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## Chapter – 7

# ENVIRONMENTALLY BENIGN MARINE ANTIFOULING COATINGS

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# ABSTRACT

The formation of biofilms of marine organisms on the surfaces of ship hulls, rudders, and propellers, heat exchangers in cooling water systems, water treatment membranes, aquatic sensors, and other equipment in contact with the marine environment is a challenging problem, associated with not only increased operation and maintenance costs, but also damage and loss of functionality caused by microbially induced corrosion. Surface modification using coatings is an approach that has been widely used to control marine biofilm formation. Until recently, marine antifouling coatings incorporated biocides that killed the microorganisms, and consequently had an unfavorable effect on the marine ecosystem. Over the past two decades, however, several environmentally friendly nanostructured polymer coatings have been developed as promising alternatives to the biocidal paints. Beginning with a brief discussion of the environmental problems arising from the use of biocides, this chapter examines the macromolecular structural design and surface science strategies used in the development of environmentally friendly nontoxic coatings. Fouling release coatings of block copolymers with fluorinated liquid crystalline side chains, silicone coatings filled with nanoparticles, hydrophilic antifouling coatings, amphiphilic block copolymer coatings, and coatings with nanoscale surface heterogeneities are discussed, along with a detailed specification of their surface properties, probed using techniques such as surface wettability analysis, near-edge X-ray absorption spectroscopy, and atomic force microscopy. Some biomimetic approaches, such as the incorporation of microorganisms that produce fouling-deterrent secondary metabolites, are also highlighted.

## 7.1 INTRODUCTION

Marine biofouling is the undesired attachment of microorganisms, seaweeds, and invertebrate animals on the surfaces of ship hulls and other artificial structures immersed in aquatic environments [1]. The corrosion and degradation of surfaces of ships by fouling organisms is a problem that is as old as the maritime industry. Until around mid-1800, timber planks were primarily used in ship construction. Wax, tar, and asphalt were probably the materials used by ancient mariners to protect the part of the hull below the waterline from decay [2]. In the context of the Indian subcontinent, an intense sea-route trade between the Roman Empire and Damirica (the ancient Tamil country) is mentioned in a first-century text called the Periplus of the Erythraean Sea [3, 4]. Trade between mariners of the Chola kingdom, particularly during the reign of Rajendra Chola I (1012–1047 CE), and China and Southeast Asia is well-documented. Not much information is available on the materials used in the construction of these merchant vessels. However, metal-sheathed hulls are mentioned in the eleventh-century Sanskrit text, *Yukti Kalpataru* [5]. The timber planks used for building the ships were also smeared with a synthetic "pitch" [6], hydrophobic in nature, for preserving the wood. The preparation of one such pitch involved heating a mixture of two parts of dammar (a triterpenoid resin) with one part of oil (extracted from fish) [7]. Another coating composition prevalent in India, consisted of plant oil mixed with hemp and lime, as reported by the thirteenth century Venetian seafaring trader, Marco Polo [8]. Lime was used as protection for wood against certain sea worms that were notorious for causing damage to the ship hulls in the gulf of Khambat, and was applied at least once a year [8].

In the late 1800s, as timber supply became scarce in Europe, particularly in England, iron began to replace wood in ship construction. Anderson et al. [9] have discussed the problem of galvanic corrosion when the iron ships were cladded with copper sheathing (that was previously successful in not only protecting wooden hulls from teredo worm, but also keeping fouling at bay). The solution of the problem required the assistance of Sir Humphry Davy, and involved cladding the iron ship hull with wood and then fixing the copper sheets to the wood, to avoid contact of the two metals. Sir Humphry Davy also demonstrated that copper dissolution in sea water prevented biofouling [2].

## 7.1.1 Tributyltin Self-Polishing Coatings

A major milestone in the history of modern marine antifouling coatings was the introduction of the "self-polishing" copolymer paints in the early 1970s, comprising of the tributyltin (TBT) biocides [10]. These paints were acrylic or methacrylic copolymers in which 50 to 80 percent by weight of the copolymer consisted of triorganotin salt (ester) of acrylic or methacrylic acid. The self-polishing effect in these coatings was by erosion, caused by hydrolysis of the polymer in the coating by moving seawater [11]. The antifouling action is through the release of biocides into the seawater in the vicinity of the eroding polymer front. These biocidal tributyltin based coatings were highly effective in solving the marine biofouling problem. Coatings with thicknesses that were optimized in relation to the ablation rate could ensure foulant-free hulls for up to five years [9]. However, environmental problems associated with biocidal TBT coatings began to appear as early as the 1980s. By 1987, most of the European countries had restricted the use of these coatings [12]. The International Maritime Organization's Convention on the Control of Harmful Antifouling Systems on Ships came into force in September 2008, and stated that "all ships shall not apply or re-apply organotin compounds, which act as biocides in antifouling systems". As of 2009, the convention was ratified by 28 nations, representing about 44 % of the world fleet [13]. Other non-signatory nations have regional regulations restricting the use of TBT-based paints.

## 7.1.2 Tin-free Biocidal Coatings

Tin-free self-polishing copolymers based on copper and zinc have been considered [11]. Several marine antifouling paints currently incorporate pigments such as cuprous oxide that can react with seawater to produce biocidal ions  $(Cu^{2+})$ . Cuprous thiocyanate and zinc oxide have also been used [2]. Because certain microfoulers such as algae are tolerant (resistant) to these coatings, secondary or booster biocides are added [14]. The co-biocides include zinc and copper pyrithione (Omadine), zinc dimethyldithiocarbamate (ziram), zinc ethylene bis(dithiocarbamate) polymer (zineb), N'-tert-butyl-

*N*-cyclopropyl-6-(methylthio)-1,3,5-triazine-2,4-diamine (Irgarol 1051), 3-(3,4-diclorophenyl)-1,1dimethylurea (DCMU, Diuron), 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine (TCMS pyridine), 2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil), *N*-dichlorofluoromethylthio-*N'*,*N'*-dimethyl-*N*phenylsulfamide (dichlofluanid), 4,5-dichloro-2-*n*-octyl-4-isothiazolino-3-one (Sea-Nine 211), triphenylborane pyridine, 8-methyl-*N*-vanillyl-6-nonenamide (capsaicin), and (*RS*)-4-[1-(2,3-dimethylphenyl)ethyl]-3*H*-imidazole (medetomidine) [2, 14, 15]. Of these compounds, Sea-Nine 211 and Zinc Omadine are approved by the US Environmental Protection Agency (EPA) for use in marine paints [16]. Nevertheless, due to concerns regarding adverse effects of biocides on non-target organisms [15], and their toxicity and persistence in the aquatic environment [12, 17], it is clear that "greener" non-biocidal antifouling coatings will be the materials of choice in the future.

