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ABC Triblock Surface Active Block Copolymer with Grafted Ethoxylated Fluoroalkyl Amphiphilic Side Chains for Marine Antifouling/ Fouling-Release Applications

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An amphiphilic triblock surface-active block copolymer (SABC) possessing ethoxylated fluoroalkyl side chains was synthesized through the chemical modification of a polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polyisoprene polymer precursor. Bilayer coatings on glass slides consisting of a thin layer of the amphiphilic SABC spray coated on a thick layer of a polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS) thermoplastic elastomer were prepared for biofouling assays with the green alga *Ulva* and the diatom *Navicula*. Dynamic water contact angle analysis and X-ray photoelectron spectroscopy (XPS) were used to characterize the surfaces. Additionally, the effect of the Young's modulus of the coating on the release properties of sporelings (young plants) of the green alga *Ulva* was examined through the use of two different SEBS thermoplastic elastomers possessing modulus values of an order of magnitude in difference. The amphiphilic SABC was found to reduce the settlement density of zoospores of *Ulva* as well as the strength of attachment of sporelings. The attachment strength of the sporelings was further reduced for the amphiphilic SABC on the "low"-modulus SEBS base layer. The weaker adhesion of diatoms, relative to a PDMS standard, further highlights the antifouling potential of this amphiphilic triblock hybrid copolymer.

Introduction

Marine biofouling is defined as the buildup of microbial slimes, plants, and animals on any surface immersed in seawater. The increase in roughness imparted by the accumulation of biofouling and the resultant increase in frictional drag leads to substantial powering penalties, even for microfouling slimes.[1] To date, the most effective method of marine biofouling control has been the use of biocidal antifouling paints, but more research effort is now being expended on developing environmentally friendly alternatives and several recent reviews have focused on the various approaches being pursued.[2−7] Meanwhile, the most successful nonbiocidal materials in commercial terms are based on polydimethylsiloxanes, the so-called fouling-release coatings.

Most of the nonbiocidal coatings being developed for marine antifouling and/or fouling release that have been reported in the literature have been based on tailored polymeric materials. Specific attention has been placed on controlling the wettability and surface energy of coatings by tuning the surface chemistry, with successful antifouling and/or fouling-release behavior demonstrated for both hydrophobic and hydrophilic systems.[3] The Young's modulus of a coating is also of significant interest, with more compliant systems showing the easy release of fouling organisms by hydrodynamic shear forces.[8−10] Thus, the fouling-release performance of hydrophobic poly(dimethyl siloxane) (PDMS)-based coating systems is due to the combination of low surface energy, high thickness, and low modulus.[11−16] Nevertheless, PDMS-derived coatings are still particularly susceptible to fouling by diatom slimes,[17] and concerns also exist about their long-term durability. With more polar surfaces, hydrophilic coatings incorporating poly(ethylene glycol) (PEG) moieties, known for their resistance to protein adsorption and cell adhesion,[18−20] have also demonstrated resistance

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to settlement and the elevated release of marine fouling organisms.[20−23]

The realization that there are desirable surface properties associated with both extremes of wettability has led several groups of researchers to the development of "ambiguous" amphiphilic coating materials incorporating both hydrophobic and hydrophilic moieties. Motivation has been driven by the desire to produce a universal antifouling and/or fouling-release coating capable of resisting settlement (attachment) as well as the ability to readily release a wide a range of fouling organisms. With this in mind, Gudipati et al. produced surface-tethered hyperbranched polymers containing both fluorinated and PEGylated groups. These materials were characterized by both low protein adsorption and high fouling release at an optimal composition of hydrophobic and hydrophilic monomers.[24] More recently, Ober and co-workers reported on the development of a polystyrene-*block*-poly(acrylic acid)-derived surface-active block copolymer with amphiphilic ethoxylated fluoroalkyl side chains capable of both resisting settlement (attachment) and enhancing the release of zoospores as well as improving the release of sporelings (young plants) of the green alga *Ulva* and the diatom *Navicula* and also deterring the settlement of barnacles.[25,26] Additionally, a similar functionalized amphiphilic polystyrene block copolymer containing ethoxylated fluoroalkyl side chains has been reported by Martinelli et al. to have the potential to control algal settlement and release.[27] The antifouling and fouling release properties of these coatings are attributed to the very low interfacial energy with water because of the PEG groups, the nonadhesive nature due to the fluoroalkyl groups, and the environmentally responsive dynamic switch in surface wettability due to conformational changes in the amphiphilic side chains.[3,25]

This study reports on further developments to the multilayer polymeric coating approach taken by Ober and co-workers to produce antifouling and/or fouling-release coatings. The Young's modulus of the coating has been controlled by the use of a thick layer of the thermoplastic elastomer polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS). A mechanically tethered thin layer of a styrenic surface-active block copolymer (SABC) imparts chemical functionality to the surface. Previous work has focused on the synthesis of hydrophobic and hydrophilic side chain polymers derived from polystyrene-*block*-polyisoprene,[21,22] amphiphilic side chain polymers derived from polystyrene-*block*-poly(acrylic acid),[25,26] and antimicrobial polymers formed from polystyrene-*block*-poly(4-vinylpyridine).[28,29] This article focuses on the synthesis and characterization of a new polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polyisoprene-derived system, specifically designed to optimize the surface segregation of side chain functional moieties. This is achieved through the presence of a 25 000 g/mol poly(ethylene-*ran*-butylene) block that serves as a "molecular spacer" that should theoretically allow the functionalized isoprene block a greater ability to explore its conformational space and segregate to the surface. The synthesis and characterization of an amphiphilic triblock SABC containing ethoxylated fluoroalkyl side chains will be described, further building on the preliminary results reported in Weinman et al.[30] Particular attention is paid to surface characterization of the resultant SABCs using dynamic water contact angle analysis and X-ray photoelectron spectroscopy (XPS). Bioassays with zoospores of the green alga *Ulva* were used to determine the antifouling (antisettlement) potential, and bioassays employing sporelings (young plants) of *Ulva* and the diatom *Navicula* were designed to determine the fouling-release potential of the surfaces. *Ulva* (syn, *Enteromorpha*) is the most common macroalga that fouls ships and other submerged structures. Dispersal is mainly through motile, quadriflagellate zoospores (approximately 7 to 8 μm in length), which are released in large numbers. On favorable substrates, spores settle (attach) through the discharge of a glycoprotein adhesive[31] and then rapidly germinate into sporelings (young plants). Sporelings, in common with most other macrofouling organisms, exhibit weak adhesion to PDMS-based coatings.[11,32,33] Two different SEBS thermoplastic elastomer base layers with Young's modulus values varying by an order of magnitude were used to determine if the release of *Ulva* sporelings could be enhanced on coatings with a low Young's modulus because the release of sporelings has been shown to be related to the modulus of PDMS.[32] The second test organism was the diatom *Navicula*. Diatoms are unicellular algae that form biofilms (slimes) on surfaces,[34] but unlike spores of *Ulva* that are motile and therefore are able to "select" where to settle, diatom cells are not motile in the water column and reach a surface through transport in currents and gravity. In laboratory assays, the cells sink rapidly and form an even covering on the test surfaces. The reason for using both *Navicula* and *Ulva* to evaluate test coatings is that apart from having different settlement characteristics, the adhesion biology of the two organisms is different. For example, in contrast to *Ulva*, diatoms adhere more strongly to hydrophobic coatings, including silicone elastomers and fluorinated block copolymers, and, conversely, adhere more weakly to hydrophilic surfaces.[20,22,33,35]

