater (ASW) was prepared by dissolving sea salts (Sigma-Aldrich) in deionized water (38.5 g/L) and filtering with a 0.22 μm filter following standard sterilization practices for microbiological experiments. Polymer-brush-modified substrates were soaked in ethanol under UV light for 15 min and washed with filtered ASW before being incubated individually in incubator flasks under sterile conditions in filtered ASW at 37 °C for up to 14 weeks. For a defined experimental time period, the substrates were removed from the medium, washed with deionized water overnight, and dried in a stream of nitrogen. No sign of microbial growth was observed during the experiment (14 weeks).
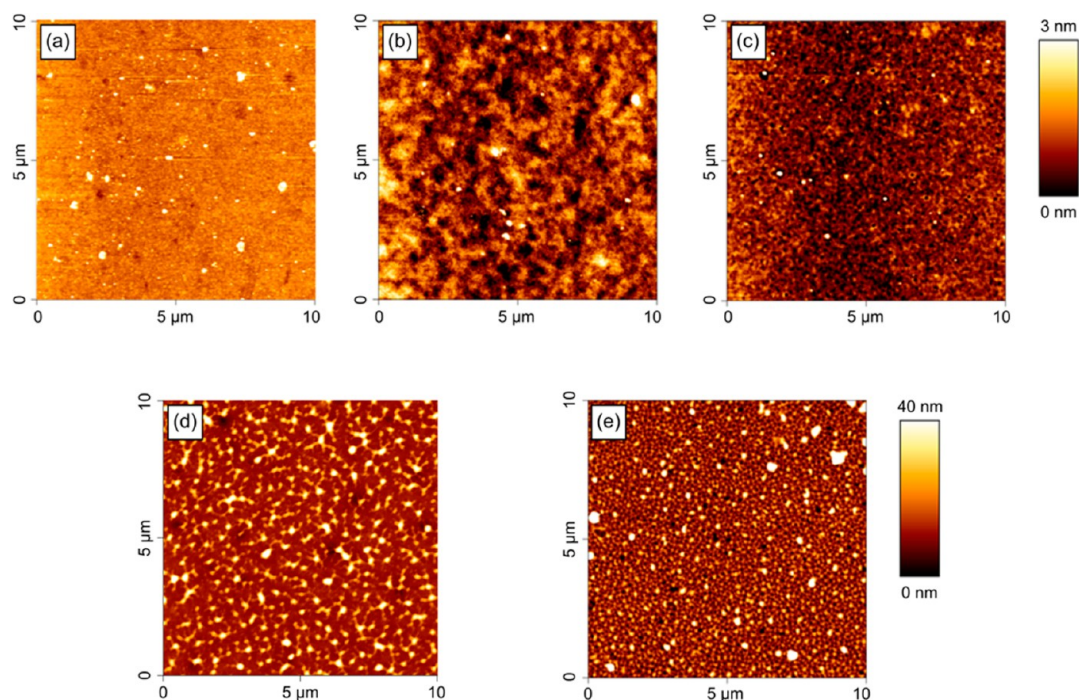
Figure 3. Tapping-mode AFM images in air of (a) PS (Ra = 1.1 nm), (b) PMMA (Ra = 0.5 nm), and (c) PSBMAm (Ra = 0.3 nm) polymer brushes and (d) PMMA-b-PSBMAm (Ra = 5.6 nm) and (e) PS-b-PSBMAm (Ra = 4.5 nm) block copolymer brushes.

Characterization. The thicknesses of SAMs and polymeric films were measured with a variable-angle spectroscopic ellipsometer (WVASE32) (J.A. Woollam Co., Inc.). Each sample was scanned with a light source wavelength ranging from 400 to 800 nm at 60, 65, and 70° angles of incidence, respectively. Experimental data was fitted against a three-layer model: Si/SiO$_2$/Cauchy layer using VASE software with atmosphere compensation. More than four different points on each sample were measured, and the average values are reported in this Article. Infrared spectra were acquired using an FT-IR spectrometer (Bruker, Vertex 80v) and a liquid-nitrogen-cooled MCT detector operating at a 4 cm^{-1} spectral resolution across the 700–4000 cm^{-1} range. The spectrometer was purged with nitrogen before vacuum was applied. Silicon substrates were measured in transmission mode, and at least 2000 scans were recorded for each sample. The X-ray photoelectron spectroscopy (XPS) study was performed with a VGScientific ESCALAB 250 spectrometer (U.K.) with a monochromatized Al Kr X-ray source (1486.6 eV). Emitted photoelectrons were detected by a multichannel detector at a takeoff angle of 90° relative to the surface. During the measurements, the base pressure was 10^{-9} to 10^{-10} Torr. Survey spectra were obtained at a resolution of 1 eV from a single scan, and high-resolution spectra were acquired at a resolution of 0.05 eV from five scans.