## 7.1.3 Cu Accumulation and Toxicity: Need for Non-Biocidal Coatings

The 2016 draft criteria of the United States EPA for dissolved copper in estuarine or marine waters [18] recommends that the Cu concentrations should not exceed the acute and chronic toxicity levels of 2.0  $\mu$ g/L and 1.3  $\mu$ g/L, respectively. (These values are based on a temperature of 22 °C, a pH of 8, a dissolved organic carbon concentration of 1.0 mg/L, and a salinity of 32 parts per thousand. Concentration limits for other conditions of pH, temperature, salinity, and DOC are estimated using a "saltwater biotic ligand model").

Elevated copper concentrations, of up to 6  $\mu$ g/L of dissolved Cu and up to 10 pM of the toxic non-chelated free Cu<sup>2+</sup>, at sites with boats, in three San Diego Bay marinas (California, USA), were found to result in copper bioaccumulation in tissues of several macrobenthic species [19]. Copper accumulation in the marine environment, combined with ocean acidification due to increasing atmospheric CO<sub>2</sub>, could be an impending environmental problem, as already manifested in the form of increased copper toxicity in mussels [20]. Antifouling strategies that do not use any biocides are urgently needed. The development of such environmentally friendly alternatives is of particular relevance to India, whose large coastal population relies on fisheries production and export for food security and livelihood. Heavy metal contamination of the coastal waters of India, and in the coastal fishes, is becoming evident and is of concern [21, 22].

Numerous reviews and edited books have been published, in recent years, on the topic of environmentally friendly marine antifouling coatings [1, 2, 9, 23–41]. A goal of this chapter is to highlight some of the main classes of biocide-free coatings designed to prevent marine biofouling, with an emphasis on understanding how the surface chemistry of these coatings imparts resistance to biofouling. The focus will be on molecular properties of the surface and how these properties influence cell adhesion. A brief introduction of the mechanism of biofouling is followed by a discussion of hydrophobic fouling release coatings, hydrophilic non-biocidal antifouling coatings, amphiphilic block copolymer coatings, and coatings with nanoscale surface heterogeneities.

#### 7.2 SETTLEMENT AND ADHESION OF MARINE FOULING ORGANISMS

The first step in marine biofouling of a clean surface that is immersed in seawater is the formation of a conditioning film consisting of dissolved organic molecules such as carbohydrates and proteins. This is followed by colonization of the surface by a wide range of marine organisms. Figure 7.1 shows the diversity in type and size of marine fouling species. Unicellular organisms such as bacteria, diatoms, and protozoa form a complex biofilm consisting of organized communities of mixed microorganisms surrounded by a matrix of extracellular polymeric substances (EPS) [42]. These biofilms are referred to as "microfouling" or "slime". Macroscopically visible algae (seaweeds) and invertebrates such as soft corals, sponges, anemones, tunicates, and hydroids are called "soft macrofouling", and shelled



**Figure 7.1** Diversity and size scales of a representative fouling organisms. Reprinted with permission from ref. [1]; Copyright 2011 Macmillan Publishers Limited.

invertebrates such as barnacles, mussels, and tubeworms are called "hard macrofouling" [1]. Bacteria, motile spores of seaweeds, and certain larvae of invertebrates can all simultaneously colonize the surface, which results in a major challenge in creating a fouling-resistant coating that can resist fouling by organisms with a range of adhesion mechanisms (including the chemical composition of the EPS adhesive) and a range of sizes of the sensing apparatus that they use to select a surface for attachment [1].

Spores of the green alga (seaweed) *Ulva* use their apical papilla and barnacle cypris larva use a pair of sensory antennules to probe the surface. When a silicon surface coated with alternating stripes of hydrophobic 1H, 1H, 2H, 2H-perfluorooctyl-trichlorosilane and hydrophilic trimethoxysilylated poly(ethylene glycol) was exposed to *Ulva* zoospores (spores capable of swimming using flagella), the spores settled at higher densities on the fluorinated stripes compared with the PEGylated stripes, showing a clear preference for settlement on hydrophobic surfaces (see Figure 7.2). Stripes of different widths were studied. The spores were able to differentiate between the hydrophobic and hydrophilic regions when the pattern size was larger than 20  $\mu$ m, but were unable to do so when the features were smaller than 5  $\mu$ m [43]. The marine bacterium *Cobetia marina* (syn. *Deleya marina*) shows a similar preference for settlement on hydrophobic surfaces [44–46].

After the organism has settled on a surface, whether it can remain attached to the surface and grow into a reproductive adult depends on how well the organism's macromolecular adhesive is bonded to the surface, which is determined by the intermolecular forces of interaction between the adhesive plaque and the surface.

#### 7.3 FOULING RELEASE (FR) COATINGS

"Fouling release" coatings are an important class of biocide-free coatings that function on the basis of weak intermolecular forces of interaction between the bioadhesive and the coating surface. These



**Figure 7.2** Autofluorescence images of settled spores on regions of silicon wafer patterned with hydrophobic FOTS and hydrophilic PEG stripes. FOTS and PEG represent coatings of  $F(CF_2)_6CH_2CH_2SiCl_3$  and  $CH_3O(CH_2CH_2O)_{6-9}(CH_2)_3Si(OCH_3)_3$ , respectively. The dotted lines indicating the boundaries between PEGylated and fluorinated areas are provided to assist interpretation. Reprinted with permission from ref. [43]; Copyright 2008 American Chemical Society.

coatings do not prevent organisms from attaching, but the adhesion strength is weakened so that the attached organisms are more easily removed by the hydrodynamic shear forces generated by the relative movement of the surface in water.

Using Kendall's model, Chaudhury et al. [47] have discussed that the pull-off force, F, required to remove a hard object attached to a thick elastomeric surface is proportional to  $(WE)^{1/2}$ , where W is the work of adhesion and E is the Young's modulus of the surface.

When the surface is nonpolar, the work of adhesion, W, between the coating and the bioadhesive is given by  $2(\gamma_s \gamma_l^d)^{1/2}$ , where  $\gamma_s$  is the surface energy of the coating and  $\gamma_l^d$  is the dispersive component of the surface energy of the liquid adhesive secreted by the marine organism [23]. Here, we have used the Dupré equation,  $W = \gamma_s + \gamma_l - \gamma_{sl}$ , for the work of adhesion, W, in terms of the surface energies,  $\gamma_s$  and  $\gamma_l$ , and the interfacial energy,  $\gamma_{sl}$ , and the Fowkes-approximation,  $\gamma_{sl} \approx \gamma_s + \gamma_l - 2(\gamma_s \gamma_l^d)^{1/2}$ , for interfacial energy between two surfaces that adhere purely by dispersive intermolecular interactions. Thus, a 0.5 order of dependence of F on the coating modulus and a 0.25 order of dependence on the coating surface energy is indicated by this analysis, which calls for soft (compliant) low surface-energy coatings to achieve easy fouling release. (Note that the order of dependence on the coating surface energy, based on this analysis, is lower than the commonly assumed value of 0.5 [9]).