Experimental Section

Materials. The polystyrene$_{8K}$-*block*-poly(ethylene-*ran*-butylene)$_{25K}$-*block*-polyisoprene$_{10K}$ (PS$_{8K}$-*b*-P(E/B)$_{25K}$-*b*-PI$_{10K}$) triblock precursor copolymer was produced using anionic polymerization and subsequent catalytic hydrogenation by Kraton Polymers at pilot-plant scale (~0.5 kg) to facilitate the preparation of the SABC.

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3-*meta*-Chloroperoxybenzoic acid (*m*CPBA, ClC_6H_4COOOH, FW 172.57, 77%), boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$, FW 141.93, 99.9%), and the ethoxylated fluoroalkyl surfactant Zonyl FSO-100 (registered trademark of E. I. du Pont de Nemours & Co., Inc., $F(CF_2CF_2)_y(CH_2CH_2O)_xCH_2CH_2OH$, x = 0−13 and y = 1−5, average $M_n \approx 725$ g/mol) were purchased from Sigma-Aldrich and used as received in the modification of the PS-*b*-P(E/B)-*b*-PI triblock precursor polymers. Anhydrous chloroform ($CHCl_3$) and α,α,α-trifluorotoluene (TFT) were also purchased from Sigma-Aldrich and used with no further purification. Chloroform, methylene chloride (CH_2Cl_2), methanol (CH_3OH), toluene, 6.25 N sodium hydroxide (NaOH), 96% sulfuric acid (H_2SO_4), 30 wt % hydrogen peroxide (H_2O_2) in water, 95% ethanol (CH_3CH_2OH), and all other reagents were used as received.

3-(Glycidoxypropyl)trimethoxysilane (GPS, 99%) was purchased from Gelest and used as received. Two separate commercially available polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS) ABA triblock thermoplastic elastomers having different chemical and bulk properties (Kraton G1652 and Kraton MD6945) and SEBS grafted with maleic anhydride (MA-SEBS, Kraton FG1901X) were generously provided by Kraton Polymers.

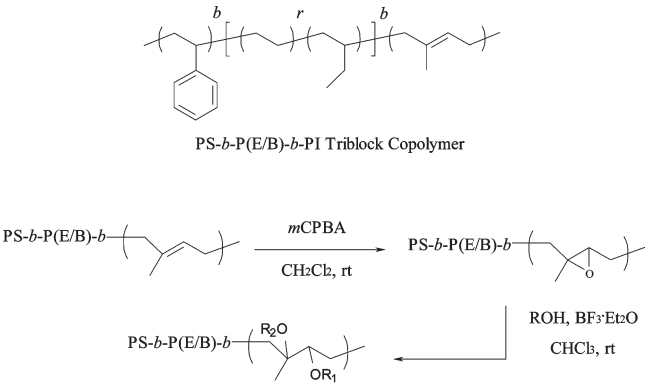
Polymer Synthesis and Characterization. The amphiphilic surface-active block copolymer was produced through a straightforward, two-step modification of the Kraton PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K} precursor polymer depicted in Scheme 1 in a similar fashion to that previously reported in Weinman et al.[30] Functionalization of the PI block of the triblock precursor was achieved through epoxidation of the residual unsaturated alkene groups in the polymer backbone followed by subsequent catalytic ring-opening etherification reactions using nonionic surfactant alcohols carrying amphiphilic functionality.

In a typical epoxidation reaction, the PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K} SABC precursor polymer (5 g, 14.5 mmol of reactive isoprene sites) was dissolved in 100 mL of dichloromethane in a round-bottomed flask. 3-*meta*-Chloroperoxybenzoic acid (*m*CPBA, 3.9 g, 17.4 mmol) was added to the mixture, and the solution was stirred vigorously for 5 h at room temperature. Subsequently, the polymer was precipitated in methanol, collected by filtration, and reprecipitated from dichloromethane to remove residual *m*CPBA and its respective byproducts. The white rubbery product was dried at room temperature under reduced pressure for 48 h to remove remaining solvent.

^{1}H NMR for epoxidized PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K} (300 MHz, $CDCl_3$, δ): 6.57, 7.07, (5H, styrene), 2.66 (br s, 1H, epoxidized isoprene, $-CH_2C\mathbf{H}(O)C(CH_3)CH_2-$), 0.80, 1.07, 1.22, 1.45, 1.57 (backbone). IR (dry film) υ_{max} (cm^{-1}): 2915, 2850 (C−H stretching); 1460, 1380 (C−H bending); 880 (C−O−C asymmetric stretching); 700 (C−H bending, aromatic).