AFM Measurements. 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. QITM mode (quantitative imaging mode) in liquid was used in a SmallCellTM fluid cell with an O-ring seal in the dry state, in DI water, and in 0.7 M sodium chloride solution. For AFM measurements, silicon probes with a gold reflex coating (Budgetsensors, model Multi75GD) were used. The nominal spring constant of the cantilever was 3.0 N/m. For quantitative imaging (QITM), the deflection sensitivities were measured, followed by the determination of the cantilever spring constants, and showed values in the range of 2.07–3.17 N/m for Multi75GD probes.

■ RESULTS AND DISCUSSION

Synthesis. For a comparison of the stability of zwitterionic polymers with different anchoring blocks, five different surfaces covered with polymeric brushes were fabricated (Table 1).
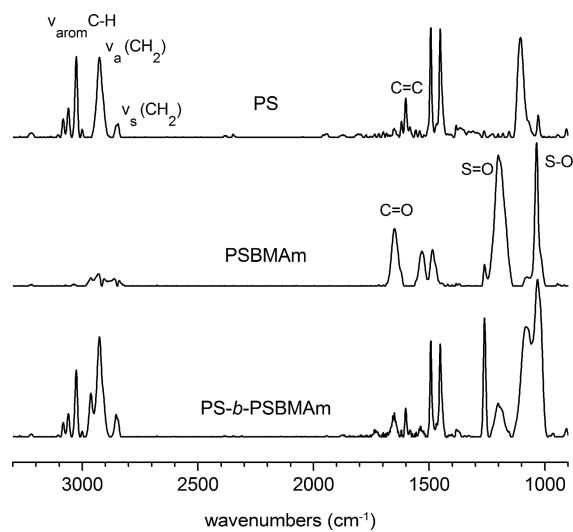

Figure 4. FT-IR spectra of PS, PSBMAm, and PS-b-PSBMAm polymer brushes.

The surface grafting procedure to prepare the block copolymer brushes is shown in Scheme 1. First, an ATRP initiator layer was fabricated by vapor deposition. Subsequently, hydrophobic polymers of either poly(methyl methtacrylate) (PMMA) or polystyrene (PS) were grafted from the initiator-modified surfaces using mild polymerization conditions. SBMAm SI-ATRP was initiated from the PMMA or PS macroinitiator to form the PMMA-b-PSBMAm or PS-b-PSBMAm diblock copolymer, respectively (Scheme 1).

The formation of the CMPS ATRP-initiator layer was characterized by ellipsometry and XPS. The value of the layer thickness was 0.8 ± 0.2 nm. In the XPS spectrum, the characteristic peaks of CMPS were observed at 284.5 (C 1s), 201.0 (Cl 1s), and 99.5 (Si 2s) eV (Figure 1). SI-ATRP of PS and

MMA was carried out in anisole at 90 °C with the PMDETA ligand and in a water/methanol mixture at room temperature with the bipyridyl ligand, respectively. Halogen exchange was used to improve the initiation efficiency of MMA ATRP from benzyl chlorine-grafted initiator in the presence of the copper bromide catalyst.[27,47,48] The zwitterionic homopolymer brush, SBMAm, was grafted directly from CMPS substrates using a water/methanol mixture and the bipyridyl ligand at 60 °C. The same reaction conditions were employed to extend PS and PMMA macroinitiators with zwitterionic blocks.