The surface energy (surface tension) values of some common liquids and polymer surfaces are compiled in Table 7.1. It is seen that, among the polymers listed, poly(tetrafluoroethylene) (PTFE) and poly(dimethylsiloxane) (PDMS) have the lowest surface energy values. PTFE is a highly crystalline polymer, with a melting temperature of about 327 °C, and is, therefore, difficult to process by conventional techniques. Moreover, PTFE has a relatively high Young's modulus at room temperature ( $\cong$  400 MPa). These properties make the PTFE homopolymer unsuitable for practical application as marine antifouling coatings.

In contrast, PDMS, a polymer with low glass transition temperature (approximately  $-121 \text{ }^{\circ}\text{C}$ ) is soft at room temperature, and its surface is nonpolar, with a relatively low surface energy of about

 $21 \text{ mJ/m}^2$ . This polymer was, therefore, among the earliest successfully used nontoxic fouling release coating for ship hulls. PDMS-based coatings are crosslinked elastomers, generally obtained by the reaction of hydroxyl-terminated PDMS oligomers with tetraalkoxysilane crosslinking agents. Low-temperature vulcanization via the hydrosilylation reaction on vinyl-terminated PDMS is also possible.

After 10 years in service, a crosslinked PDMS elastomer (PDMSe) applied on a *Tropic Lure* ship hull was found to be relatively clean, without macroalgae or barnacle adhesion, when simply maintained by high pressure washing and repair to damaged areas [9]. Some commercial silicone coatings contain small amounts of non-bonded silicone oils, such as methyl phenyl silicone, to enhance foul-release properties of the coating. It was found that these oils remained in the coating, without leaching into seawater [9].

Although PTFE is not a marine antifouling coating per se, a variety of fluoropolymer coatings making use of the low surface energy of fluoroalkyl groups have been developed. In a study comparing marine antifouling properties of two Intersleek non-biocidal silicone and fluorpolymer-modified silicone coatings (IS700 and IS900, respectively), the fluorinated coating was found to be more effective in short-term (10-day) field experiments.

For a nonpolar surface interacting with water, the surface energy,  $\gamma_s$ , is related to the water contact angle,  $\theta_w$ , by  $\gamma_s = 0.25\gamma_w^2(1 + \cos\theta_w)^2/\gamma_w^d$ , where  $\gamma_w$  and  $\gamma_w^d$  are the total surface energy of water (73 mJ/m<sup>2</sup>) and the dispersion component of its surface energy (22 mJ/m<sup>2</sup>), respectively. From this equation, it is evident that surfaces with lower water contact angle values have higher surface energies.

Material	Chemical structure	Surface energy $\gamma$ (mJ/m <sup>2</sup> )
<i>n</i> -Perfluorohexane [49]	$CF_3(CF_2)_4CF_3$	12
<i>n</i> -Perfluorononane [49]	CF <sub>3</sub> (CF <sub>2</sub> ) <sub>7</sub> CF <sub>3</sub>	15
<i>n</i> -Hexane	$CH_3(CH_2)_4CH_3$	18
Hexadecane	$CH_3(CH_2)_{14}CH_3$	28
Water	H <sub>2</sub> O	73
Poly(tetrafluoroethylene) (PTFE)	$(-CF_2CF_2-)_n$	19
Poly(dimethylsiloxane) (PDMS)	$ \begin{array}{c} CH_{3} \\ -\left(-Si - O\right)_{n} \\ CH_{3} \end{array} $	21
Poly( <i>n</i> -hexyl methacrylate)	$- \underbrace{(CH_2 - CH_3)}_{O^{< C} O^{< -}} $	30

TABLE 7.1. Surface Energy of Some Common Liquids and Polymers at Room Temperature<sup>[a]</sup>

<sup>[a]</sup> Data compiled from references [50] and [51], and other sources.

Material	Chemical structure	Surface energy $\gamma$ (mJ/m <sup>2</sup> )
Poly( <i>n</i> -butyl methacrylate)	$-\left(-CH_{2}-CH_{3}-CH_{2}-CH_$	31
Polyethylene		32
Poly( <i>n</i> -butyl acrylate)	$-\left(-CH_2-CH\right)_n$	34
Poly(2,3,4,5,6-pentafluorostyrene)	$ \begin{array}{c} -\left( CH_2 - CH \right)_n \\ F \\ F \\ F \\ F \\ F \end{array} $	35 <sup>[b]</sup>
Poly(methyl methacrylate)	$-\left(CH_2-C\right)_n^{CH_3}$	40
Polystyrene (PS)	-(CH <sub>2</sub> -CH) n	41
Poly(ethylene oxide) (PEO)	$-\left(-CH_2CH_2O\right)_n$	43
Poly(4-vinyl pyridine) (P4VP)	-(-CH <sub>2</sub> -CH) n	47 <sup>[c]</sup>

# **TABLE 7.1** (Continued)

<sup>[b]</sup> based on solubility parameter; a value of  $33 \pm 3 \text{ mJ/m}^2$  determined using contact angle measurements, is found experimentally [52]

<sup>[c]</sup> based on molar parachor and solubility parameter predictions; a value of  $68.2 \text{ mJ/m}^2$  is reported in ref. [53]

The static water contact angle on IS900 is only about 76° [48]. In contrast, IS700 has a hydrophobic surface with a water contact angle of about 99°. On the basis of this fact, IS900 would have a higher

surface energy than IS700. The superior FR performance of IS700 cannot be because of a lower  $\gamma_s$ , but probably due to nanoscale surface heterogeneities and/or an amphiphilic nature (which will be discussed separately in a following section).

Among the early fluorinated coatings designed for marine antifouling application was the one in which reactive perfluoroalkyl polymeric surfactants were crosslinked with poly(2-isopropenyl-2-oxazoline) [54]. The goal was to prepare a purely hydrophobic coating. But the advancing and receding water contact angles on these coatings were relatively low (a maximum of about 94° and 53°, respectively) due to the presence of polar functional groups at the surface. Surface reconstruction, defined as the rearrangement of chemical groups at the interface of the coating with water for the lowering of interfacial energy, is a problem when hydrophobic coatings are immersed in water. Polar groups tend to migrate to the polymer–water interface, resulting in a loss of the nonpolar character of the surface and, therefore, its "non-stick" properties. The coatings of Schmidt et al. [54], and other fluorinated polyurethane coatings discussed in ref. [23], relied on crosslinks as barriers to hinder surface reconstruction.

#### 7.3.1 FR Coatings with Fluorinated Liquid Crystalline Side Chains

Ober and coworkers [55] used the self-assembly of liquid crystalline (LC) perfluoroalkyl mesogens to design block copolymer coatings that were resistant to surface reconstruction. The block copolymers consisted of a polystyrene block and a fluorinated block, in which the perfluoroalkyl groups were attached to the polymer backbone through flexible alkyl spacers. Figure 7.3(a) shows the chemical structure of a representative block copolymer that consisted of perfluorodecyl mesogen in the side chain, connected to the polymer backbone by a nine carbon atom long alkyl spacer. A schematic of self-assembly of the mesogens is shown in Figure 7.3(b).



