

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/260231007>

# Polymer brush coatings for combating marine biofouling

ARTICLE *in* PROGRESS IN POLYMER SCIENCE · MAY 2014

Impact Factor: 26.93 · DOI: 10.1016/j.progpolymsci.2014.02.002

---

CITATIONS

33

READS

298

## 5 AUTHORS, INCLUDING:



Daniel Rittschof

Duke University

219 PUBLICATIONS 6,498 CITATIONS

[SEE PROFILE](#)

**AUTHOR QUERY FORM**

 ELSEVIER	<b>Journal:</b> JPPS <b>Article Number:</b> 858	<b>Please e-mail or fax your responses and any corrections to:</b> <b>E-mail:</b> <a href="mailto:corrections.essd@elsevier.thomsondigital.com">corrections.essd@elsevier.thomsondigital.com</a> <b>Fax:</b> +353 6170 9272
---	--	---

Dear Author,

Please check your proof carefully and mark all corrections at the appropriate place in the proof (e.g., by using on-screen annotation in the PDF file) or compile them in a separate list. Note: if you opt to annotate the file with software other than Adobe Reader then please also highlight the appropriate place in the PDF file. To ensure fast publication of your paper please return your corrections within 48 hours.

For correction or revision of any artwork, please consult <http://www.elsevier.com/artworkinstructions>.

Any queries or remarks that have arisen during the processing of your manuscript are listed below and highlighted by flags in the proof. Click on the 'Q' link to go to the location in the proof.

Location in article	Query / Remark: <u>click on the Q link to go</u> Please insert your reply or correction at the corresponding line in the proof
<u>Q1</u>	<p>Please confirm that given names and surnames have been identified correctly.</p> <p>Please check this box or indicate your approval if you have no corrections to make to the PDF file <input type="checkbox"/></p>

Thank you for your assistance.



Contents lists available at ScienceDirect

# Progress in Polymer Science

journal homepage: [www.elsevier.com/locate/ppolysci](http://www.elsevier.com/locate/ppolysci)



## Polymer brush coatings for combating marine biofouling

Q1 Wen Jing Yang<sup>a,b</sup>, Koon-Gee Neoh<sup>b</sup>, En-Tang Kang<sup>b,\*</sup>,  
Serena Lay-Ming Teo<sup>c,\*</sup>, Daniel Rittschof<sup>d</sup>

<sup>a</sup> Key Laboratory for Organic Electronics & Information Displays, Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Wenyuan Road 9, Nanjing 210046, PR China

<sup>b</sup> Department of Chemical & Biomolecular Engineering, National University of Singapore, Kent Ridge, Singapore 119260, Singapore

<sup>c</sup> Tropical Marine Science Institute, National University of Singapore, Kent Ridge, Singapore 119223, Singapore

<sup>d</sup> Duke University Marine Laboratory, Nicholas School of the Environment, 135 Duke Marine Lab Road, Beaufort, NC 28516-9721, USA

### ARTICLE INFO

#### Article history:

Received 29 August 2013

Received in revised form 4 February 2014

Accepted 11 February 2014

Available online xxx

### ABSTRACT

A variety of functional polymer brushes and coatings have been developed for combating marine biofouling and biocorrosion with much less environmental impact than traditional biocides. This review summarizes recent developments in marine antifouling polymer brushes and coatings that are tethered to material surfaces and are non-releasing of biocides. Polymer brush coatings have been designed to inhibit molecular fouling, microfouling and macrofouling through incorporation or inclusion of multiple functionalities. Hydrophilic polymers, such as poly(ethylene glycol), hydrogels, zwitterionic polymers and polysaccharides, resist attachment of marine organisms effectively due to extensive hydration. Fouling release polymer coatings, based on fluoropolymers and poly(dimethylsiloxane) elastomers, minimize adhesion between marine organisms and material surfaces, leading to easy removal of biofoulants. Polycationic coatings are effective in reducing marine biofouling partly because of their good bactericidal properties. Recent advances in controlled radical polymerization and click chemistry have also allowed better molecular design and engineering of multifunctional brush coatings for improved antifouling efficacies.

© 2014 Published by Elsevier Ltd.

**Abbreviations:** AA, alginic acid; AAm, acrylamide; AFM, atomic force microscope; AMPS, 2-acrylamide-2-methyl-1-propanesulfonate; ATRP, atom transfer radical polymerization; CBMA, carboxybetaine methacrylate; CRP, controlled/living radical polymerization; GPS, 3-(glycidoxypropyl)trimethoxysilane; HA, hyaluronic acid; HBFP, hyperbranched fluoropolymer; HEMA, 2-hydroxyethyl methacrylate; IDT, isophorone diisocyanate trimer; META, 2-(methacryloyloxy)ethyl trimethylammonium chloride; MIC, microbiologically influenced corrosion; MPC, 2-methacryloyloxyethyl phosphorylcholine; MWCNT, multi-wall carbon nanotubes; NA, noradrenaline; OEG, oligo(ethylene glycol); P4VP, poly(4-vinylpyridine); PA, pectic acid; PAA, poly(acrylic acid); PANI, polyaniline; PDMAEMA, poly(2-dimethylaminoethyl methacrylate); PDMS, poly(dimethylsiloxane); PEG, poly(ethylene glycol); PEGMA, poly(ethylene glycol) methacrylate; PEI, polyethylenimine; PFPE, perfluoropolyether; PFS, 2,3,4,5,6-pentafluorostyrene; PGMA, poly(glycidyl methacrylate); PS-*b*-P(EO-*stat*-AGE), polystyrene-block-poly[(ethylene oxide)-*stat*-(allyl glycidyl ether)]; PSPMA, poly(3-sulfopropyl methacrylate); PTMSPMA, poly(3-(trimethoxysilyl) propyl methacrylate); PVA-SbQ, poly(vinyl alcohol) with stilbazolium; QAC, quaternary ammonium cations; QAS, quaternary ammonium salts; SABC, surface-active block copolymers; SBMA, sulfobetaine methacrylate; SEBS, polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene; SI-ATRP, surface-initiated atom transfer radical polymerization; SPC, self-polishing copolymer; SQTC, semifluorinated-quaternized triblock copolymers; TBT, tributyltin; TEM, transmission electron microscopy; TPCL, polycaprolactone polyol.

\* Corresponding authors.

E-mail addresses: [checket@nus.edu.sg](mailto:checket@nus.edu.sg) (E.-T. Kang), [tmsteolm@nus.edu.sg](mailto:tmsteolm@nus.edu.sg) (S.L.-M. Teo), [ritt@duke.edu](mailto:ritt@duke.edu) (D. Rittschof).

<http://dx.doi.org/10.1016/j.progpolymsci.2014.02.002>

0079-6700/© 2014 Published by Elsevier Ltd.

## Contents

27	1. Introduction .....	00
28	2. Marine biofouling .....	00
29	3. Commercial antifouling coatings .....	00
30	4. Functional polymers for experimental fouling management coatings .....	00
31	4.1. Coupling agents and anchors for polymer brush coatings .....	00
32	4.1.1. Epoxy primers and inorganic coupling agents for antifouling coatings .....	00
33	4.1.2. Biological and biomimetic anchors for polymer brush coatings .....	00
34	4.2. Fouling-resistant polymer coatings .....	00
35	4.2.1. PEG-based polymers .....	00
36	4.2.2. Hydrogel coatings .....	00
37	4.2.3. Zwitterionic polymers .....	00
38	4.2.4. Saccharide-based coatings .....	00
39	4.3. Fouling release polymer coatings .....	00
40	4.3.1. PDMS-based polymers .....	00
41	4.3.2. Polystyrene-based diblock copolymers .....	00
42	4.3.3. Elastomers with dynamic deformation .....	00
43	4.4. Fouling-degrading polymer coatings .....	00
44	4.4.1. Antimicrobial polymers .....	00
45	4.4.2. Enzyme-based coatings .....	00
46	5. Multifunctional polymers for fouling management coatings .....	00
47	5.1. Fouling-resistant and fouling release polymer coatings .....	00
48	5.1.1. Hybrid xerogels .....	00
49	5.1.2. Perfluoropolyether-based polymers .....	00
50	5.1.3. Fluorinated amphiphilic networks and copolymers .....	00
51	5.1.4. Non-fluorinated amphiphilic polymers .....	00
52	5.2. Fouling-resistant and antimicrobial polymer coatings .....	00
53	5.3. Antimicrobial and fouling release polymer coatings .....	00
54	5.4. Bioinspired micro- and nanostructured polymer surfaces .....	00
55	6. Polymer coatings for combating marine biocorrosion .....	00
56	6.1. Antimicrobial polymers .....	00
57	6.2. Electroactive polymers .....	00
58	7. Conclusions and outlook .....	00
59	Acknowledgement .....	00
60	References .....	00
61		

## 1. Introduction

Marine biofouling, defined as the accumulation of marine micro- and macro-organisms on man-made surfaces, is a worldwide problem affecting maritime and aquatic industries [1–9]. It has detrimental effects on shipping vessels, heat exchangers, offshore rigs and jetties, aquaculture cages and other submerged structures in marine environments. In the case of ships, marine biofouling causes high frictional resistance, leading to increased fuel consumption, maintenance costs and greenhouse gases emissions. The increase in fuel consumption can be up to 40% and in-voyage overall costs as much as 77% [4,10–12]. Marine biofouling also creates a corrosive environment and causes pitting corrosion in metals, resulting in degradation and failure of materials and structures [5,13,14]. In particular, microbiologically influenced corrosion (MIC) or biocorrosion, induced by sulfate-reducing bacteria, is extremely damaging to aquatic, maritime and process industries [15–17]. It is estimated that biocorrosion and related damages cost 30–50 billion dollars annually [18,19]. In addition, vessels can serve as a source of invasive species [4,10,14]. For aquaculture farming, biofouling causes an estimated 20% increase in the cost of equipment maintenance in fish production [8].

A variety of antifouling coatings have been developed to control and manage marine micro- and macro-fouling. Effective antifouling protection will save the global maritime industry an estimated 150 billion US dollars per year [20]. Self-polishing antifouling paints incorporating tributyltin-based compounds (TBT-compounds) were used as highly effective biocide-releasing paints after 1960s. However, TBT-compounds cause imposex, intersex and sterility as well as alter shell growth in mulluscs [21,22]. Accumulation in mammals and debilitation of immunological defence in fishes have also been reported [4]. Organotin ship coatings were voluntarily withdrawn from the market in 2003 and banned in 2008 [4,10,23]. Fouling is managed in the post organotin era with copper releasing and copper ablative paint systems [4–6]. The metals are still toxic to marine organisms and may bioaccumulate in the environment, albeit to a lesser extent [5]. As copper levels rise, the solution has been to added organic biocides to enable use of lower levels of copper [5,24]. Although the effects of organic biocides have not been fully studied, their toxicity to aqueous organisms and environment are also under scrutiny. As biocide use in the marine environment is now heavily regulated in many countries, the industry has turned its attention to fouling release and non-leaching biocide coatings.

Tethering of functional polymer brushes to material surfaces provides an environmentally benign and non-releasing alternative to the ablative biocide coatings. Polymer brushes can inhibit biofouling and biocorrosion through incorporation of functional groups with anti-adhesion, antimicrobial and anti-corrosion properties rather than via release of biocides. Various functional polymer coatings have been developed in recent years. In designing antifouling polymer coatings, three main strategies are considered: (i) preventing biofoulants from attaching to surfaces (fouling-resistant coatings), (ii) reducing adhesion between marine organisms and material surfaces (fouling release coatings) and (iii) degrading/killing of biofoulants (fouling-degrading coatings).