The formation of the polymer brushes on silicon substrates was confirmed by IR spectroscopy showing the presence of distinctive stretching vibrational peaks for each polymer (i.e., carboxylic (C=O) for PMMA, C=C aromatic for PS, and S=O for PSBMAm (Figure 4)). The dry thickness of the polymer brushes was determined by ellipsometry, and values ranging from 10 to 40 nm were obtained as illustrated in Figure 2. For the PS grafted polymer, the linear relationship between brush thickness and polymerization time demonstrate the "controlled" nature of the polymerization system. SI-ATRP of both monomers, St and MMA, is exhaustively documented in the literature,[29] which facilitates the selection of the optimal reaction conditions to maintain the living characteristics of ATRP without the

addition of free initiator. The synthesis procedure we employed, together with the use of mild reaction conditions, drastically limits the formation of free polymer. As a result, only traces of polymer were present in the solution.

Tapping-mode AFM was used to measure the surface roughness of the polymeric brushes prepared by SI-ATRP (Figure 3a−c). All graft-modified surfaces had a dense, uniform polymer coating with an average roughness value of $Ra = 0.3−1.1$ nm over an area of 10 μm × 10 μm.

XPS scans also proved the presence of grafted polymers on the substrates. As an example, an XPS survey spectrum of PMMA brushes is shown in Figure 1. In addition to the characteristic peaks expected for PMMA, there were peaks at 68.5 and 77.5 eV originating from bromide (Br 3d) (Figure 1, inset). The presence of bromide indicates that halogen exchange took place to form active initiator end groups, which is essential to conducting the brush chain extension. SI-ATRP of SBMAm was initiated from a grafted PMMA or PS macroinitiator, leading to the formation of PMMA-b-PSBMAm and PS-b-PSBMAm diblock copolymer brushes, respectively. The formation of diblock copolymer brushes was further confirmed by ellipsometry, FT-IR, and XPS. As shown in Figure 2, brush chain extension with PSBMAm increased the thickness of polymer grafts with time. PSBMAm blocks with thickness values from 9 to 30 nm were prepared by varying the polymerization time. IR spectra recorded from block copolymers presented the distinctive sulfonate S=O stretching peak of the PSBMAm block as shown in Figure 4 for the PS-b-PSBMAm brush. In agreement, XPS survey spectra of PMMA-b-PSBMAm and PS-b-PSBMAm confirmed the presence of the nitrogen (N 1s) and sulfur (S 2p) atoms (Figure 5). The surface roughness values (Ra) of 28-nm-thick grafted block copolymers were between 4.5 and 5.6 nm over an area of 10 μm × 10 μm as determined from AFM surface morphology scans. A topology inspection of AFM images showed that PS-b-PSBMAm brushes covered the substrate largely by small isolated spherical clusters as compared to relatively larger clusters on PMMA-b-PSBMAm brushes.
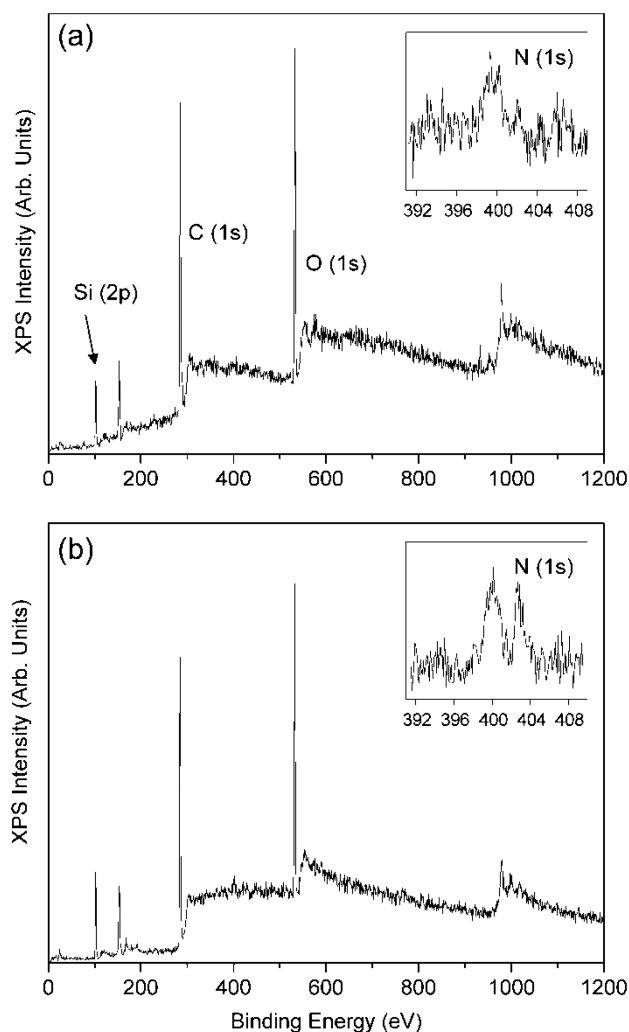