**Figure 7.3** (a) Comblike block copolymer with hydrophobic LC semifluorinated side-chains. (b) Liquid crystalline self-assembly of the semifluorinated side-chains to form a non-reconstructing hydrophobic surface under water.

The synthesis and surface properties of these block copolymers (with different lengths of perfluoroalkyl mesogens and alkyl spacers) are reviewed in ref. [23]. The rigid perfluoroalkyl groups formed a smectic LC phase in the bulk, and also at the surface of the coating. The melting point (clearing temperature) of the smectic mesophase ranged from about 20 to 100 °C depending on the lengths of the fluoroalky mesogen and alkyl spacer in the side chains. Thus, when the mesogen and spacer lengths were designed to have a melting temperature of the smectic phase that was significantly higher than room temperature, underwater surface reconstruction could be prevented. Advancing and receding water contact angles as high as 123° and 112°, and a surface energy as low as 8 mJ/m<sup>2</sup>, could be achieved using this approach.

Note that the surface energy of these polymers is lower than even that of perfluorohexane or PTFE (cf. Table 7.1) because of complete coverage of the surface with  $-CF_3$  groups, caused by LC self-assembly. Indeed, the contribution of different groups to the lowering of surface energy decreases in the order  $-CF_3 > -CF_2 - > -CH_3 > -CH_2$ . The  $-CF_3$  group with a hemispherical volume of 42.6 Å<sup>3</sup>, which is significantly higher than hemispherical volume of the-CH<sub>3</sub> group (16.8 Å<sup>3</sup>) [56], shields the surface better and minimizes the interaction of water with any underlying polar groups.

The fluorinated block copolymer of Figure 7.3(a) was soluble in organic solvents, and could be processed using techniques such as spin coating and spray coating. Figure 7.4(a) shows a tapping-mode atomic force microscopy (AFM) phase image of a coating prepared by spraying. The AFM image is consistent with X-ray scattering results that showed the formation of cylindrical nanostructures (standing up perpendicular to the substrate) by microphase separation of the polystyrene and the fluorinated blocks [see Figure 7.4(b)]. Grazing incidence X-ray scattering studies (GISAXS) indicated self-assembly over three different length scales: microphase separation of the two blocks, smectic layer formation of the fluorinated mesogens, and hexagonal packing of the mesogens within a smectic layer [57]. The smectic layers in these coatings spontaneously self-assembled to be predominantly parallel to the coating surface, as desired.

We evaluated the antifouling properties of the fluorinated block copolymer coatings for adhesion strength of *Ulva* sporelings [Figure 7.1(j)] and *Navicula* diatoms [Figure 7.1(d)], and found that these coatings resulted in only a weak adhesion of *Ulva*, but a strong adhesion of the diatoms [58]. Adhesion of diatoms is a long outstanding problem for most non-biocidal hydrophobic surfaces, including those of PDMSe. The green alga *Ulva* is resistant to copper-based antifouling paints [9] and diatom biofilms are difficult to remove from silicone coatings [31]. Therefore, new coatings that are resistant to fouling by both of these organisms are required.



**Figure 7.4** (a) Tapping-mode AFM phase image of a spray-coated surface of LC fluorinated block copolymer with a chemical structure shown in Figure 7.3. (b) Model of self-assembly in block copolymer with LC semifluorinated side chains [57,58].

Using a bilayer coating approach, the coating surface energy,  $\gamma_s$ , and modulus, *E*, could be independently varied. The modulus of the coating was controlled using a poly[styrene-*block*-(ethylene-*ran*-butylene)-*block*-styrene] (SEBS) triblock copolymer as the base layer [58]. The Young's modulus of the base layer depended on the weight fraction of the styrene block in SEBS. It was 18 MPa for Kraton G1652 and about an order of magnitude lower for Kraton MD6945 (1.2 MPa). A significantly improved fouling release behavior was observed when the softer (compliant) SEBS was used as the base layer [59]. Note that commercial PDMSe coatings such as RTV11 and Intersleek have a modulus in the range of 1 to 3 MPa.

The use of SEBS as the base layer also solved the problem of adhesion of the "non-stick" coatings to surfaces of interest. SEBS, grafted with maleic anhydride (MA) groups, adhered strongly to glass and metals, through the reaction of MA groups with the hydroxyl groups on the substrate. In addition, the fluorinated block copolymer [Figure 7.3(a)] adhered well to the SEBS base layer, due to the presence of a common polystyrene block. In this manner, a variety of coatings [58–63] remained well-adhered to the substrates, and could be tested in a turbulent flow channel at high flow rates, without the coatings peeling off from the substrates [64].

Besides modulus and surface energy, the thickness of the coating also plays an important role in fouling release performance. Theoretically, when the contact radius of an object with a coating is significantly higher than the coating thickness, the pull-off force is proportional to  $(WE/h)^{1/2}$ , where *h* is the thickness of the coating [47]. (In contrast, when the coating is significantly thicker than the size of the adhering object, there is no thickness dependence of contact force). Accordingly, Wendt et al. [65] found that the critical stress required for removing barnacles adhered to PDMSe coatings of different thicknesses (0.1 mm, 0.5 mm and 2 mm), decreased with an increase in the coating thickness.

#### 7.3.2 Developments in Silicone Fouling Release Coatings

#### Polyureas and Polyurethanes

Oil-filled PDMS elastomer coatings suffer from the problems of poor bonding to a substrate because of their low surface energy, and easy damage because of their low surface hardness. PDMS based polyurea (containing the -NHC(=O)NH- urea linkages) [66] and polyurethanes (containing the -NHC(=O)O- urethane linkages) [67], were synthesized to improve adhesion to the substrate with the help of hydrogen bonding interactions of the polar urea or urethane groups. In the case of the PDMSbased polyurea coatings, the composition containing 41 wt % of the hard polyurea segment resulted in a higher percentage removal of *Navicula* diatoms than the PDMS homopolymer coating, under the same water-jet pressure ( $\cong$  20 kPa) [66]. This coating was hydrophobic, with a static water contact angle of about 100° that decreased to about 95° after 60 days of immersion in artificial seawater. The advancing and receding water contact angles were 105° and 89°, respectively. In the design of such coatings, it is important to ensure that the surfaces present a siloxane-rich surface even after immersion in water, and that the polar urea/urethane groups that migrate to the polymer-water interface do not cause strong bonding with the adhesive secreted by the marine organisms. If the surface functional groups react or interact with the organism's EPS, the fouling release property will be lost. Consequently, in pseudobarnacle assays, the coatings containing the polyurea block showed a higher pull-off force compared with PDMS homopolymer.

#### Carbon Nanotubes and Clay Fillers

Silicone-based coatings filled with low levels (0.05 wt %) of multi-walled carbon nanotubes or sepiolite clay particles resulted in improved release of *Ulva* sporelings and reduction in the adhesion strength of adult barnacles [68]. No major changes in mechanical properties were observed by the low

amounts of filler. The observed enhancement in FR behavior was attributed to the change in the surface properties of the elastomer upon adding the filler particles. In contrast, previous studies on PDMSe coatings containing higher concentrations of fillers such as silica and calcium carbonate showed an adverse effect on FR performance, caused by the increase in the modulus of the coatings [69].