Recently, controlled radical polymerization (CRP) techniques, especially the atom transfer radical polymerization (ATRP), have been demonstrated to be effective for the fabrication of polymer brush coatings for biomedical and marine antifouling researches [25–27]. Highly efficient coupling reactions, such as azide-alkyne click reaction [28,29], thiol-ene click reactions [30,31] and activated ester-amine reactions [32,33], also play an important role in efficient synthesis and macromolecular engineering of polymer brush coatings. By employing CRP and the highly efficient click coupling reactions, a multitude of antifouling polymer coatings have been developed. This review focuses on recent development in polymer brushes and coatings for combating marine biofouling and biocorrosion. Fouling-resistant, fouling release, fouling-degrading, anti-biocorrosion and multifunctional polymer brush coatings, prepared by conventional polymerization methods, CRP techniques and click reactions are covered.

## 2. Marine biofouling

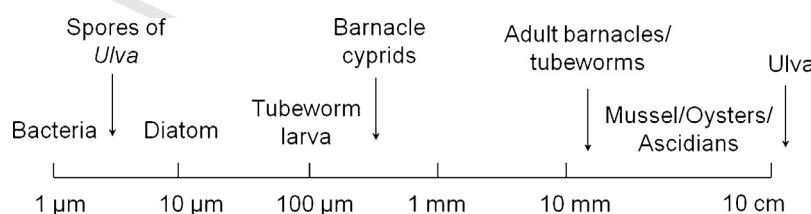
Marine biofouling involves a vast diversity of fouling organisms. It is reported that more than 4000 species have been identified on fouled structures worldwide [3,4]. Fouling organisms range in size from micrometers (bacteria, diatoms, algae spores) to centimeters (barnacles, tube-worms, oysters, mussels) (Fig. 1) [1]. It is often stated that fouling community development generally follows a linear "successional" model [4–6]. In the first stage, organic molecules, such as protein, polysaccharides and proteoglycans, adhere to the surface via physical forces. Next, reversible 'adsorption' of bacteria and diatoms occurs, followed by attachment of spores of microalgae and protozoans to form a biofilm or slime layer. In the last stage, larvae of macroorganisms settle on the surface in 2–3 weeks of immersion and then set for growth of either

macroalgae or marine invertebrates [2,4–6]. However, the sequence of biofouling may not strictly follow the linear successional model [1,34,35], as the formation of biofilm is not a prerequisite and other marine species may settle at the same time [3]. In a more balanced view, fouling ranges from successional to non-successional processes driven by the numbers and kinds of propagules in the water column [1,34,35].

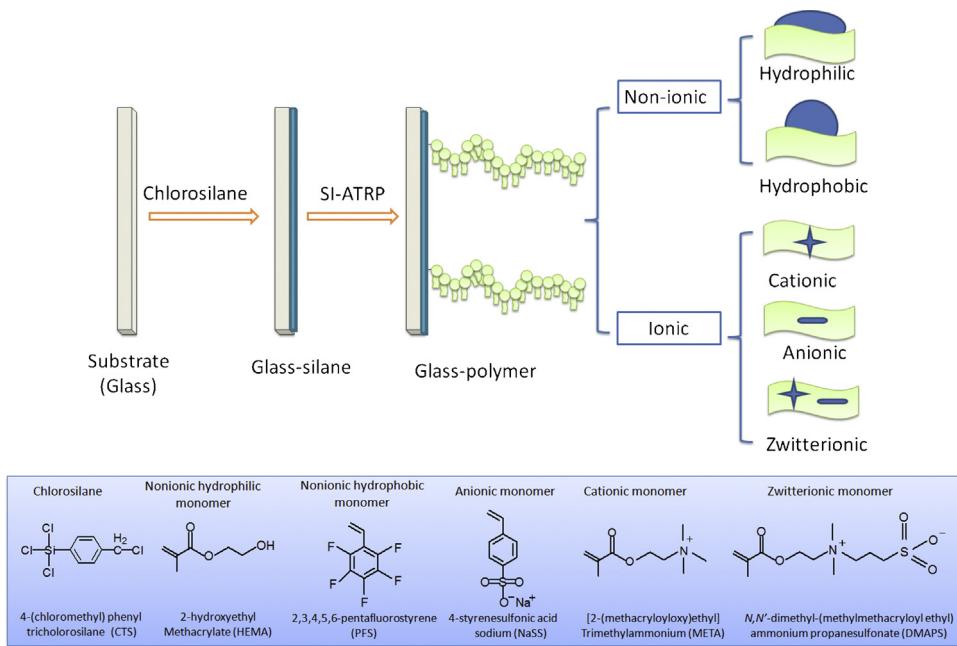
The development of marine biofouling communities are driven by several factors, including temperature, nutrient levels, flow rates, salinity and pH of the marine environment, and the properties of material surfaces [4–6]. Apart from the environmental factors, surface properties, such as surface energy and wettability [36–43], charge [42,44–51] and topography [52–58], have been shown to affect the adhesion of marine organisms. Many studies have demonstrated that surfaces with surface energy values between 20 and 30 mJ m<sup>-2</sup>, known as the 'Baier minimum', show minimal adhesion for the fouling of microorganisms [36,38,39,59,60]. In addition to surface energy, surface charge also plays an important role in the adhesion of micro- and macro-foulers [42,44–51]. Recently, a series of dense and uniform polymer brush coatings with varying degrees of hydrophilicity and charges were synthesized via surface-initiated atom transfer radical polymerization (SI-ATRP) (Fig. 2) and evaluated in both microbiofouling (protein and bacteria adhesion) and macrobiofouling (barnacle settlement) assays [45]. Protein adsorption varies on charged polymer surfaces, while the adhesion of bacteria and settlement of barnacle cyprids on the anionic polymer surfaces were highest among the cationic, zwitterionic and non-ionic hydrophilic and hydrophobic polymer surfaces. Besides surface chemistry, surfaces with complex topographies, such as those mimicking the skin of sharks and lotus leaves, exhibit biofouling inhibition or 'self-cleaning' properties [52–56].

## 3. Commercial antifouling coatings

Existing commercial antifouling coatings are first summarized in this section for comparison with the polymer antifouling coatings currently under research. Biocide-based coatings are among the most widely used commercial antifouling coatings. They can be divided into three categories according to the release mechanisms: contact leaching coatings (insoluble matrix), controlled depletion polymer coatings (soluble matrix) and self-polishing copolymer (SPC) coatings (Fig. 3) [4–6,9]. In contact leaching coatings ('hard' bottom or 'non-sloughing' bottom paints), the polymer matrix, such as vinyl, epoxy,



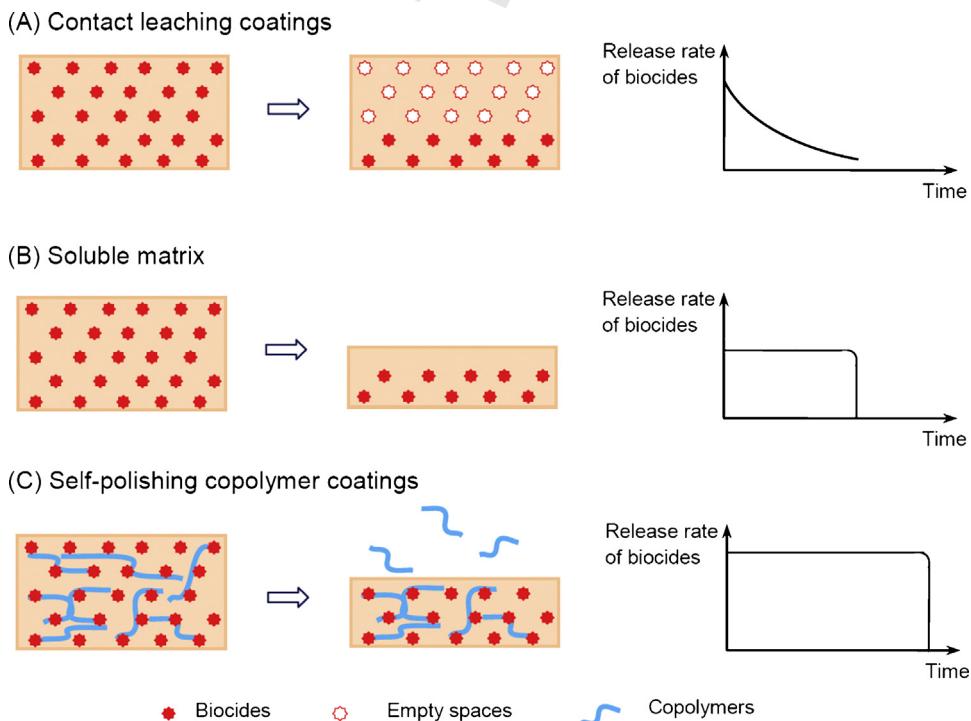
**Fig. 1.** Diversity and size scales of a range of representative fouling organisms.



**Fig. 2.** Schematic illustration of the surface-functionalization processes via SI-ATRP of nonionic hydrophilic and hydrophobic, cationic, anionic, and zwitterionic monomers [45]. Copyright 2012, Reproduced with permission from Taylor & Francis.

acrylic or chlorinated rubber polymers, is insoluble and does not polish or erode in seawater [4]. The toxicants or particles can be incorporated in the coatings and released gradually, leaving empty pores that the seawater can permeate through to dissolve the inner

toxicant particles. In this case, the toxicants released rate gradually decreases over time, reducing the protection effect [6]. The short lifetime (12–24 months) of contact leaching coatings have limited their application [6].



**Fig. 3.** Scheme illustration of the behavior of biocide-based antifouling system. (A) Contact leaching coatings, (B) soluble matrix coatings and (C) self-polishing copolymer coatings.

In order to circumvent this problem, soluble matrix coatings were developed by incorporating a large proportion of seawater-soluble binder based on rosin and its derivatives [4]. Once in contact with seawater, the biocides and soluble resins are dissolved and released. Controlled depletion polymer coatings adopt a similar mechanism by using more resistant synthetic organic resins to control the hydration and dissolution of soluble binder. The life time can be extended up to 36 months [3,6].

Self-polishing copolymer coatings erode and release the biocide over a sustained period of time. They use acrylic or methacrylic copolymers as matrix that is easily hydrolyzed in seawater, releasing the biocide and leaving the surface polished to reduce drag [4,6]. The attached fouling organisms are removed together with the decomposed matrix from hydrolysis. The release rate of biocides can be controlled by the degree of polymerization and hydrophilic properties of the copolymer binders [24]. The SPC coatings have an extended lifetime up to 5 years and account for 80% of the market for antifouling paints [6].

Commercial non-biocidal coatings range from very hard coatings for small boats that withstand harsh cleaning to foul release coatings for large ships that have low surface energy properties and additives that make them easy to clean. Fouling release coatings rely on the concept that minimizing the adhesion strength between fouling organisms and material surfaces will lead to easy removal of the biofoulants by simple mechanical cleaning or hydrodynamic stress during navigation [3,61,62]. The adhesion strength is proportional to  $\gamma E$ , where  $\gamma$  is the surface energy and  $E$  is the modulus [63]. Poly(dimethylsiloxane) (PDMS) and fluoropolymers with low energy and/or low modulus are the most common materials used as binders. However, fouling release silicones suffer from several disadvantages [3,4]. The diatoms slimes are difficult to release on PDMS even at high speed of 30 knots [3,4]. PDMS is susceptible to mechanical damage and exhibit poor adhesion to substrates [3,64]. Moreover, the leachates from fouling release silicones interact with enzymes involved in curing of biological glues for barnacles and affect the embryonic development of sea urchins and fish [65,66].

In summary, the current commercial antifouling systems are rosin-based control depletion paints, self-polishing systems and fouling release coatings [20]. Nevertheless, they suffer from many limitations. With the strong demand for improved products, various antifouling polymer coatings, ideally by non-releasing mechanism or using biocide with short environmental half-lives are being developed and researched upon in recent years.