To produce ether-linked amphiphilic side chain surface-active block copolymers, 2.1 g of epoxidized PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K} (5.8 mmol of epoxide) was taken in a round-bottomed flask in conjunction with a 4-fold molar excess (23.2 mmol) of the side chain precursor ethoxylated fluoroalkyl surfactant alcohol. The reactants were purged with argon and subsequently dissolved in ∼150 mL of anhydrous chloroform. Activated molecular sieves were added to the reaction mixture, and it was allowed to sit for ∼12 h to optimize the uptake of water. Etherification was performed through the addition of boron trifluoride diethyl etherate catalyst (0.345 g, 2.4 mmol) followed by vigorous stirring at room temperature for at least 48 h. Following the reaction, 6.25 N sodium hydroxide was added to quench any residual boron catalyst, and the reaction mixture was concentrated under reduced pressure using a rotary evaporator. The resultant SABC was precipitated into methanol, and the yellow rubbery product was collected by filtration and subsequently reprecipitated twice from chloroform to remove additional residual amphiphilic surface-active side chain alcohol. Finally, the finished sample was dried under reduced pressure at room temperature for 48 h to remove residual solvent fully.

Scheme 1. Synthesis of Ether-Linked Surface-Active Triblock Copolymers Containing Ethoxylated Fluoroalkyl-Derived Side Chains[a]



R_1, R_2 = H or R, where R = -$CH_2CH_2(OCH_2CH_2)_x(CF_2CF_2)_y$ F

[a] ROH = $F(CF_2CF_2)_y(CH_2CH_2O)_xCH_2CH_2OH$, x = 0−13 and y = 1−5, average $M_n \approx 725$ g/mol.

^{1}H NMR for PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K} functionalized with Zonyl FSO-100 ethoxylated fluoroalkyl surfactant side chains (300 MHz, $CDCl_3$, δ): 6.56, 7.07, (5H, styrene), 3.64 (br s, ∼14H, $-CF_2CH_2\mathbf{CH_2}O(\mathbf{CH_2CH_2}O)_{\sim 2.5}\mathbf{CH_2}CH_2O-$); 2.42 (m, 2H, $-O-CH_2\mathbf{CH_2}CF_2-$); 0.82, 1.06, 1.23, 1.72 (backbone). IR (dry film) υ_{max} (cm^{-1}): 3500 (O−H stretching); 2930, 2855 (C−H stretching); 1465, 1380 (C−H bending); 1245, 1220 (C−F stretching), 1150, 1135 (C−O stretching); 700 (C−H bending, aromatic).

^{1}H NMR spectra were recorded using a Varian Gemini spectrometer with deuterated chloroform. The IR spectrum of the polymer cast as a film from THF solution on a sodium chloride plate was collected using a Mattson 2020 Galaxy Series FTIR spectrometer. Gel permeation chromatography of a THF solution of polymers (1 mg/mL) was carried out using four Waters Styragel HT columns operating at 40 °C in conjunction with Waters 490 ultraviolet (λ = 254 nm) and Waters 410 refractive index detectors. The molecular weight range of the columns was from 500 to 10^7 g/mol. THF was used as the eluent at a flow rate of 1 mL/min, and toluene was used as a marker for flow calibration. The GPC was calibrated using a series of low-dispersity polystyrene standards.

Surface Preparation and Characterization. Surfaces for XPS and dynamic water contact angle analysis were prepared on silicon wafers by spin coating 3% (w/v) solutions of SABCs in TFT at 2000 rpm for 60 s. All surfaces prepared for study were annealed in a vacuum oven at reduced pressure at 120 °C for at least 12 h followed by slow cooling to room temperature.

XPS measurements were performed using a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, U.K.) with a monochromatic Al Kα X-ray source (1486.6 eV) operating at 225 W under a vacuum of 1.0×10^{-8} Torr. Charge compensation was carried out by the injection of low-energy electrons into the magnetic lens of the electron spectrometer. The pass energy of the analyzer was set at 40 eV for high-resolution spectra and 80 eV for survey scans, with energy resolutions of 0.05 and 1 eV, respectively. The spectra were analyzed using Casa XPS v.2.3.12Dev4 software. The C−C peak at 285 eV was used as the reference for binding-energy calibration.

Water contact angles were measured using a contact angle goniometer (AST Products, Inc. model VCA Optima XE) at room temperature. Dynamic water contact angle measurements were performed through the addition and retraction of a small drop of water (∼2 μL) on the surface. The advancing and receding contact angle behavior was digitally recorded, and image analysis software was used to measure the angles. Three measurements each for two different locations on the sample were taken.

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Stress−Strain Analysis of SEBS Base Layers. Samples of the Kraton G1652 and Kraton MD6945 SEBS thermoplastic elastomers were pressed at 100 °C between Teflon paper to 0.5 mm thickness and then cut into dog-bone-shaped samples. The samples were then monotonically stretched to fracture using an Instron (Norwood, MA) 1123 testing machine. All stress−strain curves were recorded at room temperature. Elastic modulus values were estimated for each sample by examining the slope of the stress−strain curve in the elastic deformation region.

Atomic Force Microscopy Analysis of SEBS Base Layers. To gain further understanding of the differences between the two SEBS base layers, surface morphology was analyzed using atomic force microscopy (AFM). Samples were prepared by spinning 5% (w/v) solutions of both Kraton G1652 and Kraton MD6945 thermoplastic elastomers on silicon wafers. Surfaces for analysis were annealed in a vacuum oven at reduced pressure for 12 h at 120 °C. Tapping-mode AFM measurements were made using a Digital Instruments Dimension 3000 atomic force microscope. Phase-contrast images were collected over 2 μm × 2 μm regions to reveal the surface morphology. The hard PS blocks appear light in a dark matrix of soft PEB blocks. Images were collected using Applied Nanostructures long cantilevers (ACL) at 1.5 Hz. Tapping was sufficiently hard to tap through the soft surface layer of the ethylene-butylene block.

Preparation of Surfaces for Biofouling Assays. Coated glass slides for biofouling assays with both *Ulva* and *Navicula* were prepared as previously reported in Krishnan et al. for the amphiphilic SABC using either Kraton G1652 or Kraton MD6945 SEBS as a thermoplastic elastomer base layer.[28] In summary, glass slides were cleaned by immersion in a 7:3 v/v mixture of concentrated H_2SO_4 and 30 wt % H_2O_2 solution, rinsed well, dried, and subsequently functionalized with a 4% w/v solution of 3-(glycidoxy)trimethoxysilane in ethanol. The silane was cured by heating the functionalized glass slides to 110 °C under reduced pressure for a minimum of 30 min. This epoxy containing silane served as an adhesion promoter for the initial SEBS layer spin coated from a 7% w/v SEBS solution in toluene (5% Kraton FG-1901X and either 2% G1652 or MD6945). The thickness of the SEBS base layer was then built up through successive spin coating of a 12% w/v SEBS solution (either Kraton G1652 or MD6945) in toluene three times. Finally, a relatively thin layer of SABC was deposited on top of the SEBS base layer through spray coating from a 3% w/v solution in TFT. The glass slides were annealed overnight at 120 °C following the conclusion of the deposition of each layer. The SEBS base-layer thickness produced was on the order of ~500 μm. Meanwhile, the SABC layer deposited onto the SEBS base layer via spray coating produced a layer on the order of ~20 μm in thickness.