#### Biocidal Silicone Coatings

As previously stated, the ultimate goal of the marine antifouling technology research is to develop coatings that will not kill marine organisms, but will repel or prevent them from settling on their surfaces. Such coatings would be not only self-cleaning, but also self-healing, similar to some of the inherently antifouling surfaces in nature [70]. Nevertheless, antifouling coatings based on biocidal action are also being actively researched, perhaps due to the inability of nontoxic coatings to satisfactorily solve the biofouling problem. The latter get heavily fouled within a few months of immersion in water. PDMSe [71] (and poly(methyl methacrylate) [72]) coatings, containing biocidal CuO and ZnO nanoparticles, were found to remain free of foulants even when there was no water flow past the surface. Other biocidal coatings include PDMS-based polyurethane containing the N-(2,4,6-trichlorophenyl)maleimide (TCM) biocide as pendant groups, tethered to the polymer backbone through the hydrolytically stable thioether group [73], and PMDS coatings with tethered quaternary ammonium salts [74]. The TCM-tethered PDMS-polyurethane coatings showed promising antifouling performance against barnacle cyprids, the marine bacterium *Micrococcus luteus*, and the diatom, Navicula. The polysiloxane coatings containing tethered quaternary ammonium salt showed antifouling behavior against the marine bacteria, Cellulophaga lytica and Halomonas pacifica, and the diatom, Navicula. In contrast, certain block copolymers with quaternary ammonium pendant groups, that we evaluated for fouling by Ulva sporelings and Navicula diatoms did not show marked algicidal activity, but they were highly effective against the airborne bacterium Staphylococcus aureus [75].

## 7.3.3 Other Fouling Release Coatings

A variety of other fouling release coatings have been reported. These include perfluoropolyether-based crosslinked elastomers [76], fluoropolymer/siloxane block copolymers and blends [77–79], fluorinated polyurethanes [80], and xerogel coatings [48, 81], including the halide permeable siloxane xerogels containing sequestered catalyst (for *in situ* formation of biocidal hypohalous acid through oxidation of the halide salts in seawater by the H<sub>2</sub>O<sub>2</sub> released by organisms in the biofilm) [82]. Details on some of these coatings are available in previous reviews [23, 24].

## 7.4 HYDROPHILIC NON-BIOCIDAL ANTIFOULING COATINGS

Hydrophilic coatings are those with surfaces that are partially or completely wetted by water and have water contact angles below 90°. The silicone and fluorinated FR coatings discussed in previous section are hydrophobic in nature. Water contact angles of up to about 126° are found for smooth compact layers of hydrophobic fluoroalkyl groups [83]. By controlling surface roughness, superhydrophobic surfaces with water contact angles as high as 175° can be obtained [84–86]. Such hydrophobic FR coatings allow easy detachment of marine organisms that settle on and adhere to the surface. However, antifouling surfaces, which can prevent biofouling right at the stage of settlement (and not after settlement and attachment, as in the case of FR coatings), are highly attractive and much required.

Research in the biomedical field has shown that hydrophobic surfaces are, in fact, favorable for initial attachment of fouling species, and that hydrophilic surfaces are required for biofouling resistance [87, 88].

#### 7.4.1 Surface Hydration and Polymer–Water Interfacial Energy

The high interfacial energy of a hydrophobic surface in contact with water is the thermodynamic driving force for adsorption of amphiphilic molecules, such as proteins, at these surfaces. Consider, for example, the fluorinated surface with a surface energy of 8 mJ/m<sup>2</sup> and water contact angle,  $\theta_w$ , of 123°. The interfacial energy between the surface and water,  $\gamma_{sw}$ , is given by  $\gamma_{sw} = \gamma_s - \gamma_w \cos \theta_w$ , which (using the surface tension of water,  $\gamma_{w}$ , equal to 73 mJ/m<sup>2</sup>) is calculated to be about 48 mJ/m<sup>2</sup>. Protein adsorption would be thermodynamically favored at this interface, because it would lead to a significant reduction in the interfacial energy. Consider, on the other hand, a hydrophilic surface such as a zwitterionic block copolymer coating reported in ref. [52]. For this coating,  $\gamma_s$  was found to be about 31 mJ/m<sup>2</sup> and the water contact angle was 66°. The interfacial energy is only about 1 mJ/m<sup>2</sup>.

Hydrophilic surfaces possessing low interfacial energy with water are resistant to protein adsorption and cell attachment. They are also resistant to settlement by larger organisms. For example, hydrophilic coatings prepared using the poly(2-methyl-2-oxazoline) dimethacrylate macromonomer were found to greatly decrease the settlement of cyprids of *Amphibalanus amphitrite* compared with bare silicon [89]. Polymer brushes (surface-tethered coating of polymer molecules) containing the zwitterionic sulfobetaine groups are highly resistant to the settlement of *Ulva* zoospores [90]. Most spores remain motile (free-swimming above the surface) and do not settle on these surfaces. In the case of the few spores that do settle and release their adhesive, the adhesive is not able to bond to the surface.

There are a few "rules" for a hydrophilic surface to be antifouling. For stable surface hydration, which is essential for preventing biofouling [91], at least two proton acceptor oxygen atoms must be present in the monomer structure, allowing strong hydration bonds in a double hydrogen bridge bonding configuration [92]. For more information on such rules (and exceptions), the reader is referred to ref. [23].

#### 7.4.2 Settlement of Ulva Zoospores on OEG and PEG SAMs

The preference of *Ulva* zoospores for settlement on hydrophobic surfaces, avoiding hydrophilic surfaces, is clearly demonstrated by the study using surfaces with micropatterned surface-wettability that was previously discussed (cf. Figure 7.2, [43]). Grunze and coworkers conducted an in-depth comparison of *Ulva* zoospore settlement on self-assembled monolayers of short chain oligo(ethylene glycol) (OEG) terminated alkane thiols and longer chain poly(ethylene glycol) (PEG) SAMs [92]. The SAMs were prepared using the thiols  $HS(CH_2)_{11}(OCH_2CH_2)_YOX$  (EG<sub>Y</sub>OX, where Y = 1–6 and X = H or CH<sub>3</sub>) and  $HS(CH_2)_2(OCH_2CH_2)_YOX$  (PEG<sub>Y</sub>OX, where Y = 44 or 112 and X = H or CH<sub>3</sub>), respectively. Glass slides coated with gold thin films were used as the substrates.

