SEMIFLUORINATED TRIBLOCK COPOLYMERS AS SURFACE ACTIVE COMPONENTS FOR MULTILAYER MARINE ANTIFOULING COATINGS

Qin Liu1, Saritraman Krishnan1, Marvin Paik2, Peter Busch1, Christopher K. Ober1, Alexander Hetzer1, Karen E. Sohn, Edward J. Kramer2, Greg L. Kowlake1 and Dean E. Wendt1

1 Materials Science and Engineering, Cornell University, Ithaca, NY, 14853
2 Department of Materials, University of California at Santa Barbara, Santa Barbara, CA 93106

Introduction

Marine fouling is a major problem in the seaborne transport of materials worldwide, and anti-fouling control is important for successful operation of a ship.1 Any fouling or buildup of marine flora and fauna on the hull of a ship will impede its ability to achieve top speed, add to the fuel expended and increase the noise generated by a ship passing through the water. Presently the most effective paints that have fouling release properties contain large quantities of copper. The environmental impact of long term leaching of copper in to marine harbors and estuaries is a serious concern.

Current state-of-the-art understanding of anti-fouling materials is that the best copper-free fouling control systems are low surface energy coatings, namely silicone or fluoropolymer-based systems that minimize the adhesive strength between fouling organisms and the specialized polymer surface. It is now apparent that adhesion strength of hard fouling organisms is proportional to \(\gamma E\gamma^2\), where \(\gamma\) is the surface energy and \(E\) is the modulus of the surface. For this reason, silicone elastomers are, as of now, the only commercial environmentally benign fouling release coatings, because they possess both low modulus and low surface energy.1 The efficacy of silicone polymers is lower than that of biocide-containing anti-fouling paints, and regular mechanical cleaning (scrubbing) of the coated surface is required adding to operational expense. It would be advantageous to use fluorinated materials to lower the surface energy of a coating and decrease its adhesive strength, but these materials are typically hard and brittle with high moduli and do not provide good biofouling control. Moreover, the hydrophobic, fluorinated surfaces often undergo rapid molecular reconstruction in polar environments, such as water, and thus lose their fouling release characteristics. This makes the creation of fluorinated, fouling-release surfaces that do not reconstruct a challenge. Several approaches toward the creation of stable surfaces have been examined, and of particular interest is the stabilization of the surface with liquid crystalline semifluorinated groups (short segments of alkyl and perfluoralkyl alkyl groups of 5-10 carbons each).1 It was anticipated that assembly of such groups onto a surface would result in stable fouling-release surfaces.

We are developing coating systems that combine both thermoplastic elastomers (TPE) and surface-active block copolymers (SABC) to exceed the current performance of fouling release silicone coatings. Commercially available TPE provides the needed mechanical strength and adhesion properties, while the SABC provides the surface and fouling release behavior. Our previous research has demonstrated that semifluorinated liquid crystalline block polymers as SABCs can form a long-term stable hydrophobic coating, with promising antifouling performances. In this paper, we will discuss our current efforts to develop simplified synthetic approaches to prepare SABCs in large quantity, as well as the fabrication of coating systems to prepare samples for biofouling test.

Experimental

Materials. Semifluorinated alcohols, 1H, 1H, 2H, 2H-perfluorodecanol (F10H2), and 1H, 1H, 2H, 2H-perfluorodecanol (FS12H2), were purchased form SynQuest Fluorochemicals. Triblock thermal plastic elastomers, poly(styrene-butadiene-styrene) (SBS) and poly(styrene-ethylene/butene-styrene) (SEBS), were kindly donated by Kraton Polymers LLC. Other chemicals were purchased from Aldrich, and used as received.

Synthesis of SABC. SBS, D-1102 (10.0 g, 0.16 mol), was dissolved in 500 mL THF in a 1000 mL flask at room temperature. Bromine (27 mL) was slowly added via an addition funnel over a period of 4 h under stir, and the reaction was maintained for 3 more hours. The product was precipitated from methanol twice to remove residual bromine. The white product was dried in vacuum oven at room temperature for 12 h. In a typical polymer side chain attachment, 15.0 g brominated SBS was dissolved in 600 mL chloroform. F10H2 (60 g), 6 g 18-crown-6 and 120 g potassium hydroxide in 600 mL water were added. The system was refluxed for at least 72 h. Finally, the product was precipitated from methanol twice to remove unattached semifluorinated alcohol. The polymer was dried in air for half hour, and then was dissolved in mixture of THF and trifluorotoluene (TFT) (w/w 30/70) for storage. The products are named as SBS-F10H2-xx or SBS-F10H2-xx, and xx denotes the weight fraction of incorporated fluorine.

Fabrication of multilayer coating system. The glass slides were cleaned using mixture of concentrated sulfuric acid and hydrogen peroxide, and then (3-glycidoxypropyl) trimethoxysilane (GPS) was coated on the surface. The GPS functionalized glass slides were spun-coated with the blend of SEBS, and SEBS with grafted maleic anhydride, and then one more thick SEBS layer. The top thin SABC layer was prepared by spray-coating SABC solution on the substrate.

Characterization. NMR spectra were recorded on a Varian Gemini 400 MHz spectrometer. Wide-angle X-ray diffraction (WAXD) was performed on a SCINTAG 0/20 diffractometer. The Ni-filtered Cu X-ray tube (Ka1 = 1.5418) was operated at 45 kV and 40 mA. DSC was performed on a TA Q100, and the sample was heated to 150 °C to remove thermal history, and then was cooled to –100 °C at a rate of 10 °C/min. The sample was heated at a rate of 10 °C/min to 150 °C, and all the report data are from the second heat. Elemental analysis was used to quantitatively analyze the incorporation of the water. The products are named as SBS-F10H2-xx or SBS-F10H2-xx, and xx denotes the weight fraction of incorporated fluorine.