#### 4. Functional polymers for experimental fouling management coatings

Surface-tethered polymers with specific functionalities have been extensively utilized in biomaterials and biomedical devices [19,26]. Thus, by concept, functional polymer brush coatings can be tethered to material surfaces as a viable alternative to biocide-releasing coatings for inhibiting marine biofouling. The polymer brush coatings can inhibit marine biofouling with the incorporation of functional groups with specific anti-adhesion, antimicrobial

and anticorrosion properties, to provide a non-biocide releasing, environmentally benign antifouling technology.

In general, three strategies have been employed in the designing of antifouling polymer coatings: preventing biofoulants from attaching to surfaces (fouling-resistant), reducing the adhesion strength of biofoulants (fouling releasing) and degrading/killing of biofoulant. Hydrophilic polymers, such as poly(ethylene glycol) (PEG), have been shown to resist protein adsorption and cell adhesion, and hence have been widely employed as effective experimental coatings to inhibiting marine biofouling [67–71]. Fouling release polymer coatings, such as fluoropolymers and silicones, allow the attached organism to be released easily from the surface because of low adhesion strength [3]. Antimicrobial polymers containing polycations have been developed for anti-biofouling in marine and biomedical application as they compromise microbes by disrupting cellular membranes [72–76]. Many more polymer coatings have been designed for improved antifouling efficacies by incorporating multiple functionalities (Section 5).

Tethering of polymer brushes to material surfaces can be accomplished by either 'grafting-to' or 'grafting-from' approaches [77–80]. Well-defined antifouling polymer coatings are attached to surfaces via physisorption or covalent bonding in the 'grafting-to' approach. On the other hand, the 'grafting-from' approach, via polymerization from initiators bound on the material surfaces (surface-initiated polymerization), allows the preparation of dense and stable polymer brushes coatings [26,79]. In particular, surface-initiated controlled radical polymerization (SI-CRP), such as atom transfer radical polymerization (ATRP), is a powerful technique for preparation of well-defined and narrowly dispersed polymer brushes of controlled architecture [25–27].

Highly efficient coupling reactions, such as azide-alkyne click chemistry, thiol-ene click reactions and activated ester-amine reactions, provides convenient and versatile approaches for efficient polymer synthesis and macromolecular engineering [28–32,81–83]. The azide-alkyne click reaction has excellent reaction specificity, high efficiency and good functional group tolerance [28,29]. The resultant cyclic 1,2,3-triazole linkages are resistant to hydrolysis, oxidation, and reduction, making the click reaction of particular interest in the preparation of highly robust polymer structures. Thiol-ene click reactions can proceed under mild reaction conditions with good efficiency and fast kinetics [30,31]. An activated ester, such as pentafluorophenyl ester, exhibits high reactivity toward primary and secondary amines under mild conditions with no known side reactions [32,33]. ATRP and the highly efficient click coupling reactions have contributed significantly to the fabrication of robust antifouling polymer brushes coatings (Table 1).

##### 4.1. Coupling agents and anchors for polymer brush coatings

###### 4.1.1. Epoxy primers and inorganic coupling agents for antifouling coatings

In shipping industries, epoxy primers are usually used to obtain a good adhesion of the antifouling top-coat to steels

**Table 1**

Marine antifouling polymer coatings and surfaces prepared via ATRP and click coupling reactions.

Approaches	Methods	Applications	Monomers/coupling units	References
'Grafting-from'	ATRP	Fouling-resistant	HEMA, SBMA, CBMA, PFS	[45,87,88,200]
		Antimicrobial Anti-corrosion	META 4VP, DMAEMA, TMSPMA, GMA	[45] [84,85,204,206]
'Grafting-to'	ATRP	Amphiphilic	PEGylated-fluoroalkyl monomer, PFS	[123,157,158]
	Thiol-ene	Fouling-resistant	PEG with vinyl end and thiol cross-linker	[101,161]
		Amphiphilic	PS- <i>b</i> -P(EO- <i>stat</i> -AGE) and perfluoroctanethiol, polyester and PEG	[161,171]
	Azide-alkyne	Fouling-resistant and antimicrobial	PEGMA and META	[178]
	Pentafluorophenyl ester-amine	Amphiphilic	HBFP and PEG	[157–159]

[6]. For fouling release coatings, a three-layer system has been employed, including the primer, tie-coat and top-coat [3]. The tie coat is to ensure good adhesion between the primer and top-coat.

Interfacial coupling agents or anchors are indispensable when tethering polymer brushes and coatings to the substrate surfaces. Take SI-ATRP for example, a layer of ATRP initiators, such as alkyl bromide and chloride, on the substrate surface is necessary. Inorganic coupling agents, such as bromomethyl- or chloromethyl-terminated silanes [84,85] and bromomethyl-terminated thiol agents [86–88], are extensively used as ATRP initiators in SI-ATRP process (Fig. 4A–E). Poly(sulfobetaine methacrylate) (PSBMA) and poly(carboxybetaine methacrylate) (PCBMA) antifouling coatings were prepared on glass surfaces modified with the bromomethyl-terminated silane for preventing attachment of algal zoospores, diatoms and barnacle cyprids [87,88].

#### 4.1.2. Biological and biomimetic anchors for polymer brush coatings

In addition to inorganic coupling agents, some novel anchoring methods have been developed in recent years. Dopamine (Fig. 4F), inspired by mussel adhesive, has been successfully employed as a biomimetic anchor for polymer brushes in both SI polymerization and 'grafting-to' process [89–94]. Dopamine contains catechol functional group that exhibits versatile adhesion to a wide range of substrates. In SI-ATRP processes, an ATRP initiator containing the catechol functional group (Fig. 4G) can be synthesized a priori [89,90], or the alkyl bromide ATRP initiator can be introduced by the reaction of 2-bromoisobutryl bromide with the dopamine-coated substrates [91–94]. Moreover, various copolymers with side-chain catechol group have been developed for anchoring polymer brushes to substrates in the 'grafting-to' processes. A poly(dopamine acrylamide)-co-poly(propargyl acrylamide) (PDA-*co*-PPA) copolymer (Fig. 4H), containing alkyne- and catechol-functionalities were prepared for anchoring on titanium surfaces to provide the 'clickable' alkyne sites for

subsequent functionalization via azide-alkyne click reactions [95].

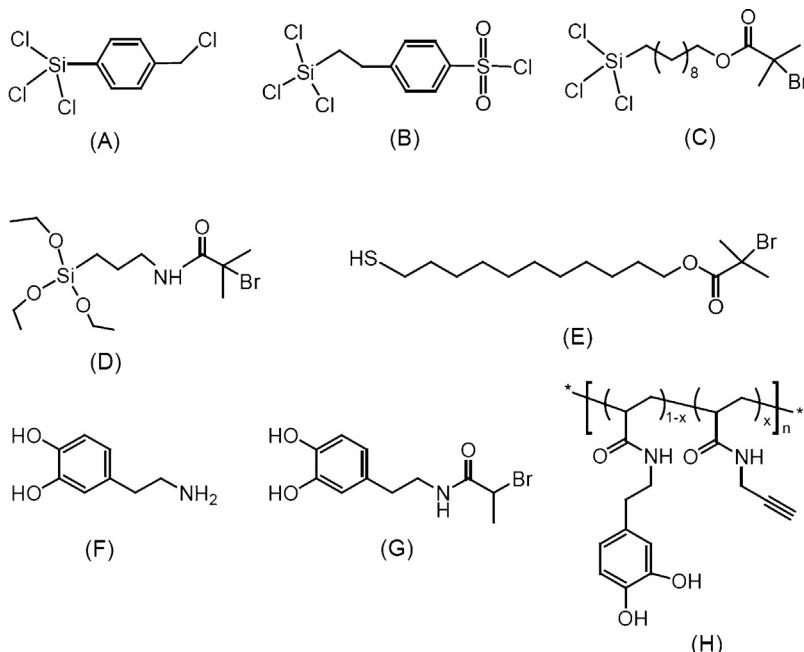
Recently, barnacle cement, a biological adhesive from barnacles, has been beneficially applied as a versatile surface anchor due to its strong adhesion, environmental friendliness and chemical reactivity [96,97]. Antifouling and antimicrobial polymer brush coatings have been anchored on barnacle cement in both the 'grafting-from' and 'grafting-to' processes (Fig. 5). A bifunctional polymer brush coating containing poly(2-hydroxyethyl methacrylate) (PHEMA) and chitosan (CS) has been prepared via SI-ATRP using barnacle cement as an initiator anchor [96]. In addition, barnacle cement has also been employed as a surface anchor for introduction of 'clickable' moieties for subsequent functionalization with various polymer brushes via click chemistry [97].

#### 4.2. Fouling-resistant polymer coatings

Fouling-resistant polymer coatings are usually prepared from hydrophilic polymers. Hydrophilic polymers have low polymer–water interfacial energies. The high degree of hydration increases the energetic penalty of removing water when biofoulants attach, resulting in resistance to protein adsorption and settlement of fouling organisms [7]. Several hydrophilic polymer coatings, such as PEG, hydrogel, zwitterionic polymers and polysaccharides, have been developed as marine antifouling coatings.

##### 4.2.1. PEG-based polymers

PEG-based polymers have been widely used as antifouling materials. Due to their large exclusion volume, high mobility of hydrated chains and steric hindrance effect, PEG units effectively resist protein and platelet adhesion, and reduce cell attachment and growth [67,68]. Their anti-biofouling efficacies in the marine environment have also been explored [69–71]. Correlation between settlement of algal cells and ethylene glycol chain length and terminal groups has been investigated for oligo(ethylene glycol) (OEG) and PEG-modified surfaces prepared from



**Fig. 4.** (A–D) Bromomethyl or chloromethyl-terminated silanes, (E) bromomethyl terminated thiol, (F) dopamine, (G) ATRP initiator containing catechol group and (H) PDA-co-PPA copolymer.

self-assembled monolayer [70,71]. PEG with long chain length exhibits better antifouling efficacy than OEG, and different antifouling mechanisms for PEG and OEG coatings have been proposed. The OEG-modified surface reduced adhesion between spores and surfaces, leading to an easy release through minor hydrodynamic force, while PEG inhibits spore settlement (Fig. 6) [71]. Furthermore, the number of adhered zoospores *Ulva linza* and diatom *Navicula perminuta* cells are dependent on the end-group termination of hexa(ethylene glycol), increase as the wettability decreases [70].

In addition to self-assembled OEG and PEG monolayers, methoxyl-terminated PEG polymers were anchored to the titanium surface by conjugation with the L-3,4-dihydroxyphenylalanine adhesive [69]. The resulting hydrophilic PEG-functionalized surface exhibited a significant decrease in the attachment of diatom *N. perminuta* and zoospores *U. linza*. In spite of good anti-adhesion efficacy, PEG is a polyether that autoxidizes easily, especially in presence of oxygen and transition metal ions, and is also susceptible to thermal degradation [98,99]. These problems need to be addressed for it to be used for long-term applications of PEG in the marine environment.