Although the *Ulva* zoospores settled on the surfaces of EG<sub>6</sub>OH, shed their flagella, and secreted their adhesive, the adhesive was unable to irreversibly bond to the surface. The strength of adhesion of the settled spores was so low that even small shear forces (generated by small displacements of the substrates in the assay dishes, or by removal of the substrates through the water–air interface) was sufficient to remove the attached spore from the surface. The weak adhesion of the spores to the short chain length OEG SAMs was attributed to the remarkable strength of the bifurcated hydration bond of water to the OEG chain. In contrast, on the longer chain PEG surfaces, most of the spores did not settle at all. They did not secrete their adhesive and continued swimming above the surface of the SAM. The ability of PEG to inhibit spore settlement is because of steric repulsion of the loosely packed polymer layer with high water content [24]. Similarly, while the EG<sub>6</sub>OCH<sub>3</sub> SAM, with a water contact angle of  $33^{\circ}$ , there was hardly any effect of the terminal group (H or CH<sub>3</sub>) on the spore settlement density in the case of the

thicker PEG<sub>Y</sub>OX SAMs. Both the hydroxyl- and methoxy-terminated PEG coatings prevented the spores from settling.

 $EG_6OH$  SAMs also showed remarkable resistance against attachment of *Cobetia marina* [44].

#### 7.4.3 Antifouling Coatings with PEGylated Side Chains

In our initial studies on developing hydrated antifouling polymer coatings, diblock copolymers with methoxy-terminated PEG side chains, containing an average of 11 mers of ethylene glycol in each side chain, were evaluated for fouling by Ulva zoospores and Navicula diatoms [58]. Although the growth of sporelings on the PEGylated surfaces were significantly lower, and the release of Navicula diatoms was much higher, compared with the PDMSe coatings, the expected cell-repellent behavior of hydrophilic PEGylated surfaces, that is, their ability to completely prevent the settlement of Ulva zoospores, was not observed. There was no significant difference in the amount of Ulva sporelings between hydrophobic fluorinated and hydrophilic PEGylated block copolymer coatings. After a detailed investigation of the surfaces using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, that probes surface composition in the top 3 nanometers of a polymer surface, it became clear that a significant amount of the polystyrene block was present at the surface, even after using spray-coating solvents and processing conditions that would lead to surface enrichment of the hydrophilic PEG groups. The presence of both PEG and polystyrene at the surface is due to comparable surface energies of dry PEO and polystyrene (43 and 41 mJ/m<sup>2</sup>, respectively; see Table 7.1). Because of the slightly higher surface energy of PEG, a preferential segregation of polystyrene would occur when the coating is prepared in air (or analyzed in vacuum).

## 7.4.4 Analysis of Surface Composition Using NEXAFS Spectroscopy

NEXAFS spectroscopy is a synchrotron-based X-ray absorption spectroscopy technique that is highly sensitive to the composition and orientation of chemical bonds at the surface. The surface is irradiated with a beam X-ray photons of different energies (e.g., 270 to 320 eV in increments of 0.1 eV, in C 1s NEXAFS spectroscopy) and the intensity of the emitted Auger electrons, called the partial electron yield (PEY), is recorded for each photon energy. Figure 7.5 shows the C 1s NEXAFS spectra of four different polymer coatings.

The spectral features of each polymer in this set are remarkably distinct from those of the other polymers. The  $C \ 1s \rightarrow \sigma_{C-F}^*$  resonance peak is prominently seen near 293 eV in the spectrum of the fluorinated block copolymer coating. The peak near 285.5 eV seen in the polystyrene spectrum is due to the  $C \ 1s \rightarrow \pi_{\Phi}^*$  resonance. The relative intensities of the peaks in the block copolymer surfaces at this energy are proportional to the surface styrene contents. The  $C \ 1s \rightarrow \pi_{\Phi}^*$  peak intensity, and therefore, the surface concentration of the polystyrene block is small in the case of the fluorinated block copolymer [see chemical structure in Figure 7.3(a)], whereas it is higher for the block copolymer grafted with 11-mer long methoxy-terminated PEG groups. Figure 7.5(d) is the NEXAFS spectrum of SEBS (Kraton G1652). The low intensity of the  $C \ 1s \rightarrow \pi_{\Phi}^*$  peak, from the polystyrene block, indicates that the surface of the SEBS coating is composed mainly of the lower surface energy poly(ethylene-*ran*-butylene) central block.

## 7.4.5 Surface Delivery Vehicles

Surface delivery vehicles or surface anchor groups are used to bring functional groups with high surface energy to the surface of a coating [93]. Figure 7.6 illustrates the idea using representative cases of linear and comb-like diblock copolymers. Figure 7.6(i) shows the simplest case of a diblock





**Figure 7.5** C 1s partial electron yield vs. X-ray photon energy NEXAFS spectra of (a) polystyrene, (b) block copolymer with LC semifluorinated side chains, (c) block copolymer with poly(ethylene glycol) side chains, and (d) polystyrene-*b*-poly(ethylene-*r*-butylene)-*b*-polystyrene (SEBS) coatings. All spectra were obtained using X-ray incidence angle of  $55^{\circ}$  [58].

copolymer coating, in which the surface is covered by the lower surface energy B block. However, the higher energy A block may be forced to be present at the surface by end-functionalization of the A block with a low-energy surface-anchor group C. In addition to the difference in surface energy values, the ability of the C group to drag the higher surface energy block to the surface depends on factors such as the lengths of the A and B blocks, and the polymer–polymer interaction parameter,  $\chi_{AB}$ .

We investigated the strategy of end-functionalization, shown schematically in Figure 7.6(ii), using polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymers [53]. The objective was to bring the higher surface energy P4VP block to the surface of the coating. Toward this goal, the P4VP block was end-functionalized with (heptadecafluoro-1,1,2,2-tetrahydrodecyl)-dimethylsilane groups that contained the low-energy perfluorooctyl surface anchor [94]. However, NEXAFS spectroscopy showed that the surface of the thermally annealed block copolymer film was covered mostly by the PS block. The relatively small perfluorooctyl group at the end of the polymer chain was not able to drag the P4VP block to the surface.



**Figure 7.6** Schematic of surface-energy dependent surface composition of: (i) a diblock copolymer with surface energy of B block lower than that of the A block; (ii) a diblock copolymer with a low surface-energy surface anchor group, C, tethered to the end of the high surface energy block, A; (iii) a comb-like block copolymer in which side-chains or grafts G are present in one of the blocks; and (iv) a comb-like block copolymer in which the grafts, G, are end-capped with low surface-energy groups, F. The surface energies,  $\gamma_A$ ,  $\gamma_B$ ,  $\gamma_C$ ,  $\gamma_D$ ,  $\gamma_F$ , and  $\gamma_G$  are relative to the medium that the coatings of the block copolymers are in contact with. The conformation of the polymer backbone and the side chains depends on the chemical details of the constituent groups, and can be, for example, flexible random coil or rigid rod depending on how the backbone bonds can rotate under steric constraints present in the molecular unit.