The rationale behind testing MD6945 in addition to G1652 (which has typically been used in previous studies) was that the elastic modulus of MD6945 is very similar to that of PDMS, which is known to possess excellent fouling-release properties against *Ulva*. For biofouling assays, glass microscope slides coated with a poly(dimethylsiloxane) elastomer (PDMS), Silastic T2 (Dow Corning), prepared as described by Schumacher et al.,[36] were used as standards. G1652 SEBS and MD6945 SEBS were also included as controls.

Settlement of Zoospores and Strength of Attachment of Sporelings of *Ulva*. Nine replicates of each test sample were equilibrated in a 30 L tank of recirculating deionized water at ~20 °C for 48 h. The slides were transferred to artificial seawater 1 h prior to the start of an experiment. Zoospores were released from fertile plants of *Ulva linza* and prepared for assay as described previously.[37] In brief, 10 mL of the zoospore suspension (1×10^6 spores per mL) was pipetted into individual compartments of Quadriperm polystyrene culture dishes (Greiner Bio-One), each containing a test slide. The test slides were incubated in the dark at ~20 °C for 1 h and gently washed in seawater to remove zoospores that had not settled (that were still swimming). Three slides were fixed using 2.5% glutaraldehyde in seawater, and spores were counted by the fluorescence of chlorophyll as previously reported.[38]

Sporelings (young plants) of *Ulva* were cultured in nutrient-enriched seawater for 7 days on the remaining six replicates of each coating.[32] Growth was estimated by the direct measurement of fluorescence from chlorophyll contained within the chloroplasts of the sporelings using a Tecan plate reader (GENios Plus).[33,39] Fluorescence was recorded in relative fluorescence units (RFU) from direct readings. The slides were read from the top, 300 readings per slide, taken in blocks of 30 × 10. The strength of attachment of the sporelings was determined by exposure to a range of impact pressures from a calibrated, automated water jet.[40] The range of impact pressures used was chosen to provide maximum information on the strength of attachment of the sporelings, with one replicate slide being exposed at each of five impact pressures. RFU readings (80 per slide) were taken from the central part of the slide that was exposed to the water jet. The percentage removal was calculated from the mean RFU reading before and after exposure to the water jet. From the percentage removal data, the critical water pressure required to remove 50% of the sporeling biomass was derived.

Attachment and Adhesion Strength of *Navicula*. Cells of *Navicula* were cultured in F/2 medium contained in 250 mL conical flasks. A log-phase suspension of cells was diluted to give a suspension with a chlorophyll$_a$ content of approximately 0.25 μg/mL. Ten milliliters of cell suspension was added to individual compartments of Quadriperm polystyrene culture dishes (Greiner Bio-One), each containing a test slide. After 2 h at ~20 °C on the laboratory bench, the slides were gently washed in seawater without exposure to air (a submerged wash) to remove cells that had not attached to the surface. Cells were fixed and counted as described for spores of *Ulva*. To determine the strength of attachment, slides were exposed to a wall shear stress of 23 Pa in a calibrated water channel.[41] The percentage removal of cells was calculated by comparing cell counts on slides not exposed to shear with those on slides after exposure to shear.

Results and Discussion

Polymer Synthesis and Characterization. The synthesis of ether-linked side chain SABC with pendent ethoxylated fluoroalkyl groups was followed using both infrared spectroscopy and ^{1}H NMR spectroscopy. Following the epoxidation reaction, ^{1}H NMR spectroscopy clearly showed that there was no longer evidence of any protons associated with unsaturated alkene groups on the polymer backbone (~1.7, 2.0, and 5.1 ppm), and a significant peak at ~2.7 ppm appeared, indicating the presence of protons in the newly formed oxirane rings on the polyisoprene backbone. Additionally, infrared spectroscopy clearly showed the appearance of a disubstituted epoxide asymmetric stretching peak at roughly 880 cm^{-1} associated with the epoxide ring[42] and the disappearance of the C=C absorption at 960 cm^{-1}. This indicated that most of the residual unsaturated alkene groups were success-

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fully converted to their epoxidized form. Subsequent catalytic ring-opening using ethoxylated fluoroalkyl alcohol led to the disappearance of the epoxide proton peak in the ^{1}H NMR spectra. Further analysis of the ^{1}H NMR spectra showed the appearance of peaks at ~2.4, 3.6, and 3.8 ppm for the Zonyl-functionalized sample demonstrating successful attachment of the side groups. These findings were supported by infrared spectroscopy that demonstrated the appearance of two strong peaks at ~1125 cm^{-1} corresponding to C−O and C−O−C stretching, indicating the formation of both ether and alcohol groups from ring opening of the epoxy in conjunction with the presence of the ethylene oxide groups of the ethoxylated fluoroalkyl side chain. A strong C−F stretching peak at ca. ~1220 cm^{-1} suggesting the presence of the semifluorinated amphiphilic side chain moieties further supported successful attachment.

The percentage of attachment of the ethoxylated fluoroalkyl side chain was estimated by ^{1}H NMR integration. Specifically, this was done by comparing the total number of aromatic protons (associated with the PS block) in the ^{1}H NMR spectra with the number of protons associated with the PEGylated section of the amphiphilic side chain. The number of repeat units associated with the PEGylated section of the attached Zonyl ethoxylated fluoroalkyl side chains was checked in an analogous fashion and confirmed to be similar to those reported in Krishnan et al.[25] This analysis suggested the attachment of side chains on the order of ~45% relative to the epoxy functionality. Using GPC, the polydispersity of the sample was found to increase from 1.06 for the PS-*b*-P(E/B)-*b*-PI precursors to ~1.12 for its epoxidized form. Finished, substituted SABC samples containing ethoxylated fluoroalkyl side chains were found to have PDI values of ~1.3. This rise in polydispersity combined with the observation of complete reaction of the epoxide despite less than 100% attachment suggested that some of the epoxide was most likely lost to intermolecular branching reactions. Additionally, intramolecular "loop-forming" reactions in combination with epoxide ring-opening by any residual water molecules left in the reaction mixture may have contributed to this lowered observed attachment. Because this work spanned several batches of functionalized SABC polymer, the chemical characterization of each batch was done independently. Nevertheless, chemical analysis demonstrated very similar results from batch to batch, suggesting that the functionalization reaction was easily repeatable. Thus, the values given here are representative of the several samples tested, all made from the same precursor triblock copolymer.