Results and Discussion

In our previous research, several families of semifluorinated LC block copolymers were developed as SABCs for multilayer marine antifouling coatings.2-4 To further test the potential of semifluorinated polymers as SABC, we have developed a simplified approach to large quantity synthesis of SABCs (Figure 1). Commercially available triblock copolymers, Kraton SBS D1102 (polystyrene 30 wt% and 20 mol%), was selected as the parent polymer using modification and functionalization of double bonds in the central polybutadiene block. Modification was achieved using bromine (conversion ~ 98 %, indicated by 'H NMR spectrum). Moreover, commercially available semifluorinated alcohol, F8H2 or F10H2, was incorporated into the block copolymer via nucleophilic substitution reaction. Elemental analysis was used to quantitatively analyze the incorporation of semifluorinated side chains (Table 1). A high efficiency (> 90%) of attachment was achieved by the method described in the experimental section. In the final products, there is a low level of residual bromine. Currently, we do not know if residual bromine affects the antifouling performance or long term stability of the polymers. An efficient method to remove residual bromine is being established.

To maintain a long term hydrophobic surface under water requires the semifluorinated side chains to form mesophases stable at room temperature. DSC analysis indicated that the semifluorinated side chains from F8H2 and F10H2 have a strong tendency to mesophase formation, and even a low content of semifluorinated side chains (fluorine 10 wt%) formed very stable LC phases which possess transition temperature and transition heat (after calibrated by the weight fraction) similar to polymers with a higher content of
semifluorinated side chains (Table 1). For SBS-F10H2-12, two transitions were observed by DSC analysis. Based on our prior research and results from polarized light microscope, the first transition can be assigned to the transition from smectic B LC phase to a smectic A mesophase, and the second transition is the transformation from the smectic A LC phase to an isotropic liquid. Mosaic textures, were observed by DSC analysis. Based on our prior research and results from polarized light microscope, the first transition can be assigned to the transition from a smectic B LC phase to a smectic A mesophase. As a conclusion, the semifluorinated side chains in the central block formed a smectic B LC phase at room temperature. The stable LC mesophase inhibits surface reconstruction making these films suitable as marine antibiofouling coatings.

<table>
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<tr>
<th>Sample</th>
<th>Br%</th>
<th>F%</th>
<th>TA (°C)</th>
<th>TA* (°C)</th>
<th>ΔH (J/g)</th>
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<tr>
<td>SBS-F8H2*</td>
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<tr>
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<td>10.1</td>
<td>23</td>
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<td>SBS-F10H2-52</td>
<td>9.5</td>
<td>52.1</td>
<td>------</td>
<td>81</td>
<td>34.9</td>
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</table>
*theoretical product with 100% conversion; † liquid crystalline transition; ‡ calibrated by the weight fraction of CF2 and CF3

A multilayer system was used to fabricate coating systems suitable for testing (Figure 2). A thick thermoplastic elastomer (TPE) layer between the substrate and SABC provides a sufficiently low modulus for antibiofouling performance. Moreover, the SEBS elastomers used with a triblock structure similar to the SABC also provided a good adhesion between the TPE layer and SABC. To improve adhesion between the substrate (glass) and the SEBS layer, the glass was functionalized using GPS, and then coated with a thin layer of maleic anhydride grafted SEBS. A test with brine shrimp (procedures in reference 5) demonstrated that this coating system did not leach toxic chemicals.

Figure 2. Multilayer Coating System

Spray coating by device in Figure 3 was used to apply a thin SABC layer on the top of the SEBS layer to produce a hydrophobic surface with high water contact angles (advancing: 121°; receding: 95°). AFM analysis revealed a uniform, fully covered SABC layer on top of SEBS layer. The roughness measured by interferometry was below 500 nm. The orientation of the semifluorinated side groups at the surface. The highly ordered semifluorinated side chains formed stable structures on the coating surface, which provided the resistance to the surface reconstruction under water.

Figure 3. Spray Coating Device

Figure 4. NEXAFS Analysis of SBS-F10H2-10/SEBS Coating

Conclusions
A simplified synthetic approach involving the chemical modification of styrene-diene-styrene block copolymers was established for the preparation of semifluorinated triblock copolymers for use as surface active block copolymers (SABC). The incorporated semifluorinated side chains have a strong tendency to form smectic B LC phases that are stable at room temperature. A multilayer coating for marine anti-fouling applications containing no leachable toxic chemicals was fabricated using this material. A styrene-ethylene butylene-styrene (SEBS) triblock thermoplastic elastomer substrate layer provides not only good adhesion but also soft modulus for antibiofouling performance. Spray-coating an SABC solution on the SEBS layer resulted in a uniform, fully covered hydrophobic semifluorinated surface.

Acknowledgements.

The authors acknowledge support from the Office Naval Research (award N00014-04-1-0257), and Strategic Environmental Research and Development Program (SERDP, PP-1454). The donation of triblock copolymers and helpful discussion from Dr. Dale Handlin and KRATON Polymers LLC are highly appreciated. We also thank the NIST/DOW materials end station at the National Synchrotron Light Source at Brookhaven National Laboratory for NEXAFS analysis.

References
(1) Anon, Propeller 2001, 12, 8.

Table 1. Results of Elementary and Thermal Analysis

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