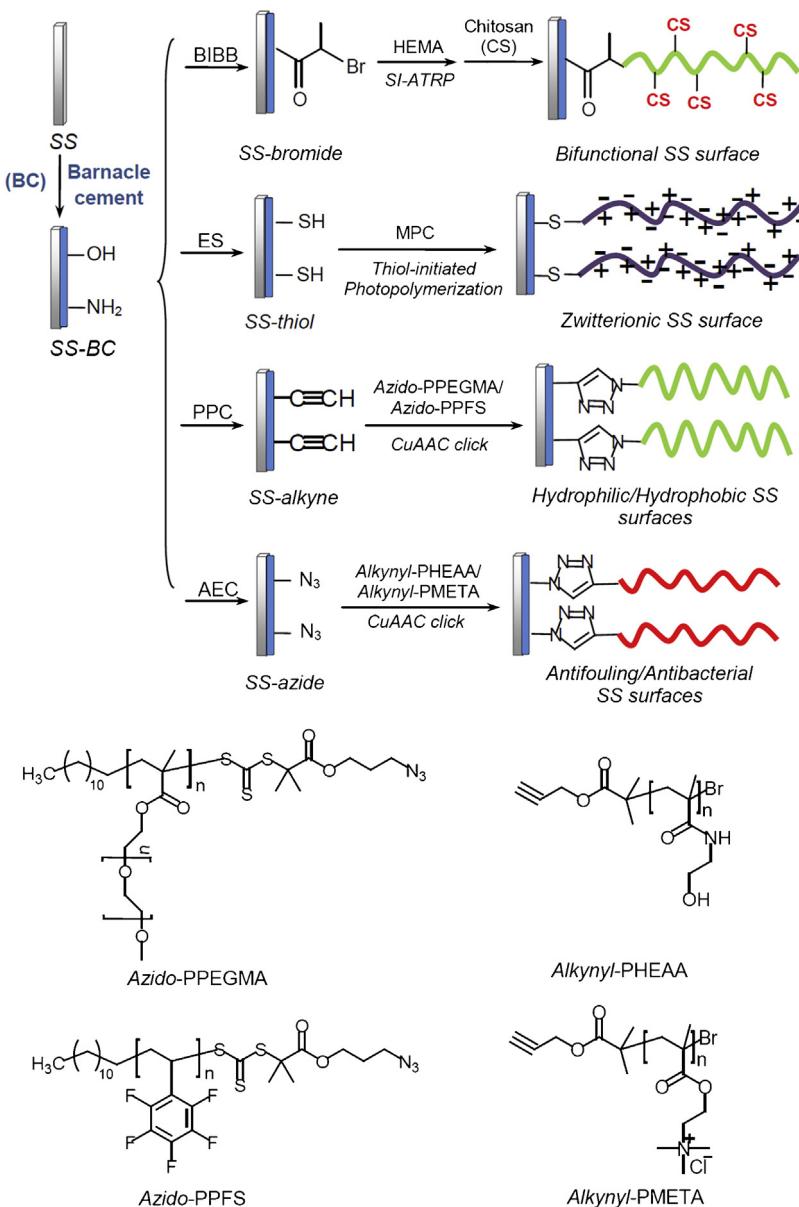
#### 4.2.2. Hydrogel coatings

Hydrogels refer to networks of hydrophilic polymer chains. They are distinguished from solid materials by the abundant composition of water [100]. Recently, a library of PEG hydrogel coatings with different structural compositions, varying PEG length, vinylic end-group and thiol cross-linker, has been prepared via thiol-ene click reaction (Fig. 7A) [101]. The step-growth mechanism of thiol-ene reaction with relative insensitivity to oxygen inhibition

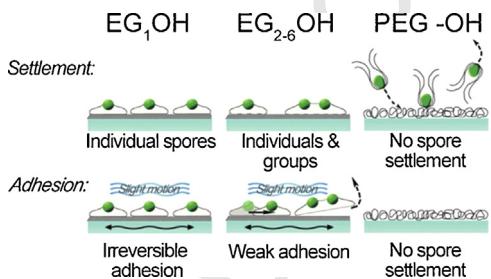
enables the built up of a homogeneous network, suggesting that thiol-ene systems are ideal for coating applications. The hydrogel coatings with long PEG chains outperformed the coatings with short PEG chains in reducing adhesion of diatom *Amphora coffeaeformis* [101].

Hydrogel antifouling coatings based on poly(ethylene glycol) methacrylate (PEGMA) and 2-hydroxyethyl methacrylate (HEMA) have been fabricated by UV-initiated free radical polymerization (Fig. 7B) [102]. Similar to PEG, the hydrophilic HEMA polymer (PHEMA) exhibits excellent resistance to protein and cell adhesion and barnacle cyprids settlement, because the PHEMA chains can become highly extended and oriented to physically exclude the biofoulants [26,45,103]. The hydrogels exhibited excellent antifouling properties against a spectrum of aquatic fouling organisms, including three bacteria species (*Cobetia marina*, *Marinobacter hydrocarbonoclasticus* and *Pseudomonas fluorescens*), diatoms (*N. perminuta*), algal zoospores (*U. linza*) and barnacle larvae (*Balanus amphitrite*). Degradation of the hydrogel coating was slow over a six-month period in artificial seawater. The apparent stability of the hydrogel may be attributed to cross-linked polymer structures formed during the UV-irradiation process.

Apart from neutral hydrogel coatings, some charged hydrogels have also been synthesized for antifouling purpose. These hydrogels, including alginate (highly anionic), chitosan (highly cationic), poly(vinyl alcohol) substituted with light-sensitive stilbazolium groups (PVA-SbQ, weakly cationic) and agarose (neutral) have been prepared and tested [46–48]. The antifouling performance varies among gels of different charges. Among all the gel coatings, the PVA-SbQ hydrogel (weakly cationic, Fig. 7C) exhibited the



**Fig. 5.** Barnacle cement used as a surface anchor for the preparation of functional polymer brush coatings by SI-ATRP and click chemistry.



**Fig. 6.** The different responses of spores of *Ulva* to OEG and PEG surfaces. [71] Copyright 2009, Reproduced with permission from the American Chemical Society.

best antifouling efficiency. Not only did it inhibit the adhesion of marine bacterial *Pseudomonas* sp. NCIMB2021 and settlement of barnacle *B. amphitrite*, it also reduced the attachment of diatom *A. coffeaeformis*. Similarly, a series of synthetic polymer gels, including non-charged, positively charged, negatively charged and double network gels, have been prepared and tested for barnacle cyprids (*B. amphitrite*) settlement both *in vitro* and in marine environment [100,104,105]. All the gel surfaces exhibited a low settlement rate of barnacle cyprids in the laboratory environment, independent of surface hydrophilicity and charges. The mechanically tough gels, poly(vinyl alcohol) gel (Fig. 7D) and double network gel consisting of poly(2-acrylamide-2-methyl-1-propanesulfonate) and

polyacrylamide (Fig. 7E), exhibited good antifouling activity against marine sessile organisms for 330 days in the marine environment [105].

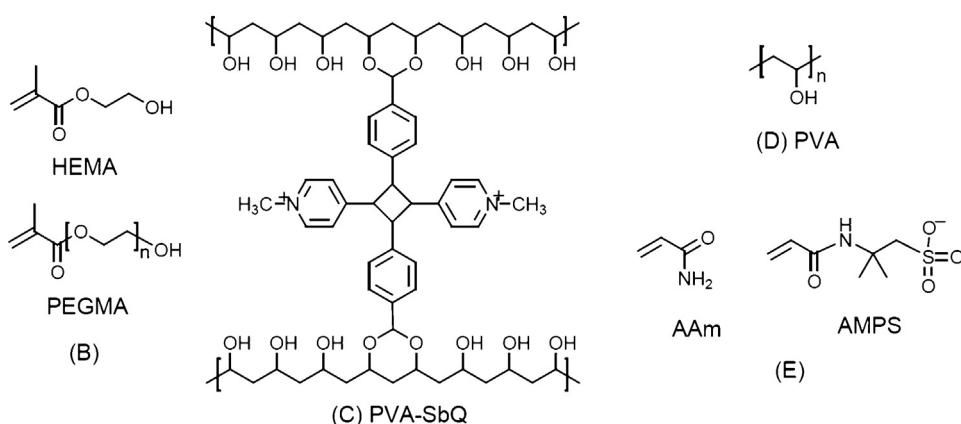
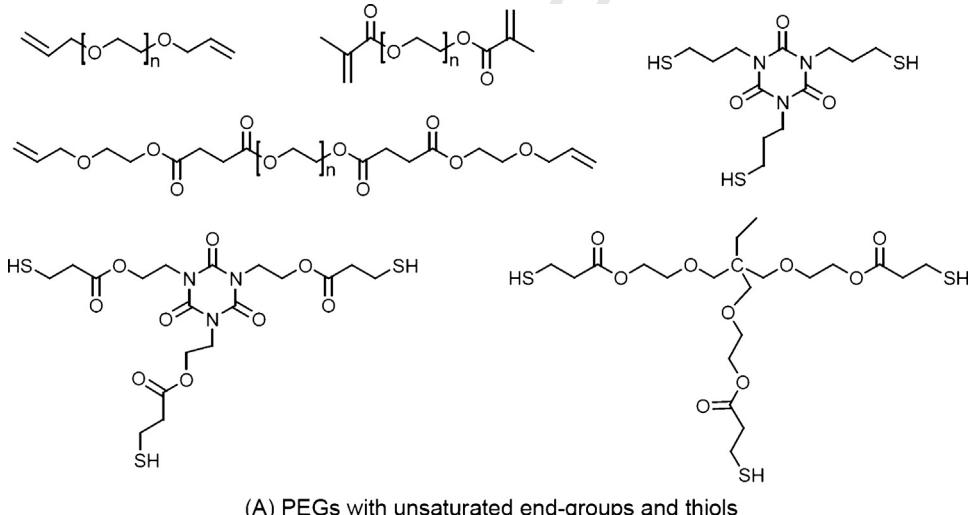
#### 4.2.3. Zwitterionic polymers

Zwitterionic polymers, such as sulfobetaine, carboxybetaine and phosphorylcholine, contain a mixture of anionic and cationic pendent groups (Fig. 8A) [106]. In comparison to the hydration of PEG and other nonionic hydrophilic polymers via hydrogen bonding, the electrostatically induced hydration of zwitterionic polymers is more pronounced [107,108]. Therefore, zwitterionic polymers are expected to have better antifouling efficacies as they can bind water molecules even more strongly, making the polymer ‘prefers to be’ in contact with water rather than biological matters [106–108]. The fouling-resistant zwitterionic coatings have been developed to inhibit biofouling of zoospores of green alga *Ulva*, diatoms *N. perminuta* and *Nitzschia closterium* and barnacle *B. amphitrite* cyprids [87,88,109]. SBMA polymer (PSBMA)-functionalized surface was prepared via SI-ATRP for resisting settlement

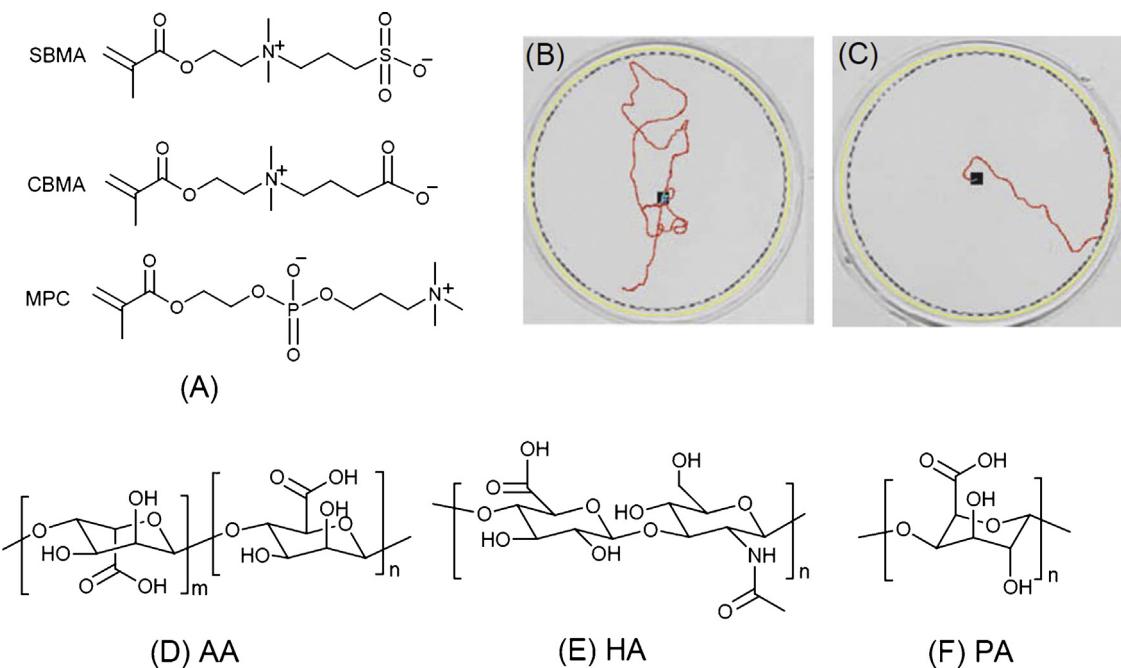
of algal zoospores and diatoms [88]. The settlement of spores *Ulva* on the PSBMA coating was low and adhesion strength of the adhered spores was weak. The diatoms *N. perminuta* were unable to attach to the PSBMA coating [88]. Both PSBMA and poly(carboxybetaine methacrylate) (PCBMA) (Fig. 8A), prepared via SI-ATRP, also exhibited high resistance against the settlement of barnacle cyprids. Interestingly, two-dimensional tracking results of cyprids behaviors on the two surfaces were quite different. On the PSBMA-modified surface, the cyprids explored the surface but were unwilling or unable to settle (Fig. 8B), whereas the cyprids did not attempt exploration and left quickly from the PCBMA-functionalized surface (Fig. 8C) [87].