Dynamic Water Contact Angle Analysis. Dynamic water contact angle analysis of the spin-coated amphiphilic ethoxylated fluoroalkyl SABC sample on a Si wafer indicated the presence of low-surface-energy, hydrophobic fluorinated moieties at the surface with $\theta_{w,\ advancing} = 107 \pm 2°$. High-contact-angle hysteresis was observed with $\theta_{w,\ receding} = 26 \pm 2°$. This suggests a dynamic surface capable of facile reordering of the side chains to readily orient the hydrophilic PEGylated groups at the surface. This is similar to what was observed for the ethoxylated fluoroalkyl polystyrene-*block*-poly(acrylic acid)-derived SABC reported by Krishnan et al.[25] but with significantly higher contact angle hysteresis (81° versus 60°) observed for the PS-*b*-P(E/B)-*b*-PI triblock-derived SABC. The lower receding angle (26°) is evidently due to the hydrophilic hydroxyl groups present in the polymers of this study that were absent in the polymer reported in Krishnan et al. ($\theta_{w,\ receding} \approx 34°$). The higher advancing water contact angle (107°) can be attributed to the hydrophobic poly(ethylene-*ran*-butylene) block in the present polymers, which was absent in the previously reported diblock copolymer ($\theta_{w,\ advancing} \approx 94°$).

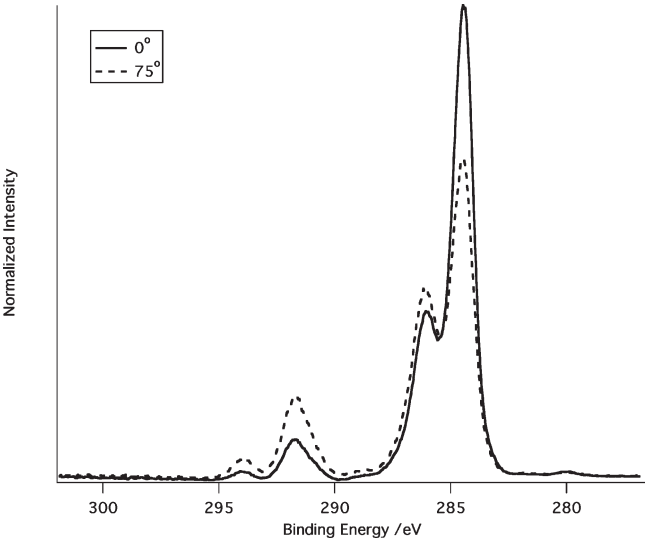

Figure 1. XPS C 1s spectra of the surface of the amphiphilic SABC with ethoxylated fluoroalkyl side chains derived from the PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K} precursor polymer spin coated on Si taken at both 0 and 75° angles of incidence.

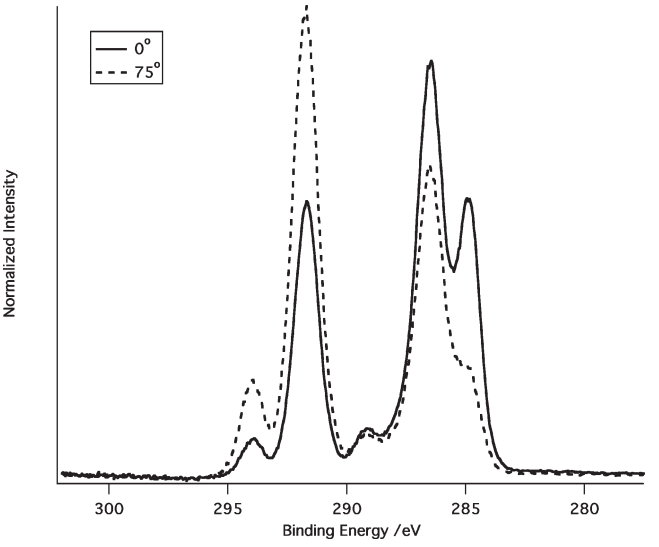

Figure 2. XPS C 1s spectra of the surface of the amphiphilic SABC with ethoxylated fluoroalkyl side chains derived from the PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K} precursor polymer spray coated onto MD6945 SEBS thermoplastic elastomer taken at both 0 and 75° angles of incidence.

X-ray Photoelectron Spectroscopy (XPS). Figure 1 depicts typical high-resolution C 1s XPS spectra of amphiphilic SABC derived from the PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K} precursor with ethoxylated fluoroalkyl side chains when spun directly on Si. The strong-intensity peak near 284.5 eV associated with C−C and C═C bonds is most likely indicative of the presence of the polymer backbone. The peak associated with C−O−C groups present near 286.5 eV meanwhile is indicative of the PEGylated groups of the amphiphilic side chain. Finally, the peaks at 292 and 294 eV are indicative of CF_2 and CF_3 groups, respectively, further suggesting the successful segregation of the ethoxylated fluoroalkyl side chains to the surface of the polymer coating. One can also note that the peaks associated with the side

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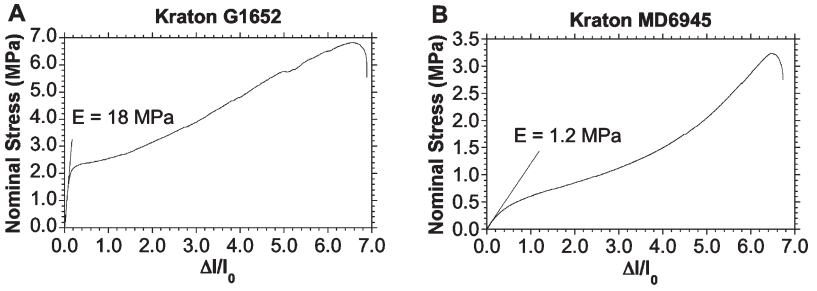

Figure 3. Measured stress−strain curves for SEBS thermoplastic elastomers Kraton G1652 and Kraton MD6945. Young's modulus (E) values are estimated from the slope of the stress−strain curve during elastic deformation.

chain (CF_3, CF_2, and C−O−C) show higher intensities at a 75° angle of incidence than at a 0° angle of incidence. This suggests the preferential segregation of the side chains to the surface as desired.