Instead of end-functionalization, if the surface anchor groups were grafted to the polymer backbone—by quaternization reaction of the pyridine group with 1-bromohexane and/or 6-perfluorooctyl-1-bromohexane (see Figure 7.7)—X-ray photoelectron spectroscopy, NEXAFS spectroscopy, and water contact angle measurements showed that the high-energy pyridinium block was drawn to the surface by the low-energy hexyl and perfluorooctyl side chains. This approach is illustrated schematically in Figures 7.6(iii) and 7.6(iv), for comb-like polymers. A characteristic

feature of such amphiphilic coatings, consisting of a combination of low and high surface energy groups, is that their surfaces exhibit a large hysteresis in water contact angles, that is, their advancing water contact angle is significantly higher than the receding water contact angle.



**Figure 7.7** Diblock copolymer (a) and terpolymer (b) with low-energy alkyl and fluoroalkyl surface anchor groups in the side chains [94]. Two different degrees of polymerizations were studied: (i) m = 105, n = 200 and (ii) m = 600, n = 630.

#### 7.5 AMPHIPHILIC BLOCK COPOLYMER COATINGS

We used the approach of surface anchoring to prepared PEGylated antifouling surfaces using block copolymer coatings [60]. By attaching low-energy fluoroalkyl groups to one end of the PEG grafts, we were able to enrich the surfaces of these coatings with the higher energy PEG segments. Figure 7.8 shows the chemical structures of the block copolymers with fluoroalkyl-terminated PEGylated side chains. Two different block copolymers were initially investigated. Atomic force microscopy (AFM) of the surface was performed both in air, and under water (phosphate-buffered saline solution). The block copolymer with m = 82 and n = 23 showed lamellar morphology with a uniform surface layer of the PEGylated block (see the AFM image in Figure 7.9). The block copolymer with m = 369 and n = 43 exhibited cylindrical microdomains at the surface [95]. The water-swollen films showed a domain size of the order of 35 nm.



**Figure 7.8** Block copolymers with fluoroalkyl-tagged PEG side groups. The number average degrees of polymerization in the block copolymers studied were: (i) m = 82, n = 23 [60] and (ii) m = 369, n = 43 [95]. The average values of x and y were about 3.5 and 3, respectively.



**Figure 7.9** Tapping mode AFM topography (left) and phase (right) images of the block copolymer of structure shown in Figure 7.8, with m = 82 and n = 23 [60]. The dark spots are "holes" [97] formed because of the mismatch between the film thickness and the periodic lamellar domain spacing in the diblock copolymer film.

The coating with block lengths m = 82 and n = 23 showed higher removal of *Ulva* sporelings than PDMSe, and more remarkably, a higher removal of *Navicula* diatoms as well (more than 80 % removal, compared with only about 10 % removal from PDMSe) [60]. Although perfect antifouling behavior, in terms of low settlement density of the *Ulva* zoospores, was not demonstrated with this block polymer architecture, the block copolymer coating with m = 369 and n = 43 showed excellent resistance to protein adsorption in fluorescence microscopy assays and adhesion force measurements (using AFM) [95]. Subsequent studies, using block copolymers with different architectures, for example, an ABC triblock copolymer consisting of polystyrene, poly(ethylene-*ran*-butylene) and a third block grafted with the fluoroalkyl-terminated PEG side chains [59], and surface anchor groups of different compositions, e.g., alkyl groups [63], or grafts of short PDMS groups [96], demonstrated good inhibition of the settlement of *Ulva* zoospores as well. The settlement density of the *Ulva* zoospores on these surfaces was significantly lower than that on PDMSe.

Other architectures, employing the low-energy fluoroalkyl groups as surface anchors, have been reported for PEGylated block copolymer coatings. The chemical structure of one such polymer is shown in Figure 7.10 [98]. This diblock terpolymer consisted of a PS block and a second PEO block in which some of the mers were derivatized with perfluorohexyl surface anchor groups. NEXAFS spectroscopy showed that there was no PS at the surface when at least 8 mol % of the mers in the PEO block were fluorinated. The settlement density of *Ulva* zoospores on the surfaces of the block copolymer coatings with 8 and 17 mol % of fluorinated mer, was significantly lower compared to the block copolymer without any fluoroalkyl anchor and also compared to PDMSe. Furthermore, the removal of *Ulva* sporelings after exposure to water flow (24-Pa wall shear stress) was high for these coatings.



**Figure 7.10** Poly(ethylene oxide) (PEO) based diblock terpolymer containing fluoroalkyl surface anchor groups: (i) m = 105, n = 1140, y = 8 mol %; (ii) m = 105, n = 840, y = 17 mol % [98].

The fluoroalkyl-terminated PEG groups were successfully used as surface delivery vehicles for high surface energy zwitterionic groups in carboxybetaine and sulfobetaine derivatized block copolymers, resulting in coatings that were resistant to both positively and negatively charged protein molecules [52].

## 7.5.1 Surface-Wettability of Amphiphilic Coatings

Stable (non-reconstructing) hydrophobic surfaces are characterized by high advancing water contact angles and low contact angle hysteresis. In contrast, a surface of an amphiphilic polymer, such as that shown in Figure 7.7, 7.8, or 7.10 exhibits a large contact angle hysteresis, attributed to surface reconstruction when the dry coating comes in contact with water. This reconstruction is reversible and occurs over a time period that spans two different orders of magnitude [60]. Changes in the molecular composition of the surface up on immersion in water have been probed using techniques such as captive bubble contact angle measurement [60], NEXAFS spectroscopy [99, 100], and AFM [95].

The advancing and receding contact angles on the amphiphilic block copolymer surface with m = 82, n = 23 were 94° and 34° [60]. This difference in the water contact angles is caused by surface restructuring that happens over a short time scale, e.g., the flipping of the fluoroalkyl-tagged PEG side chains, such that the fluoroalkyl groups moves away from the water interface, exposing the PEG segments at the interface. The captive bubble contact angle decreased from 55° immediately after immersion in water to a value of about 31° after 2 weeks. This slower process is attributed to reconstruction of the block copolymer microstructure at the water interface. The hydrophilic block will preferentially move to the interface and the hydrophobic PS block will more away from the interface. By also measuring the equilibrium underwater octane contact angle (55° measured on the water side), it was possible to estimate the polymer–water interfacial energy. The interfacial energy was fairly low, 4 mJ/m<sup>2</sup>, as would be theoretically necessary for the surface to be resistant to adsorption of proteins.

# 7.6 COATINGS WITH NANOSCALE SURFACE HETEROGENEITIES

## 7.6.1 Hyperbranched Fluoropolymer–PEG Copolymer

Wooley and coworkers [101] postulated that surfaces of compositionally variant, nanoscopically resolved morphologies and topographies would be unfavorable for adsorption and unfolding of adhesive proteins if the dimensions of the topographical features are comparable to those of the proteins. The coatings, obtained by reacting a hyperbranched polyfluorinated benzyl ether polymer with bis(3-aminopropyl)-terminated PEG, were found to undergo a kinetically trapped phase segregation of the chemically incompatible PEG and hyperbranched fluoropolymer. Tapping-mode AFM showed a surface topography that was dependent on the weight percentage of PEG in the coating, and which changed upon incubation in artificial seawater due to the migration of PEG-rich domains to the water interface. Coatings with high concentrations of PEG (45 to 55 %) were effective against settlement of the *Ulva* zoospores.