#### 4.2.4. Saccharide-based coatings

An alternative to synthetic hydrophilic polymers is the use of natural macromolecules with intrinsic hydrophilicity, such as polysaccharides, to achieve fouling-resistant properties. Saccharides and polysaccharides exhibit resistance to mammalian cells, certain classes of bacteria [110–112] and marine organisms [113–115]. Three acidic



**Fig. 7.** Functional monomers used in the synthesis of hydrogels (A) PEGs with unsaturated end-groups and thiols, (B) PEGMA: poly(ethylene glycol) methacrylate, HEMA: 2-hydroxyethyl methacrylate, (D) PVA: poly(vinyl alcohol), (E) AAm: acrylamide, AMPS: 2-acrylamido-2-methyl-1-propanesulfonate and (C) PVA-SbQ hydrogel.



**Fig. 8.** (A) Chemical structures of sulfobetaine methacrylate (SBMA), carboxybetaine methacrylate (CBMA) and 2-methacryloyloxyethyl phosphorylcholine (MPC). Track of cyprid behavior on (B) PSBMA and (C) PCBMA surfaces [87]. Copyright 2010, Reproduced with permission from Taylor & Francis; Polysaccharides used as antifouling coatings: (D) alginic acid (AA), (E) hyaluronic acid (HA) and (F) pectic acid (PA).

polysaccharides hyaluronic acid (HA), alginic acid (AA) and pectic acid (PA) (Fig. 8D–F), containing repeating units of disaccharide  $\beta\text{-N-acetylglucosamine}-\beta\text{-D-glucuronic acid}$ , were assayed for adhesion of protein, hematopoietic cells and settlement of marine organisms, including green alga spores *U. linza* and barnacle *B. amphitrite* cyprids [113]. The three polysaccharide coatings reduced the attachment of zoospores of *Ulva* in comparison to the acid-washed glass standard. For barnacle cyprids, the reduction was only significant for HA coatings. However, inhibition of settlement of marine organisms was less pronounced in comparison to proteins and hematopoietic cells. This phenomenon might be attributed to the presence of bivalent ions, such as calcium and magnesium in the marine environment, which plays a major role in biofilm formation [116].

#### 4.3. Fouling release polymer coatings

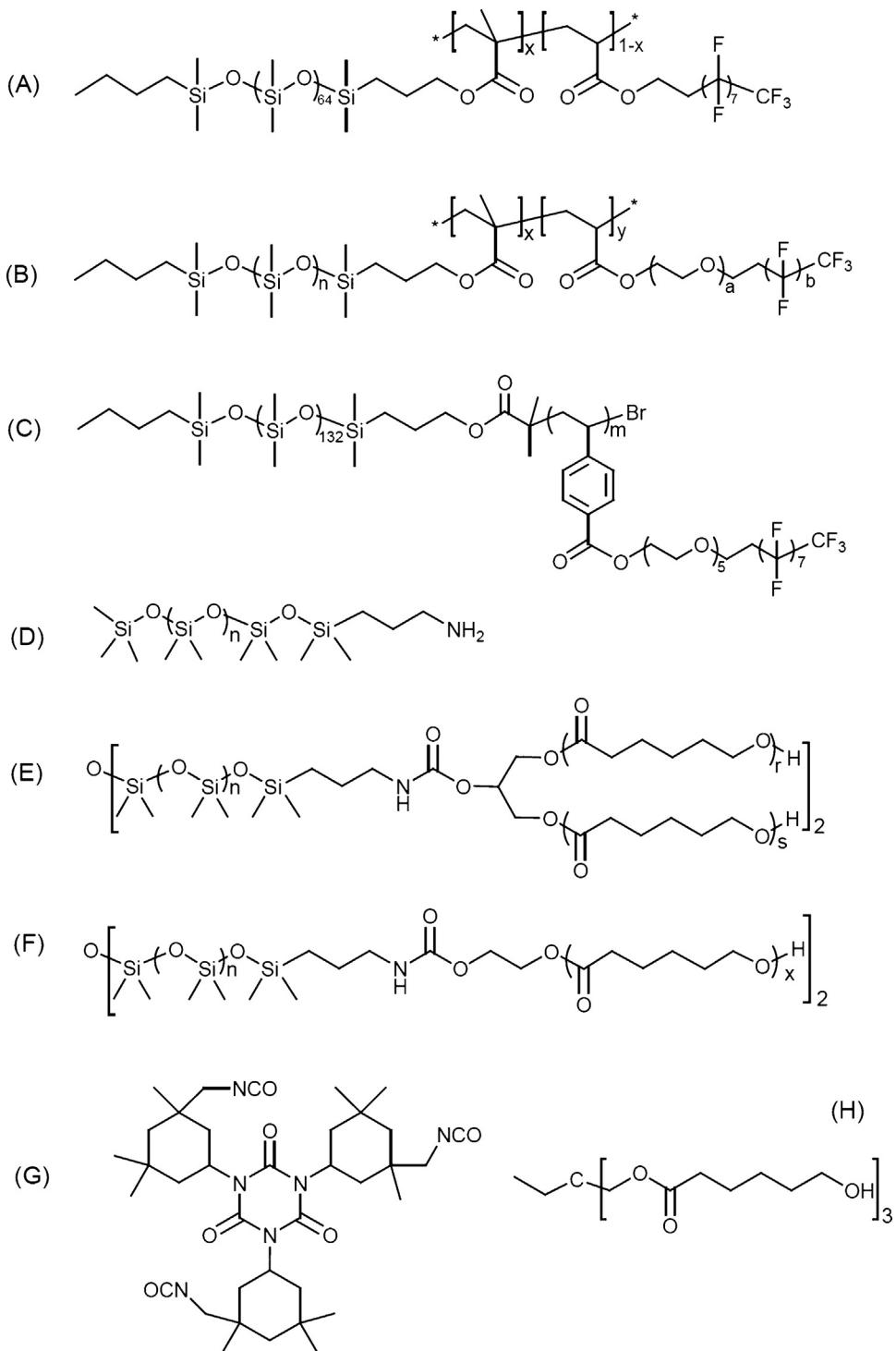
Fouling release coatings rely on the idea that by minimizing the adhesion strength between fouling organisms and material surfaces, fouling may be easily removed by simple mechanical cleaning or hydrodynamic stress during navigation [3]. The adhesion strength is dependent on the surface energy ( $\gamma$ ) and the modulus ( $E$ ). Therefore, polymers with low energy and/or low modulus, especially the PDMS-based polymers, have been developed as fouling release coatings.

##### 4.3.1. PDMS-based polymers

PDMS elastomers, with low surface energy, low modulus, low micro-roughness and low glass transition temperature, reduce adhesion of marine organisms

[3,117,118]. However, PDMS suffers from several disadvantages [3,4]. They are susceptible to mechanical damage and exhibit poor adhesion to the coating substrate [3,64]. In addition, the diatoms slimes are difficult to remove even at the high speed of 30 knots [3,4]. In view of these facts, the PDMS-based polymer coatings, blended or covalently cross-linked with fluoropolymers, nanofillers and polyurethane, have been developed to improve fouling release performance.

Fluoropolymers are low surface energy materials with non-porous and non-stick properties [4,119]. Blending of fluoropolymers with PDMS imparts low modulus characteristics of PDMS with low surface tension and thus improves fouling release efficacy of PDMS [120–123]. Fluorinated-siloxane copolymers (Fig. 9A), prepared via free radical polymerization of monomethacryloxypropyl-terminated PDMS and 1H,1H,2H,2H-perfluorodecyl acrylate, were blended with PDMS to produce a fouling release coating [120]. Apart from fluorinated siloxane copolymers, amphiphilic copolymers containing PEG-fluoroalkyl side chains (Fig. 9B and C), prepared by ATRP of PEGylated-fluoroalkyl monomer using a bromo-terminated PDMS macroinitiator, were blended with PDMS release of macroalgae *U. linza* and prevent barnacle settlement [123]. The relatively long PDMS block was used to improve the dispersion of copolymer in the elastomer matrix. Two block copolymers (Fig. 9C,  $m=6$  and 12) were blended with PDMS matrix in different weight loadings (1–10%). In comparison to the PDMS control, all the blended coatings showed a 3–14 fold improvement in the release of *Ulva* sporelings. The adhesion strength between biofoulants and polymer coatings increased with increase in the length of

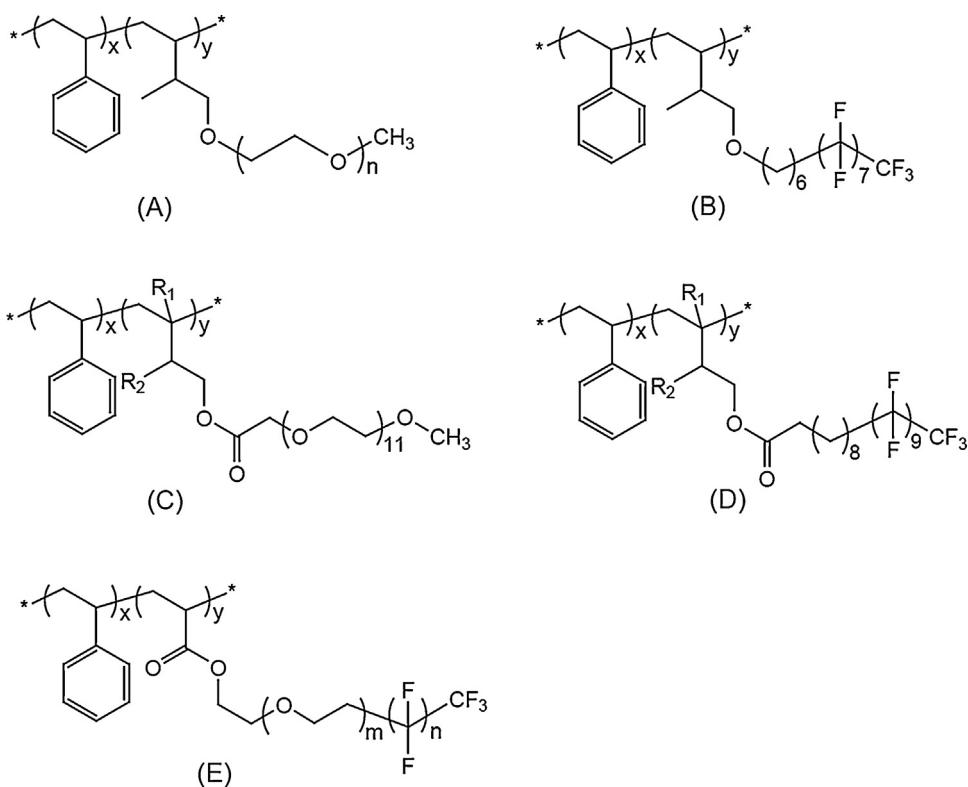


**Fig. 9.** (A) Fluorinated/siloxane copolymer and (B and C) amphiphilic fluorinated/siloxane copolymers for blending with PDMS. (D–F) PDMS macromers, (G) isophorone diisocyanate trimer and (H) polycaprolactone polyol used for preparation of siloxane-polyurethane coating.

the amphiphilic block in the copolymer for a given blend composition, but decreased at higher loading of the block copolymer in the blend [123].