Figure 5. XPS survey spectra of 28-nm-thick grafted block copolymer brushes of (a) PMMA-b-PSBMAm and (b) a PS-b-PSBMAm. (Insets) High-resolution spectra of regions associated with peaks from N 1s.
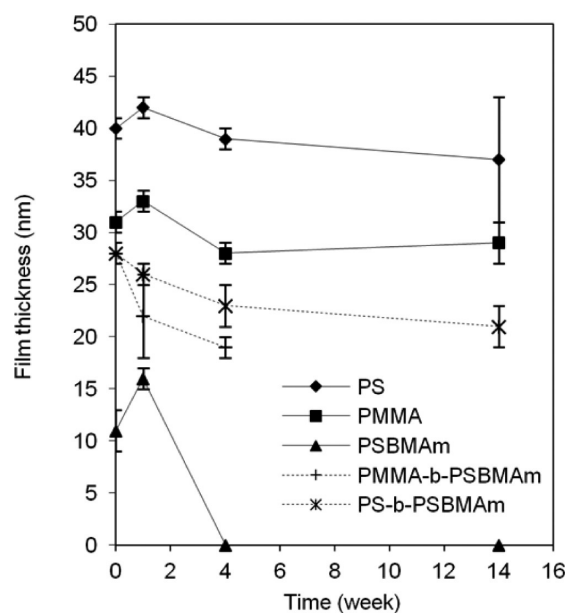

Figure 6. Brush stability test. Change in the grafted polymer thickness on a silicon wafer as a function of incubation time in ASW (pH 8.2 ± 0.1 and 31 PSU).

Brush Stability in a Seawater Environment. Modified surfaces with homoblock and diblock copolymer brushes were subjected to a 3 month seawater immersion challenge in sterilized ASW (pH 8.2 ± 0.1 and 31 PSU). A comparative study of the brush thickness evolution is summarized in Figure 6. Hydrophilic polymer brushes grafted from SiO_x substrates have been reported to show limited stability against degrafting in aqueous media,[35,36] and this is also clearly illustrated in the presented case of zwitterionic homo-PSBMAm polymers. Surfaces covered with PSBMAm brushes showed evident deterioration after 3 months (Figure 7). After 4 weeks,
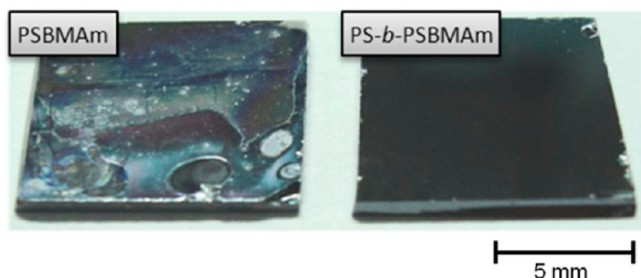

Figure 7. Optical images of modified silicon 10 mm × 10 mm surfaces with grafted PSBMAm and PS-*b*-PSBMAm brushes after 3 months of immersion in artificial seawater at 37 °C.

ellipsometric measurements were in this case unsuccessful as a result of the high levels of noise in the signal. This can be attributed to the surface irregularities created as a consequence of coating degradation on the nanoscale level. AFM topographical measurements (Figure 8a) detected a large increase in

the average surface roughness (*Ra*) from the initial value of 0.3 to 18.7 nm after 4 weeks of immersion. The roughness value was higher than the initial brush thickness of 11 nm, which indicates the complete removal of polymer brushes and the corrosion of the silicon substrate by seawater. The AFM statistical height histogram (Figure 8d) clearly evidenced up to 10-fold increases in surface heterogeneity and roughness between initial and degraded samples. This trend was not observed for the diblock copolymer brushes (Figure 8c) after 4 weeks of immersion, showing almost no differences in surface morphology (in comparison with Figure 3e) and a similar statistical height histogram (Figure 8d) similar to that of the sample before immersion in ASW. The absence of pinholes on the degraded surface may indicate that brush cleavage occurred via random initiation along the entire surface without any local preference.