## 7.6.2 Microphase Separation in Amphiphilic Block Copolymers

Galli and coworkers [61] investigated the role of nanoscale surface heterogeneities on marine antifouling properties of block copolymer coatings. Block copolymers similar to that shown in Figure 7.8, but with styrenic (instead of acrylic) backbone, were synthesized with different combinations of block lengths (m and n). The surface compositions, and the microphase separation of the two blocks in the bulk of the coating, were investigated using NEXAFS spectroscopy, XPS, AFM,

dynamic water contact angle measurements, and GISAXS [100]. Figure 7.11 shows tapping-mode AFM images of the surfaces of representative block copolymer surfaces, wherein cylindrical and spherical nanodomains are clearly seen. In these coatings, discrete nanodomains of polystyrene were dispersed in the continuous matrix of the amphiphilic block. However, turbulent flow channel assays for adhesion of *Ulva* sporelings and *Navicula* diatoms did not show any correlation between adhesion strength and the microstructure of the dry block copolymer film, evidently because both the block copolymer chosen for the study contained the amphiphilic block at the surface. There were no significant differences in the water contact angle or surface energy values either.



**Figure 7.11** Tapping mode AFM phase images of thin films of block copolymers with fluoroalkyl-tagged PEG side chains: cylindrical morphology (left) and spherical morphology (right) with nearest neighbor spacings of 20 and 22 nm, respectively [100].

In contrast, Grozea et al. [102] found that nanopatterned surfaces with hydrophobic and hydrophilic domains, prepared using polystyrene-*block*-poly(2-vinyl pyridine) (PS-*b*-P2VP) and polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymers, inhibited settlement of *Ulva* zoospores (cf. Figure 7.12). The comparison was with unpatterned surfaces of poly(styrene-*ran*-2-vinyl pyridine) random copolymer, and PS and P2VP homopolymers. The diblock copolymer coatings showed self-assembled cylindrical structures, which were retained after immersion in water.



**Figure 7.12** (a) AFM height image of a crosslinked PS-*b*-P2VP film in air, after 8 days of immersion in water;  $1000 \times 1000$  nm, *z*-range 40 nm. The block copolymer, with about 3:1 weight ratio of the PS and the P2VP blocks, was crosslinked using UV light and benzophenone photoinitiator. (b) The density of attached *Ulva* spores on

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polymers on silicon wafers on PS homopolymer. Reprinted with permission from [102]; Copyright 2009 American Chemical Society.

In addition to the studies discussed herein, using block copolymers, several different polymer architectures, incorporating hydrophobic, fluorinated or silicone polymers, and hydrophilic, PEG based polymers, have been explored as marine antifouling and FR coatings. The free-radical crosslinking of methacryloxy-functionalized hydrophobic perfluoropolyethers with methacryloxy-functionalized hydrophilic PEGs yielded elastomeric amphiphilic coatings [103]. The critical water pressure required for 50 % removal of attached *Ulva* sporelings was in the range of 40 to 80 kPa for these coatings. The corresponding water pressure, for a PDMSe reference, was about 25 kPa. In another study, a silicone-modified epoxy polymer, crosslinked with 2-amino propyl terminated poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol), was evaluated for macrofouling in a Mumbai harbor [104]. The coating was completely covered by algal slime, and other macrofouling organisms (barnacles, oysters, polychaetes, and ascidians) after 60 days of immersion. However, compared with an unmodified epoxy adipate resin that served as the reference, the silicone-modified epoxy coating exhibited good release of adhered organisms when cleaned with a water hose.

# 7.7 CONCLUSION

In this chapter, we have discussed design principles for non-biocidal polymer coatings that can resist fouling by marine organisms. The interaction of the polymer surfaces with the adhesive pad of the marine organism is discussed in terms of molecular composition of the surface of the coating. The key conclusions can be summarized as follows:

- Low surface energy fluorinated or silicone elastomers are promising as fouling release coatings. The incorporation of LC perfluoroalkyl groups with a relatively high clearing temperature, as side chains in comb-like block copolymer architecture, results in the formation of a stable low-energy surface that is resistant to underwater reconstruction. The solvent-soluble and amorphous polystyrene block of these copolymers makes the coatings easier to process than fluoropolymers such as PTFE.
- The fluorinated and silicone FR coatings discussed in this chapter will be useful in situations where periodic cleaning, (e.g., using a water jet or scrubbing), is possible. Because of the good chemical stability of the polymers, these coatings are expected to have long service life. Current concerns with certain perfluorinated compounds as persistent drinking-water contaminants necessitate that the perfluoroalkyl groups be attached to the polymer backbone by hydrolytically stable linkages such as ether groups.
- The incorporation of hydrophilic groups such as PEG in fluorinated or silicone coatings results in the formation of amphiphilic surfaces that are resistant to a broader spectrum of marine organisms, including diatom slimes, compared with coatings with purely hydrophobic or hydrophilic characters. Such amphiphilic coatings are found to retain the FR properties of the fluorinated or silicone coatings. For long-term durability of the amphiphilic coating, it must not swell and soften greatly after immersion in water.
- The coatings must not contain surface functional groups that can irreversibly bond with functional groups such as phosphorylated serines and hydroxylated tyrosines (DOPA) present in the bioadhesives secreted by marine organisms [105].
- Coatings with spontaneously formed nanoscale chemical heterogeneity at the surface have been explored as antifouling surfaces. The currently available data on the effectiveness of surface nanopatterns in imparting fouling resistance are not conclusive. No significant effect of block

copolymer morphology (cylinders vs. spheres) was observed in one study, whereas a decrease in the settlement density of *Ulva* zoospores was reported in another study.

In spite of the significant advances made over the past decade in the design of antifouling coatings, a biocide-free coating that can completely inhibit settlement of fouling organisms over long-term immersion in the marine environment is still being sought. A wide range of tin-free biocides are available, and are currently being used. Biomimetic approaches [70] such as topographically patterned surfaces mimicking the skins of sharks and whales [26, 106, 107], nontoxic self-polishing coatings which mimic the sloughing of polysaccharide mucus that some marine organisms use against fouling [108], and coatings with surface-immobilized enzymes and bioactive fouling-deterrent molecules [109–111], are some alternative strategies that are being explored. Aiming for a minimal adverse impact on the marine ecology, the secondary metabolites of certain naturally occurring marine macro-and microorganisms have themselves been explored for inclusion as fouling repellents in polymer coatings. Commercial silicone based paints seeded with *Pseudoalteromonas* marine bacteria were found to be less fouled compared with control surfaces [112]. Such further advances in environmentally benign marine antifouling coatings are possible by fully understanding the mechanisms that nature uses in controlling adhesive interactions at interfaces.

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