Nanofillers, such as multi-wall carbon nanotubes (MWCNT) [64,124], natural sepiolite [64] and

organo-modified montmorillonite [125], have also been incorporated in the PDMS coatings. Incorporating of a small amount of MWCNT (less than 0.1 wt%) within the coating enhanced fouling release performance against both macroalga *Ulva* and barnacle *Balanus amphitrite* cyprids

**Fig. 10.** Diblock polystyrene-based copolymers as fouling release coatings.

without markedly changing the bulk properties [64,124]. The fouling release efficacy was correlated with both the extent of MWCNT loading and the dispersion state, with the maximum efficacy obtained at 0.1 wt% of MWCNT and the masterbatch approach to dispersion [124].

Urethane polymers have also been incorporated in silicone fouling release coatings to improve the poor mechanical properties and low substrate adhesion [126–129]. A series of siloxane-polyurethane coating formulations with different molecular weights and weight fractions of PDMS were prepared by cross-linking of the PDMS-containing components (Fig. 9D–F), isophorone diisocyanate trimer (IDT, Fig. 9G) and polycaprolactone polyol (TPCL, Fig. 9H) [127,128]. The coatings with low molecular weight PDMS allow easy removal of algal sporelings *Ulva*, diatom *Navicula incerta* and live barnacles *B. amphitrite*.

#### 4.3.2. Polystyrene-based diblock copolymers

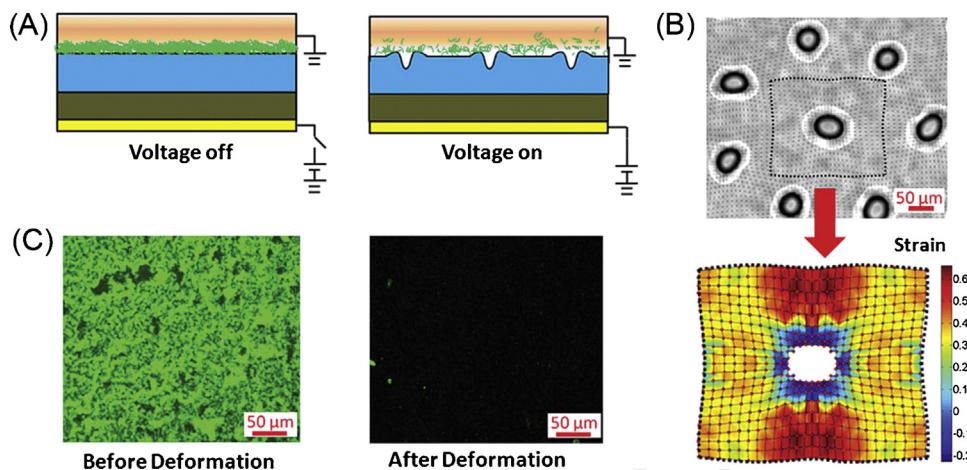
The fouling release properties of hydrophobic polystyrene-based diblock copolymers have been assayed with alga zoospores and diatoms (Fig. 10) [130,131]. The influence of wettability of polystyrene-based diblock copolymers on fouling release efficacy of diatom *N. perminuta* and green alga *U. linza* was investigated by including fluorinated and PEGylated side chains in the copolymers (Fig. 10A–D) [130,131]. It was found that *Navicula* cells were released more readily from the more hydrophilic surfaces, whereas *Ulva* sporelings had a higher removal rate from the more hydrophobic surfaces [131].

In particular, in order to avoid structural reconstruction of the polymers after immersion in water, semi-fluorinated liquid crystalline side-chains were used in the diblock copolymers to produce a stable hydrophobic and highly non-polar surface (Fig. 10D).

Due to the difference in fouling release efficacies of alga *U. linza* and diatom *N. perminuta*, a comb-like block copolymer with amphiphilic side chains (Fig. 10E) was thus developed to release both marine organisms by combining the hydrophilic and hydrophobic properties [132]. The attachment strength of *Navicula* was lowest, with a removal efficacy of  $81 \pm 5\%$ , compared to  $69 \pm 3\%$  for glass and  $11 \pm 4\%$  for PDMS. The removal of *Ulva* sporeling from the amphiphilic surface was comparable to that from PDMS.

#### 4.3.3. Elastomers with dynamic deformation

Recently, a new mechanism was proposed for effectively detaching micro- and macro-foulers adhered to surfaces by dynamically changing the surface area and topology [133]. Based on this concept, an elastomer surface capable of dynamic deformation in response to external stimuli, including practical electrical and pneumatic stimuli, was synthesized [133]. Over 95% and 80% of the marine bacterial biofilms of *Cobetia marina* were detached, respectively, under electrically induced and mechanically induced deformation (Fig. 11). Dynamic deformation of the polymer reduced the adhesion strength of barnacles (*Amphibalanus* (=*Balanus*) *amphitrite*), leading to a reduced shear force required for the detachment.



**Fig. 11.** Detachment of bacterial biofilms from dielectric elastomers under voltages. (A) Schematic illustration of the laminate structure, actuation mechanism, and the detachment of a bacterial biofilm. (B) The applied electric field can induce significant deformation of the elastomer surface as given by the contours of the maximum principal strain. (C) The deformation detaches over 95% of a biofilm (*Cobetia marina*) adhered to the elastomer surface, which is periodically actuated for 200 cycles within 10 min [133]. Copyright 2013, Reproduced with permission from Wiley-VCH.

#### 4.4. Fouling-degrading polymer coatings

##### 4.4.1. Antimicrobial polymers

Coating of substrate surfaces with antimicrobial polymers has been widely employed for combating biofouling in biomaterial and biomedical application [72–74,134]. Cationic polymer containing quaternary ammonium compounds (QAC) are among the best known antimicrobial polymers. QAC provides good bactericidal activity by disrupting the bacteria cellular membranes [73,76]. Dense cationic polymer brush coatings were prepared via SI-ATRP of 2-(methacryloyloxy)ethyl trimethylammonium chloride (META) for inhibiting marine bacterial (*Pseudomonas* sp. NCIMB 2021) adhesion and barnacle cyprids (*B. amphitrite*) settlement [45]. In comparison to the uncoated glass surface, the META polymer (PMETA) coating reduced barnacle cyprid settlement by 85% [45]. Reduced settlement of barnacle cyprids on QAC-functionalized surface was also observed on the self-assembled monolayer of *N,N,N-trimethyl-(11-mercaptopoundecyl)* ammonium chloride [44]. In contrast to the biocide-releasing antimicrobial coatings, the prepared PMETA coatings exhibited lethal effect to bacteria through a surface contact mechanism without the release of biocides. The bactericidal effect of QAC-modified surface can be correlated with the charge density and chain length of quaternary ammonium groups [73,74,76].

##### 4.4.2. Enzyme-based coatings

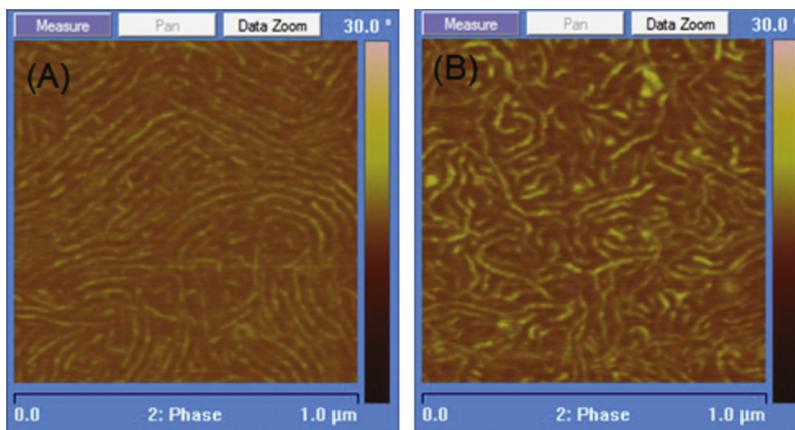
The idea of using enzymes as alternatives to toxic biocides has attracted increasing interest in recent years [135,136]. Enzymes affect the settlement and adhesion of fouling organisms in different ways [135,136]. They reduced the settlement event by attacking the adhesive of settling organisms, or degrading the polymers in the biofilm matrix formed by proliferation of the settled organisms. They may also be used to catalyze the release of antifouling compounds from the matrix. Moreover, some

specific enzymes can obstruct the intercellular communication (quorum sensing) during colonization of a surface [136,137].

A fouling-degrading polymer coating, based on enzyme Subtilisin A and hydrophilic and swellable poly(ethylene-alt-maleic anhydride) copolymer, has been developed. The enzyme Subtilisin A was employed to prevent the settlement of barnacle *B. amphitrite* cyprids [138,139]. The barnacle cyprids secrete temporary adhesives for exploration of surface and subsequently induce settlement for barnacles. This temporary adhesive of cyprids is proteinaceous and sensitive to hydrolysis by proteolytic serine proteases [140,141]. The protease Subtilisin A is a serine protease with high specificity for the hydrolysis of proteins in aqueous media [142] and thus can degrade the proteinaceous temporary adhesive of the cyprids and prevent the settlement of barnacle cyprids. Accordingly, the bioactive poly(ethylene-alt-maleic anhydride) copolymer layer containing Subtilisin A was able to interfere with the settlement of cyprids and their permanent fixation on the surface. With increasing enzyme activities, barnacle cyprids settlement decreased gradually and with an increase in the post-settlement adhesion failure [138]. The challenge for enzyme technology is to achieve controlled release and stability of the enzymes when incorporated into a coating [139,143].

#### 5. Multifunctional polymers for fouling management coatings

A critical challenge in the development of antifouling polymer coatings is the presence of a vast diversity of marine fouling organisms. It is difficult to find generalization as fouling organisms respond differently to different surface properties. For example, the diatom *N. perminuta* is released more easily from hydrophilic surfaces, while the green alga *U. linza* is from hydrophobic surfaces [131]; barnacles settle in higher percentage on



**Fig. 12.** AFM phase images of the amphiphilic triblock copolymers with grafted (A) Brij 72 side chain and (B) Brij 76 side chain [164]. Copyright 2011, Reproduced with permission from the American Chemical Society.

surfaces with higher initial wettability, while bryozoans on surfaces with lower initial wettability [144,145]. Thus, a promising approach may lie in design of coatings with multiple synergistic surface functionalities. A multitude of multifunctional polymer coatings have been developed and evaluated for marine antifouling efficacies.