Further characterization by XPS to determine if these model surfaces formed by spin coating were similar to those formed in the fabrication of samples for biofouling assays was performed. Figure 2 depicts typical high-resolution C 1s XPS spectra of amphiphilic SABC derived from the PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K} precursor with ethoxylated fluoroalkyl side chains when sprayed on top of the MD6945 SEBS thermoplastic elastomer for biofouling assays. Whereas the same set of chemical signatures is present for the spray-coated samples as for the spin-coated samples, peak intensities associated with the ethoxylated fluoroalkyl side chains greatly increased across the board. Particularly striking was that at the 75° angle of incidence the contribution from the polymer backbone was so minimal that the C−C peak simply appeared as a shoulder on the much stronger C−O−C peak. Initially, this led to concerns about residual ethoxylated fluoroalkyl side chain precursor alcohol being left in the sample as a result of incomplete purification. However, additional stepwise reprecipitations followed by bulk chemical characterization suggested that any loose ethoxylated fluoroalkyl alcohol molecules were already fully removed from the sample.

Determination of the Elastic Modulus for SEBS Base Layers. Figure 3 shows the measured stress−strain curves for the Kraton G1652 and Kraton MD6945 SEBS thermoplastic elastomers. Kraton G1652 was found to have a measured elastic modulus (E) of ∼18 ± 0.3 MPa whereas the measured value of E for Kraton MD6945 was an order of magnitude less, ∼1.2 ± 0.3 MPa. This demonstrates that MD6945 has a modulus much closer to that of PDMS, which is dependent on the degree of polymerization and cross-linking but is reported to be between 1.4 and 3.0 MPa for commercial PDMS elastomers RTV11 and Intersleek.[43]

AFM Analysis of SEBS Base Layers. Figure 4 depicts the AFM phase images of surfaces of the two different Kraton SEBS thermoplastic elastomer base layer polymers. Kraton MD6945 (Figure 4A) demonstrates spherical surface morphology whereas Kraton G1652 (Figure 4B) reveals mostly lying-down cylinders. The manifested difference in microstructure can likely be attributed to significant differences in the relative block length of polystyrene in comparison to that of poly(ethylene-*ran*-butylene). The spherical structure of MD6945 when taken into account with its lower modulus relative to that of G1652 suggests a much higher relative amount of the compliant poly(ethylene-*ran*-butylene) block in comparison to the amount of glassy polystyrene block for this polymer.

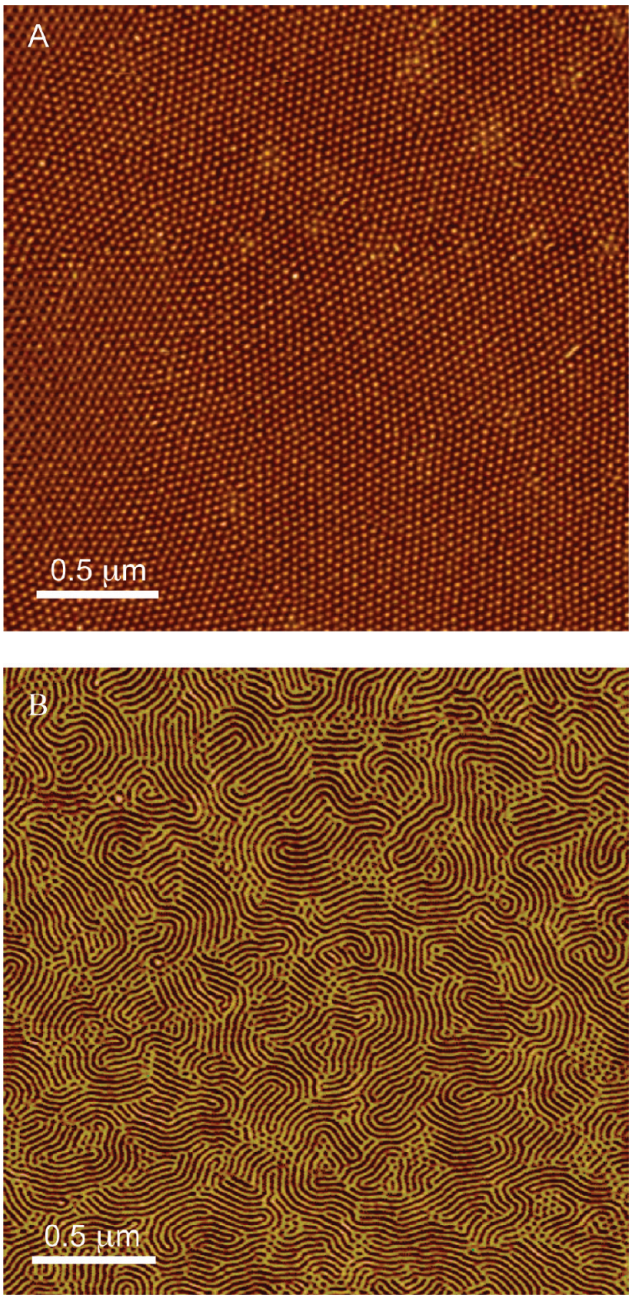

Figure 4. AFM phase images of (A) Kraton MD6945 and (B) Kraton G1652 SEBS.