In contrast, the visual appearance of surfaces covered with PS-*b*-PSBMAm block copolymer brushes did not change after long exposure to ASW. The brush with anchoring points protected with a PS block was shown to be slightly less affected by immersion in ASW than when protected by PMMA. This trend was more evident when attempts to determine the brush thickness of PMMA block copolymer by ellipsometry became unsuccessful for samples immersed for 3 months. Also, this result pointed out the role of the hydrophobicity of the anchoring block to improve the long-term stability of the grafted hydrophilic polymers, which is in agreement with the results presented recently by the Klok group for PMMA-*b*-PMAA block copolymers incubated in a cell culture medium.[26,35] Hydrophobic PS and PMMA brushes used as reference in this study did not significantly reduce their thickness upon exposure to an ASW environment.
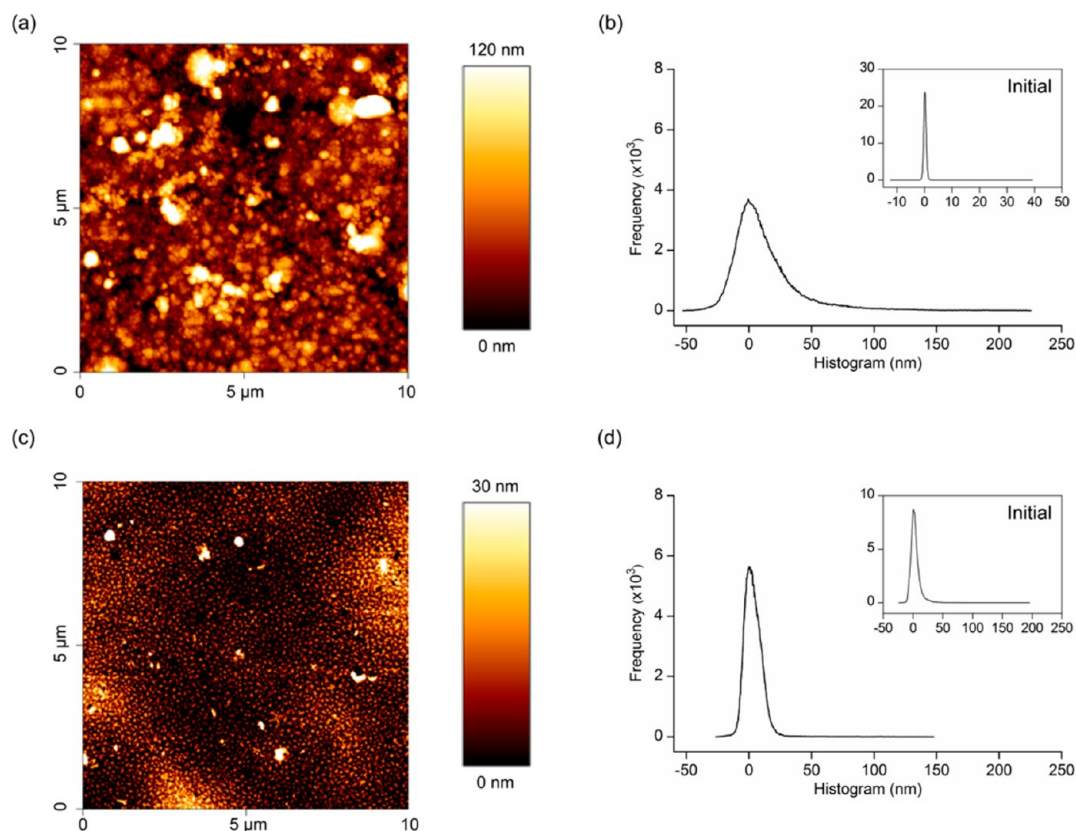
Figure 8. AFM images (10 μm × 10 μm) of silicon surfaces covered with (a) PSBMAm brushes (*Ra* = 18.7 nm) and (c) PS-*b*-PSBMAm block copolymer brushes (*Ra* = 5.4 nm) after 4 weeks of immersion in artificial seawater. Insets in graphs b and d represent AFM height histograms of initial surfaces, before immersion (Figure 3a,e, respectively).