### 5.1. Fouling-resistant and fouling release polymer coatings

#### 5.1.1. Hybrid xerogels

Organosilica-based xerogels have been developed from hydrocarbonsilyl, aminopropylsilyl and fluorocarbonsilyl-containing precursors for combating biofouling [41,49,146–150]. The xerogel coatings exhibit anti-adhesion and fouling release effects toward the zoospores *Ulva*, diatom *N. perminuta* and barnacle larvae (*B. amphitrite*). Interestingly, the adhesion of macrofoulers and microfoulers on xerogel surfaces follows opposite trends on surface wettability/surface energy. Barnacle cyprids show reduced settlement on hydrophobic xerogel coatings over the more hydrophilic coatings [148], while the percentage of removable of diatom *N. perminuta* increases as surface wettability is increased [41]. After incorporation of the long-chain hydrocarbonsilyl and fluorocarbonsilyl components in the xerogels, chemical segregations at nanometer and micrometer domains were generated and investigated by atomic force microscope (AFM) [149,150]. These nano- and micro-textures can further contribute to the fouling release performance of xerogels [150]. Therefore, the xerogel surfaces can be fine-tuned with long-chain alkyl and fluorinated components to provide the desirable wettability and topography for improving antifouling efficacies.

#### 5.1.2. Perfluoropolyether-based polymers

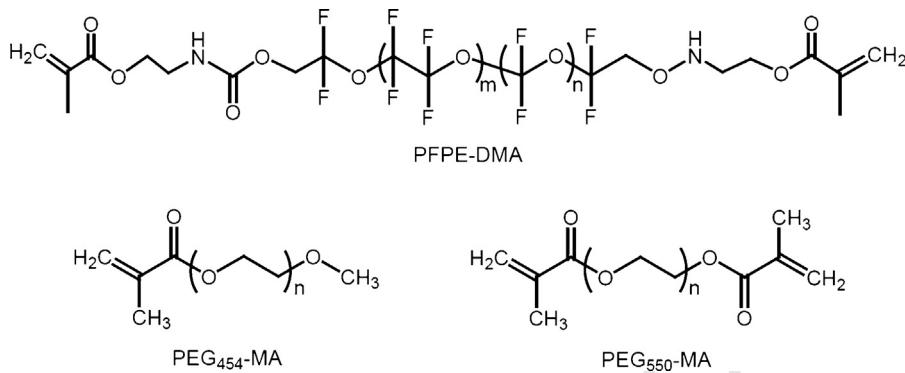
Perfluoropolyether-based terpolymers were designed as good fouling-resistant and fouling release materials [151,152]. Initially, perfluoropolyether (PFPE) macromonomer, alkyl (meth)acrylate monomer and glycidal methacrylate as the curing monomers were thermally

cross-linked to give rise to a PFPE graft terpolymers [151]. These terpolymer-modified surfaces reduced settlement of macroalgae *Ulva* markedly to approximately 10% and 25% of those on glass and PDMS elastomer, respectively. The percentages of removal of spores from the modified surfaces were also greater than that from the PDMS elastomer standard. The synthesis process was later improved by using a more energy efficient and solvent-free photochemical cross-linking reaction [152]. The resulting PFPE terpolymer-modified surfaces are highly hydrophobic, with surface tensions of  $13\text{ mN m}^{-1}$  to  $17\text{ mN m}^{-1}$ . The settlement density and attachment strength of *Ulva* were thus reduced substantially on these modified surfaces.

#### 5.1.3. Fluorinated amphiphilic networks and copolymers

The ‘ambiguous’ amphiphilic polymers incorporate both hydrophilic and hydrophobic components, and are expected to be capable of resisting biofouling and releasing of fouling organisms [153]. Many of the amphiphilic polymer materials are comprised of hydrophilic poly(ethylene glycol) (PEG) and hydrophobic fluoropolymers [153–163]. Apart from fouling-resistance of PEG and fouling release nature of the fluoroalkyl groups, phase-segregation of the amphiphilic copolymers with a mosaic of hydrophilic and hydrophobic domains on the surface are believed to have contributed to the antifouling performances (Fig. 12) [163–165].

A series of amphiphilic polymer networks, based on the photochemically cross-linked hydrophobic PFPE and hydrophilic PEG (Fig. 13), were prepared for inhibition the attachment of alga and barnacles [154–156]. Flexible monofunctional PEG (PEG<sub>454</sub>-MA) and restricted difunctional PEG (PEG<sub>550</sub>-DMA) were employed to investigate the effect of flexibility of PEG in the amphiphilic network on fouling release performance (Fig. 13) [154]. The flexible PEG chains (PEG<sub>454</sub>-MA) migrated out to the surface in a hydrophilic environment and therefore provided enhanced anti-adhesion efficacy. Besides the flexibilities, the influence of the PEG chain length in the amphiphilic networks on the antifouling performance has also been investigated, using PEG macromonomers of respective molecular weights of 300, 475 and 1100 g mol<sup>-1</sup> [156]. The



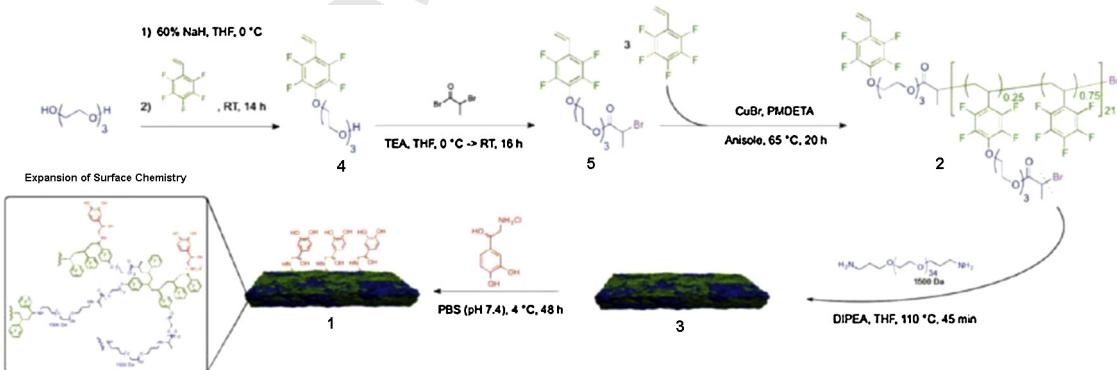
**Fig. 13.** The molecular structures of PFPE-DMA and PEG-MA for the preparation of amphiphilic polymer network.

amphiphilic PFPE-PEG networks with the highest molecular weight PEG (PEG 1100) exhibited the best performance in deterring the settlement of alga *Ulva*, diatom *N. permixta* and barnacles *B. amphitrite* cyprids. This phenomenon may be attributed to the faster segmented diffusion of PEG 1100 to the polymer-water interface than that of other two shorter PEG segments. The curing environment was also important in determining antifouling efficiency. The concentration of PEG on the surface was enhanced when the amphiphilic PFPE-PEG polymer network was cured under high humidity [155], resulting in improved non-fouling characteristics against adhesion of spores of green alga *Ulva*.

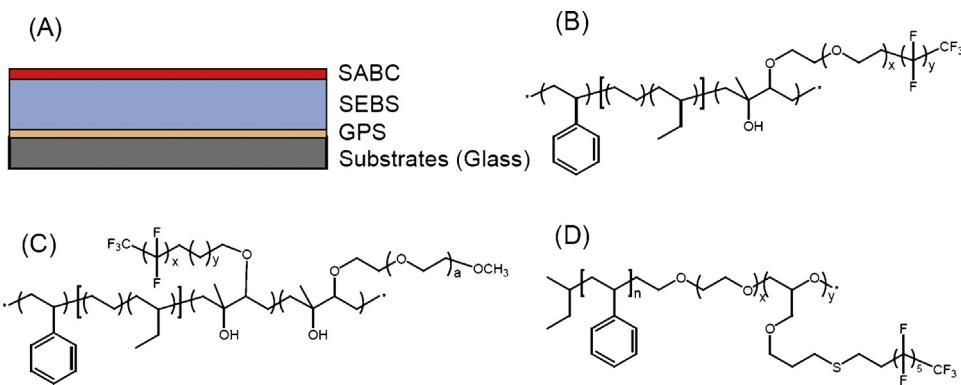
Hyperbranched cross-linked amphiphilic networks have been synthesized recently by the cross-linking of hyperbranched fluoropolymer (HBFP), which was prepared by atom transfer radical polymerization (ATRP), with a bis-amino functionalized PEG. These amphiphilic networks exhibited fouling-resistant and fouling release properties against the settlement of barnacle *B. amphitrite* cyprids [157–159]. As for the fouling release efficacy, diatoms *N. incerta* can be removed two- to three-times more easily from the HBFP-PEG surfaces than from a poly(dimethylsiloxane) (PDMS) elastomer surface. However, in tests with algal spores *U. linza*, only two formulations, among the four HBFP-PEG surfaces, displayed good fouling release performance. It is believed

that nanoscopic complexity in surface chemistry, morphology and topography may account for the resistance to biological adhesion of marine fouling organisms. A settlement sensory deterrent, noradrenaline (NA), was also immobilized in the HBFP-PEG network to produce a dual-mode antifouling polymer (Fig. 14) [158]. It is known that barnacle cyprids lose their settlement behavior and metamorphose into normal juvenile adults when exposed to NA solution [166]. The settlement of barnacle cyprids on the NA-incorporated HBFP-PEG surface was significantly reduced as compared to the unmodified HBFP-PEG surface.

Various surface-active block copolymers (SABC), which are amphiphilic and fluorinated, have been prepared as marine fouling-resistant and fouling release coatings [153,160–162]. The strategy for immobilization of SABC on surfaces involves using an elastomeric primer layer of polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) (Fig. 15A) [153,160–162]. The bilayer coating approach produces a sufficiently thick polymer film without using excessive amounts of SABC [130,167]. More importantly, the adhesion strength of hard fouling organisms is related to the surface energy and modulus [63,130,168]. The thermoplastic elastomers SEBS primer layer (~500 μm) offers good mechanical properties with low modulus [130], while the thin SABC layer (~20 μm) on top of the SEBS primer layer has a low surface energy. In fact, by employing the same top SABC layer,



**Fig. 14.** Synthesis of noradrenaline-functionalized HBFP-PEG thin films (NA-HBFP-PEG) [158]. Copyright 2012, Reproduced with permission from the American Chemical Society.



**Fig. 15.** (A) Tow-layer strategy for the preparation of antifouling and fouling release coatings. (B–D) Chemical structures of amphiphilic SABC copolymers. SABC: Surface active block copolymer, GPS: 3-(glycidoxypropyl)trimethoxysilane, SEBS: polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene thermoplastic elastomer.

the attachment strength of *U. linza* sporelings was lower on the ‘low’-modulus primer layer than on the ‘high’-modulus primer layer [153]. Therefore, the fouling release properties can be enhanced by incorporation of a low-modulus underlayer, while the fouling-resistant efficacies are improved by the amphiphilic SABC layer.

The amphiphilic SABC copolymers can be prepared via chemical modifications of the side chains of polystyrene-block-poly(ethylene-ran-butylene)-block-polysoprene precursor [153,160]. The triblock SABC copolymers, containing ethyoxylated fluoroalkyl amphiphilic side chains [153] (Fig. 15B) or mixed hydrophobic semi-fluorinated hydroxyl and hydrophilic PEG side chains [160] (Fig. 15C), can reduce the settlement of zoospores of *U. linza* and decrease the attachment strength of *Ulva* sporeling and diatom *N. perminuta* [153]. In addition to modification of side chains in the triblock copolymers, a diblock copolymer with poly(ethylene oxide) in the backbone and perfluorinated side chains (Fig. 15D) has been prepared via thiol-ene click reaction for antifouling application [161]. The resulting amphiphilic copolymer exhibited good resistance and fouling release properties against green macroalga *Ulva*. Furthermore, a coating blending triblock fluorinated amphiphilic copolymer (Fig. 15C) and the soft thermoplastic SEBS elastomer has been demonstrated to reduce biofouling of *Ulva* and *N. perminuta* [162].