Settlement of Zoospores and Release of Sporelings of *Ulva*. Figure 5A shows the settlement density of spores of *Ulva* on PDMS, G1652 SEBS, and the amphiphilic SABC multilayer

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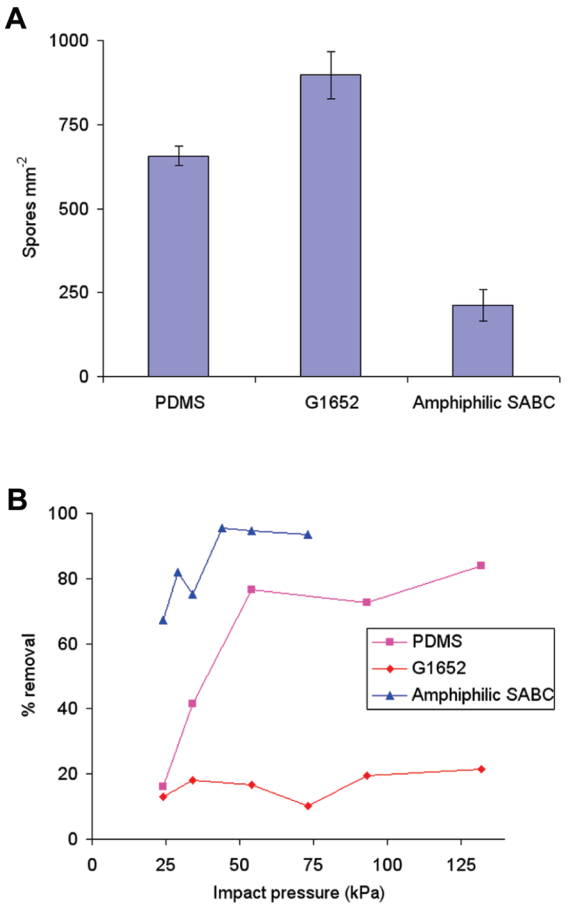

Figure 5. Results of biofouling assays with *Ulva* on glass, G1652 SEBS, PDMS, and the multilayer PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K}-derived amphiphilic SABC coating with ethoxylated fluoroalkyl side chains on a base layer of G1652 SEBS. (A) Density of settled spores. Each point is the mean from 90 counts on 3 replicate slides. Bars show 95% confidence limits. (B) Percentage removal of sporelings. Slides were exposed to a water jet over a range of pressures. One slide was used for each reported pressure.

coating derived from the PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K} precursor and the ethoxylated fluoroalkyl nonionic surfactant on a G1652 SEBS base layer. The lowest spore settlement density was recorded for the amphiphilic SABC. Spores of *Ulva* usually settle preferentially on hydrophobic, low-energy surfaces including PDMS.[44] The lower settlement density on the amphiphilic SABC suggests that the surface reorganized in the polar aqueous environment, as has been shown for other amphiphilic SABCs.[25,27]

Spores germinated and grew well on all surfaces, which were covered with a green lawn of sporelings after 7 days. The percentage removal of sporelings from the surfaces at a range of applied water jet pressures is given in Figure 5B. There was negligible removal of biomass from the SEBS base, even at the highest tested impact pressure of 130 kPa. The amphiphilic SABC demonstrated robust fouling-release behavior, releasing ~67% of biomass at an applied water jet pressure of 24 kPa and almost complete removal at 44 kPa. Release of biomass from the standard, Silastic T2, coating was less efficient than from the amphiphilic SABC coating. The combination of the favorable spore settlement and sporeling release results led us to question whether the release of sporelings could be improved by substituting the new, softer Kraton MD6945 thermoplastic elastomer in

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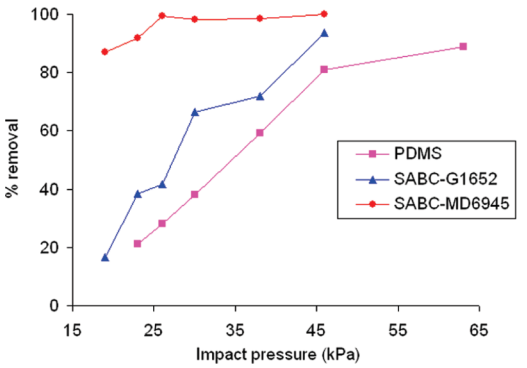

Figure 6. Percentage removal of sporelings of *Ulva* from PDMS (Silastic T2) and the PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K}-derived amphiphilic SABC with ethoxylated fluoroalkyl side chains on both G1652 and MD6945 thermoplastic elastomer base layers. Slides were exposed to a water jet over a range of pressures. One slide was used for each reported pressure. The plots for the two base layers (G1652 and MD6945) are not included because of the high impact pressures required (Table 1).

place of Kraton G1652. Whereas multiple studies have been published previously equating a lower modulus with the enhanced release of pseudobarnacles and living "hard" macrofouling organisms such as barnacles,[10,45–48] little data have been reported on "soft" fouling organisms such as *Ulva* and *Navicula*. Chaudhury et al. examined a range of PDMS coatings with different degrees of polymerization for the release of sporelings of *Ulva* under hydrodynamic shear and determined that there was a reduction in fouling-release performance at modulus values above 2 MPa,[32] which suggested that further reduction of the Young's modulus of the amphiphilic SABC coating could prove advantageous to its fouling-release performance.

Coatings of the amphiphilic SABC containing ethoxylated fluoroalkyl side chains were again prepared; this time they were sprayed on both the high-modulus G1652 SEBS and the low-modulus MD6945 SEBS base layers to determine their effect on spore settlement and the release of sporelings. The density of settled spores was not significantly different between amphiphilic SABC on high-modulus G1652 SEBS (416 spores ± 38/mm^2) and low-modulus MD6945 SEBS (449 spores ± 58/mm^2). This result concurs with previous observations that showed that there were no differences in the density of spores settled on PDMS coatings spanning a 50-fold range of modulus values.[32]

Figure 6 depicts the percentage removal of *Ulva* sporelings from the two experimental surfaces at a range of different applied water jet pressures. As seen previously, the amphiphilic SABC on both the high-modulus G1652 and low-modulus MD6945 base layers showed high release of biomass, but the percent removal from the latter was higher at the lower impact pressures. At an applied water jet pressure of 19 kPa, the amphiphilic SABC coating on a base layer of the low-modulus MD6945 demonstrated ~87% removal of sporeling biomass compared to ~17% removal for the amphiphilic SABC on a base layer of the high-modulus G1652. The critical pressures for removing 50% of the biomass (CP50) are shown in Table 1. The two SEBS base layers essentially showed no fouling-release properties, with CP50

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Table 1. Estimated Critical Applied Water Jet Surface Pressure for 50% Removal (CP50) of *Ulva* Sporeling Biofilm Derived from the Curves in Figure 6

sample	(CP50, kPa)
G1652	152
MD6945	> 270
PDMS	34
amphiphilic SABC − G1652	26
amphiphilic SABC − MD6945	< 10

values being 4−8 times higher than that for Silastic T2. The results suggest that the order-of-magnitude drop in modulus between high-modulus G1652 and low-modulus MD6945 resulted in enhanced fouling-release efficacy. These results agree with results for PDMS where the ease of removal of sporelings increased for substrates with a modulus below 2.7 MPa.[32] To our knowledge, the present results are the first to indicate that the release of soft fouling organisms from thin coatings can be facilitated through the use of a low-modulus (3 MPa or less) underlayer.

