Antifouling Block Copolymer Surfaces that Resist Settlement of Barnacle Larvae

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INTRODUCTION

Marine biofouling is a serious problem caused by the accumulation and settlement of barnacles, macroalgae, and microbial slimes on the hulls of seafaring vessels. Biofouling can significantly increase drag, leading to startling consequences with regards to fuel consumption. Environmentally compatible solutions to biofouling are being sought as traditional metal-based systems of fouling control are being phased out due to their inherent toxicity. Further exacerbating the problem of environmental conditions experienced throughout the world. This renders the biofouling is the vast range of fouling organisms and environmental

Previously, Krishnan et al. demonstrated the ability of multilayer coatings based on modified polystyrene-block-poly(acrylic acid) (PS-b-PAA) and modified polystyrene-block-polysoprene to resist fouling by two different species of marine algae known to show opposite attachment strengths on hydrophobic and hydrophilic surfaces. Navicula diatoms were found to show stronger adhesion to hydrophobic semifluorinated surfaces versus hydrophilic PEGylated surfaces, while Ulva sporelings were more easily removed from the hydrophobic surfaces. Coatings based on surface active block copolymers functionalized with the amphiphilic PEGylated fluoroalkyl groups were unique however in their ability to serve as an effective fouling release coating for both Ulva sporelings and Navicula diatoms.

Surface preparation and characterization. Surfaces for NEXAFS spectroscopy and contact angle measurements were prepared on silicon wafers by spin-coating 3% (w/v) solutions of the block copolymers in chloroform (using Cee model 100CB spin coater). Surfaces for barnacle-larvae-settlement assays were prepared by spray-coating 3% (w/v) solutions on glass microscope slides covered with Krypton SEBS (G1652) thermoplastic elastomer. Chloroform was used as the solvent for the PEG550 and Zonyl polymers, while the F8H2 polymer was dissolved in TFA. The SABC surface-coverage was 1.7 mg/cm². All the surfaces were annealed in a vacuum oven at 120 °C for 12 h followed by cooling slowly to room temperature. Dynamic water contact angles were measured using an NRL contact angle goniometer (Rame-Hart model 100-00). NEXAFS experiments were performed on the U7A NIST/Dow materials characterization end-station at the National Synchrotron Light Source at Brookhaven National Laboratory, as described in Krishnan et al. The partial electron yield (PEY) C 1s spectra were normalized by subtracting a linear pre-edge baseline and setting the edge jump to unity at 320 eV.

Barnacle settlement assay. The glass test slides were placed in filtered natural seawater for six days to collect any leachates. This water was tested for any negative physiological effects by subjecting brine shrimp nauplii larvae (Artemia sp.) to the leachate for two days and observing their relative mortality. The settlement assay consisted of placing a 0.4 mL drop of seawater containing 20-40 barnacle cypris larvae on the experimental coatings. The larvae were allowed to settle for 72 hours, or until the settlement rate on the glass control surfaces reached 50%. At this time, the number of barnacles that had settled on each surface was counted and compared to the settlement rates on the experimental controls. Glass and PDMS (Silastic T2, a fouling release silicone elastomer from Dow Corning) were used as control surfaces.

RESULTS AND DISCUSSION

Polymer synthesis. Esterification of the PS-b-PAA₅₀ precursor resulted in a high degree of attachment for all three surface active
block copolymers. Acrylic monomers with functional side groups can be polymerized directly to obtain block copolymers with styrene. For example, Hikita et al. have reported the synthesis of polystyrene-block-poly(2-perfluorooctyl ethyl acrylate) by ATRP. However, using the polymer analogous method reported herein, a precise control over the lengths of the surface-active blocks is possible, which is otherwise difficult during polymerization of monomers with widely different solubility and kinetic characteristics.

Contact angle analysis. Contact angle analysis on spin coated surfaces of PS38kPAA3k-Zonyl found \( \theta_{\text{adv}} = 86 \pm 2^\circ \) and \( \theta_{\text{rec}} = 41 \pm 2^\circ \). This was similar to previously observed contact angles and suggests rapid surface reorganization. For PS38kPAA3k-F8H2, \( \theta_{\text{adv}} = 121 \pm 1^\circ \) and \( \theta_{\text{rec}} = 70 \pm 1^\circ \), suggesting a hydrophobic, fluorinated surface.

NEXAFS spectroscopy. Figure 2 shows the C 1s partial electron yield NEXAFS spectra of the block copolymer surfaces spin-coated on silicon. The PS38kPAA3k-F8H2 surface exhibited the characteristic C 1s → \( \pi^* \) peak, arising from the C atoms of the perfluorooctyl groups of the side chains. The surfaces with PEG and PEGylated fluoroalkyl (Zonyl) side-groups showed NEXAFS spectra similar to those reported previously. It should be noted that although all three surface-active polymers were prepared from the same PS38k-b-PAA3k precursor, and had the same PS block molecular weight, the intensity of the C 1s → \( \pi^* \) peak at 285.5 eV was the lowest for the PS38kPAA3k-F8H2 surface and the highest for the PS38kPAA3k-PEG550 surface. This can be attributed to surface segregation of the low-surface-energy fluorinated block in the former, displacing the higher surface energy PS block from the surface. The PS38kPAA3k-Zonyl surface also showed a similar surface-segregation of the fluoroalkyl groups, resulting in a lower \( \pi^* \) signal compared to the PS38kPAA3k-PEG550 surface. Because the surface energy of PEG is slightly higher than that of PS, we expect a preferential presence of PS at the surface of PS38kPAA3k-PEG550. Further work is being carried out to explore if there are differences between surfaces prepared by spin coating and spray coating.

Barnacle settlement results. The results of the leachate test indicated no significant difference between mortality of brine shrimp subjected to the leachate of experimental coatings and mortality from glass controls (ANOVA, \( F=0.560, p=0.6515 \)). There was a significant difference observed between cypriis larve settlement on experimental coatings of PS38kPAA3k-F8H2, PS38kPAA3k-Zonyl, and PS38kPAA3k-PEG550 and settlement on controls of glass and Silastic T2 PDMS (ANOVA, \( F=84.454, p<0.0001 \)). Silastic T2 was selected as a standard since its fouling-release efficacy against barnacles has already been established. Subsequent tests indicate that all three experimental coatings had significantly lower settlement than glass and PDMS controls as demonstrated in Figure 3.

CONCLUSIONS
All three surface-active polymers functioned as foul-deterring surfaces with regards to fouling by barnacles larvae. The settlement was significantly lower than on a widely studied fouling releasing Silastic T2 PDMS elastomer. Of particular note was the performance of the amphiphilic block copolymer which showed almost no settlement of cypriis larve. Contact angle analysis in combination with NEXAFS spectroscopy demonstrated successful segregation of the fluorinated groups to the surfaces of our multilayer coating system.

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