SURFACE HYDRATION IN DI WATER AND NACL SOLUTION

To understand better the limited stability of zwitterionic polymers in seawater, a comparative AFM study on the swelling behavior of brushes was conducted. The Solvation of PSBMA brushes has been reported to be thickness-dependent with an interesting wettability switching behavior between hydrophilic and hydrophobic.[49−51] This switch, which has an onset region comprising dry brush thickness values between 50 and 80 nm,[49] has been attributed to the effective disassociation of the strong intermolecular and intramolecular dipolar interactions caused by the extremely high dipole moment of zwitterionic groups.[52] To the best of our knowledge, the hydration behavior of PSBMA or PSBMAm zwitterionic brushes in aqueous media with ionic strengths similar to that of seawater has not been reported.

Brush behavior in a solution of high salinity was investigated on a model 130-nm-thick PSBMAm polymeric film using AFM measurements in a liquid cell. Extended thickness was chosen to compare with results reported for PSBMA, which showed almost no swelling in DI water.[49]

In Table 2, the results obtained from the measurement of brush thickness by the scratching method[53] in DI water and

Table 2. PSBMAm Polymer Thickness (*d*) Measured by AFM in Dry and Wet Environments and Their Swelling Ratios

	thickness (nm)			swelling ratio	
	air	water	0.7 M NaCl	water	0.7 M NaCl
PSBMAm	130	160 (149)[a]	286 (248)[b]	1.2	2.2

[a] After immersion in 0.7 M NaCl (second switch). [b] After immersion in water (second switch).

0.7 M NaCl solution are summarized. The swelling ratio (*σ*) was estimated to be the coefficient of brush thickness (*d*) in dry and wet environments (d_{wet}/d_{dry}). PSBMAm showed only limited swelling in DI water, which can be attributed to the self-association of the brush suggested for PSBMA.[49,50] This behavior is a consequence of the strong intermolecular and intramolecular dipolar interactions of zwitterionic functional groups.[54] In the high-ionic-strength solution, the brush thickness values increased up to 120%. Because the value of the effective Debye length of electrostatic interactions is inversely proportional to the ionic strength of the solution,[55,56] this effect can be attributed to the screening of charges and the disruption of interchain interactions.[57] Increasing salt concentration breaks ion paring, which leads to a nonassociated state in which polymer brushes are highly solvated and stretched. This observation supports well the findings of Huck et al.[49,50] that indicate that adjacent zwitterionic chains interact strongly with each other despite their ability to self-compensate for charges within a single repeating unit.

This switch in brush thickness was found to be reversible by changing from salt water to DI water and vice versa. These results indicate that PSBMAm brushes in seawater will be highly stretched. In such a state, the effect of osmotic stress along the polymer brush backbone may lead to chain rupture in the brush or induce additional tension in the anchoring point and promote the hydrolysis of the anchoring linkage, leading to the detachment of the polymer brush.[35]

CONCLUSIONS

Zwitterionic polymeric brushes based on low fouling polysulfobetaines with monoblock and diblock architecture were synthesized by SI-ATRP and compared for stability in a seawater environment. Ellipsometry and spectroscopy measurements proved the extension of polymeric chains and the formation of diblock copolymers from PMMA and PS macroinitiators grafted from Si wafers. We demonstrate that diblock zwitterionic brushes, constructed with a hydrophobic anchoring segment (PS, PMMA), are much more stable than the corresponding pure PSBMAm and withstand ASW tests for at least the 3 months of exposure. The stability is correlated with the hydrophobicity of the protecting block, with PS being more effective than PMMA.

Experiments on the hydration of zwitterionic brushes in high-ionic-strength solutions concluded with the observation that the supercollapsed state reported previously for those polymeric structures in water[49,50] evolves to the nonassociated state in salt water as interchain ion pairs become dissociated and the brush thickness increases up to 120%. These results provide important insights, indicating the weakness of the homopolymeric zwitterionic brush when it is exposed to the marine environment. As an alternative, protected zwitterionic brushes may be used in order to increase the brush anchoring-point stability and avoid the unwanted enhancement of osmotic stress along the brush backbone.

ASSOCIATED CONTENT

Ⓢ Supporting Information

XPS survey spectra of grafted PS brushes and grafted PSBMAm brushes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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