Attachment Strength of Diatoms. Because diatoms reach a surface by sinking through the water column under the influence of gravity, at the end of the settlement period there are the same number of cells on all test surfaces. Gentle washing under water removes cells that are not attached to the surface. Differences in the number of cells therefore reflect the ability of cells to adhere to specific surface chemistries. Glass was included as an additional standard in this assay because diatoms adhere weakly to hydrophilic surfaces. Figure 7 shows the number of cells of *Navicula* on amphiphilic SABC with ethoxylated fluoroalkyl side chains on a base layer of G1652 SEBS, glass, plain G1652 SEBS, and the Silastic T2 standard. Significantly fewer cells are attached to amphiphilic SABC and glass surfaces compared to the number attached to the hydrophobic Silastic T2 standard and the G1652 SEBS base layer control (one-way analysis of variance with Tukey tests $F\ 3,\ 356 = 98.5 P < 0.05$). The percent removal data (Figure 7B) inversely correlates to the initial attachment data (i.e., the highest removal is associated with the samples that had the lowest number of attached cells for which weak adhesion was implied). The most important comparison is that whereas the PDMS elastomer showed only ∼5% removal of the cells, amphiphilic SABC on G1652 SEBS demonstrated ∼51% removal. The results are consistent with previous studies that have shown that diatoms adhere tenaciously to hydrophobic surfaces including PDMS.[20,22,33,35,49]

The results reported for the amphiphilic SABC coating are consistent with previous studies that have shown that amphiphilic coatings can function as antifouling and fouling-release coatings for higher algae such as *Ulva* as well as deter the attachment and adhesion of diatom slimes.[24,25,27] We can only speculate about the reasons for the low adhesion of both algae to the amphiphilic coatings. We would anticipate that reconstruction of the surface takes place following immersion in water, leading to nanoscale roughness as shown for related surfaces.[27] Although there are no systematic studies regarding the effects of nanoroughness on the release of the test organisms used here, recent studies have implicated surface heterogeneity and nanoroughness in reducing the number of spores settling on surfaces[50] and reducing the adhesion strength of young plants of *Ulva*.[51] We also know that

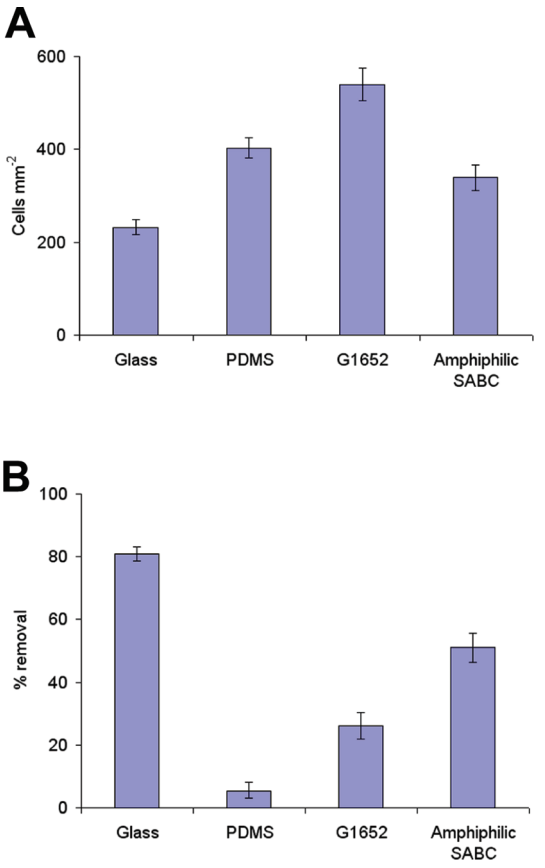

Figure 7. (A) Initial attachment after gentle washing of cells of *Navicula* to PS_{8K}-*b*-$P(E/B)_{25K}$-*b*-PI_{10K}-derived amphiphilic SABC with ethoxylated fluoroalkyl side chains on a G1652 SEBS base layer. (B) Percentage removal of cells of *Navicula* from the same SABC as a result of exposure to a shear stress of 23 Pa. Each point is the mean of 90 counts on 3 replicate slides. Bars show 95% confidence limits.

subtle changes in molecular structure, order, and crystallinity of self-assembled monolayers have a profound influence on the adhesion of spores of *Ulva* and cells of *Navicula*[20,52] and that spores also respond to microscale patterns of different surface chemistry and wettability.[44] We therefore hypothesize that molecular and assumed nanotopographic ambiguity of the surfaces reported here lowers the driving forces for the adsorption of the adhesive molecules secreted by the organisms, thereby reducing their adhesion strength. Lack of knowledge about the chemistry of the adhesives means that such a mechanistic interpretation has to remain speculative. The improvement in the release of sporelings of *Ulva* when the amphiphilic SABC was applied over a low modulus base layer suggests that the release of hard fouling organisms such as barnacles may also be facilitated.

Conclusions

Amphiphilic surface-active block copolymers with ethoxylated fluoroalkyl side chains were successfully produced through polymer modification of a polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polyisoprene precursor. Resultant polymers were characterized using a combination of ^{1}H NMR spectroscopy and Fourier transform infrared spectroscopy, confirming the successful attachment of the amphiphilic surface-active groups. Dynamic water contact angle analysis in conjunction with X-ray photo-

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electron spectroscopy suggested a surface highly populated by the amphiphilic moieties with hydrophobic fluorinated species present in an air (nonpolar) environment that could readily reorient to bring PEGylated moieties to the surface upon immersion in a hydrophilic, polar environment such as water. The settlement and ease of removal of two types of ubiquitous marine fouling algae were evaluated through a series of bioassays. The amphiphilic coating had both antifouling and fouling-release attributes. Reducing the elastic modulus of the thermoplastic elastomer base layer used in the coating enhanced the release of sporelings of *Ulva* by hydrodynamic shear and demonstrates for the first time that tuning the Young's modulus of a thin coating system can be achieved.

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