#### 5.1.4. Non-fluorinated amphiphilic polymers

Instead of fluorinated polymers, other hydrophobic components, such as hydrocarbons (Fig. 16A and B), PDMS (Fig. 16C) and polyester (Fig. 16D), have also been employed to prepare amphiphilic polymer coatings for fouling-resistant and fouling release purpose [164,169–171]. Amphiphilic polymer networks, based on alkene-modified dendritic polyester (Fig. 16D) and PEG tetrathiol (Fig. 16E), have been prepared via thiol-ene click chemistry [171]. The settlement densities of zoospores *Ulva* on the amphiphilic surfaces were much lower than that on the PDMS surface. Restructuring of the amphiphilic surface after immersion changes the surface nanostructure, which probably makes it more difficult for spores to ‘detect’ and adhere to the surface [171,172]. As for the fouling release

ability, the adhesion strength decreases with increasing PEG content from 0 to 15 PEG wt%.

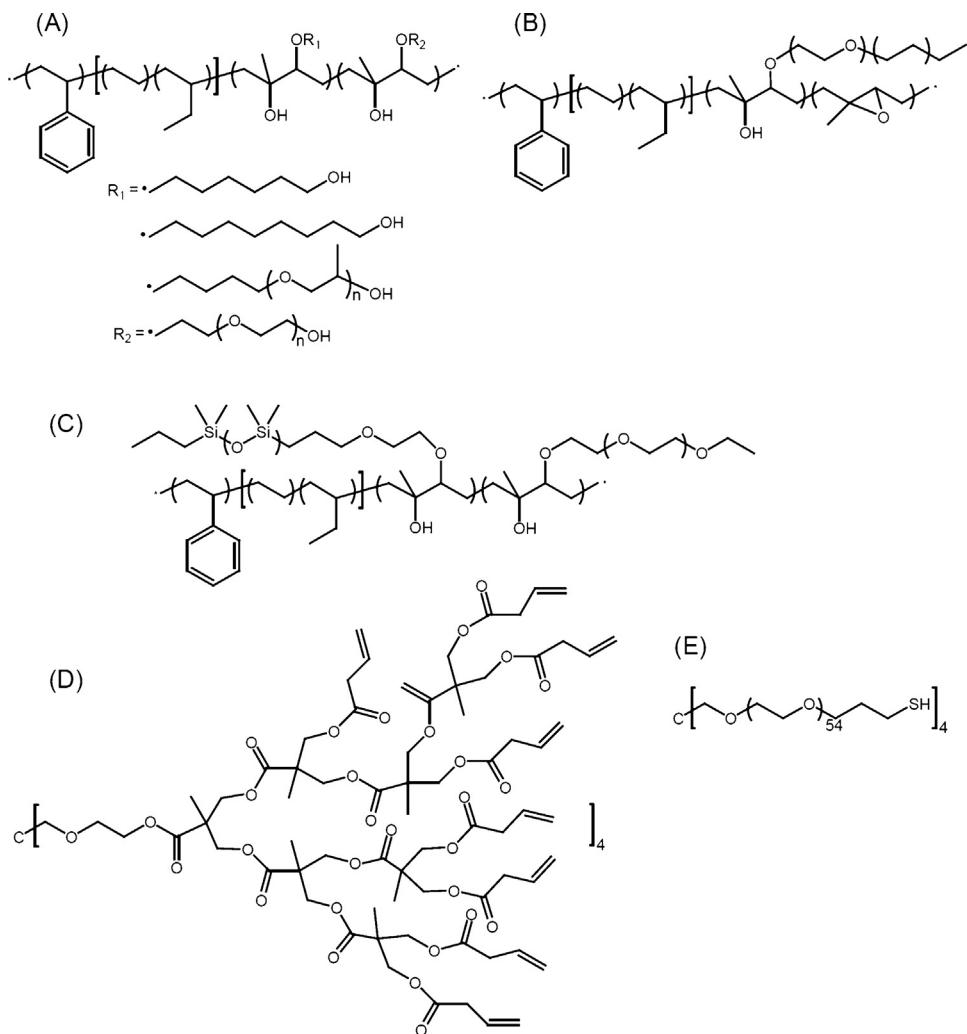
#### 5.2. Fouling-resistant and antimicrobial polymer coatings

To develop an effective coating, it is desirable to combine anti-macrofouling and anti-microbial properties. Based on this concept, poly(2-hydroxyethyl methacrylate) hydrogels containing quaternary ammonium compounds (QAC) were developed for inhibiting marine biofouling [173–177]. The hydrogel component functions as a hydrophilic material to deter biofouling, while QAC acts as an antimicrobial agent. The hydrogel coatings not only exhibit good resistance to microfouling of algal, *Enteromorpha* (=*Ulva*) *intestinalis* and *Melosira nummuloides* [175], but also inhibit macrofouling by barnacle cyprids (*Semibalanus balanoides*) and mussels (*Mytilus edulis*) [177].

Antifouling and antimicrobial multi-layer polymer coatings have also been developed recently (Fig. 17) [178]. The fouling-resistant poly(ethylene glycol) methyl ether methacrylate-based polymer chains and antimicrobial 2-(methacryloyloxy)ethyl trimethyl ammonium chloride-based polymer chains were click-assembled layer-by-layer via azide-alkyne click reaction [178]. The multilayer polymer coatings are resistant to bacterial adhesion and are bactericidal to *Pseudomonas* sp. NCIMB 2021. Settlement of barnacle *B. amphitrite* cyprids on the multilayer coatings was reduced by up to 80%. The antifouling efficacy of the polymer coatings was correlated with the number of deposited polymer layers, improving as the layer number was increased.

#### 5.3. Antimicrobial and fouling release polymer coatings

Polysiloxane coatings containing chemically tethered quaternary ammonium moieties have been designed to prevent marine biofouling through the combined fouling release and antimicrobial actions [179–181]. The bifunctional PDMS-quaternary ammonium salt (PDMS-QAS) coatings (Fig. 18A) were prepared by condensation of the silanol groups in QAS-functional alkoxy silane, silanol-terminated PDMS and methyltriacetoxysilane cross-linker.

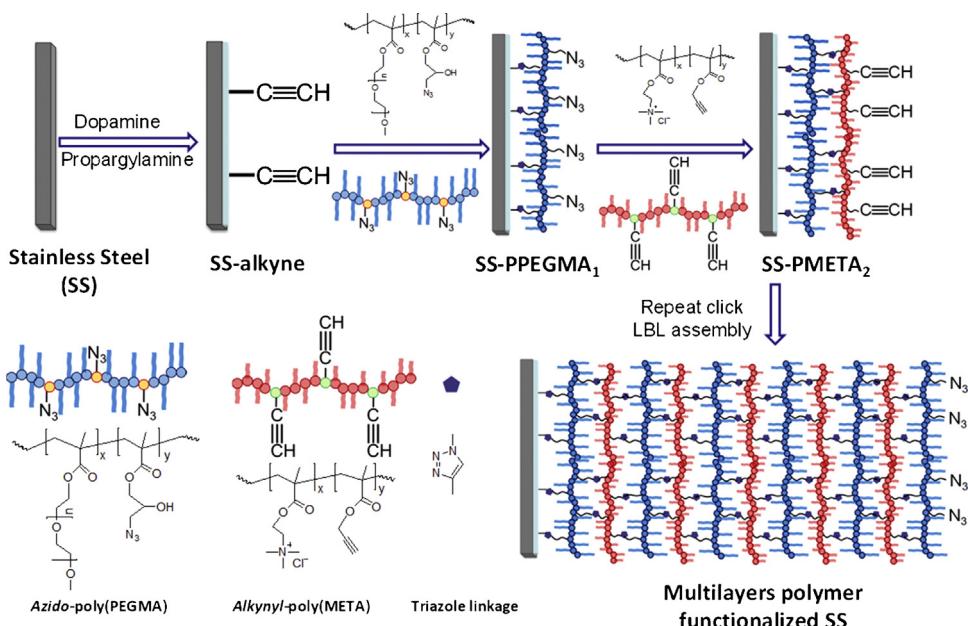


**Fig. 16.** (A) Amphiphilic copolymers containing hydrophobic aliphatic (linear hydrocarbon or propylene oxide-derived groups) and hydrophilic poly(ethylene glycol) side chains, (B) amphiphilic copolymers containing hydrophobic aliphatic groups and hydrophilic poly(ethylene glycol) side chains, (C) amphiphilic copolymers containing mixed poly(dimethylsiloxane) and poly(ethylene glycol) side chains, (D) alkene-modified Boltorn polyesters and (E) 4-armed poly(ethylene glycol) tetrathiol.

The PDMS-QAS-functionalized surface revealed a heterogeneous two-phase morphology, resulted from phase separation of the polar QAS molecules from the non-polar PDMS units [181,182]. It exhibited antimicrobial activity against marine bacteria *Cellulophaga lytica* and *Halomonas pacifica*, and diatom *N. incerta*. The antimicrobial activity was a function of the alkyl chain length in the QAS moieties [179]. In addition to alkyl chain length, the coatings with ethoxysilane-functional QAS provided enhanced antimicrobial property as compared to those with methoxysilane-functional QAS [181]. The fouling release performance was assessed by alga *Ulva*. A correlation between surface nano-roughness and fouling release efficacy was suggested by the observation that the surface coatings with the best fouling release performance also displayed the highest surface roughness.

A semifluorinated-quaternized triblock copolymer (SQTC, Fig. 18B) was synthesized to impart the fouling

release fluoropolymer coating with antimicrobial activity [183]. The SQTC-functionalized surface showed very high antibacterial activity against the airborne bacterium *Staphylococcus aureus*, but only limited algicidal activity against the marine alga *Ulva*. A superhydrophobic film containing silver nanoparticles in multi-layered polyelectrolytes was prepared for prevention of marine bacteria fouling [184]. The multi-layered polyelectrolytes were prepared from polyethyleneimine (PEI) and poly(acrylic acid) (PAA) in the form of hierarchical nanostructures. Silver nanoparticles were enclosed in the polyelectrolytes multilayers to improve the antimicrobial activity. Finally, a layer of tridecafluoroctyl triethoxysilane was deposited on top to increase the hydrophobicity. The resulting superhydrophobic surface, which mimics the bioinspired combination of low surface energy and hierarchical topography, reduced biofilms of the sulfate-reducing bacteria, *D. salexigens*.

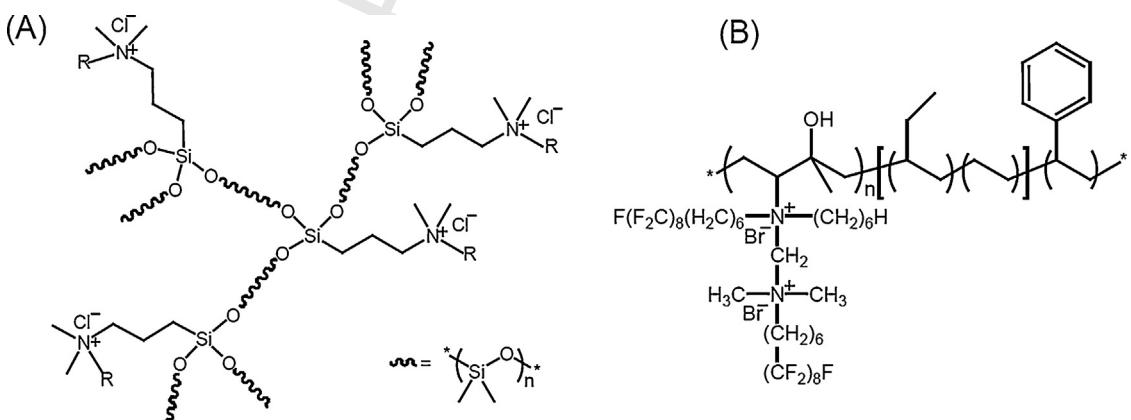


**Fig. 17.** Schematic illustration of the preparation of antifouling and antibacterial polymer multilayer coatings via layer-by-layer click deposition [178]. Copyright 2012, Reproduced with permission from the American Chemical Society.

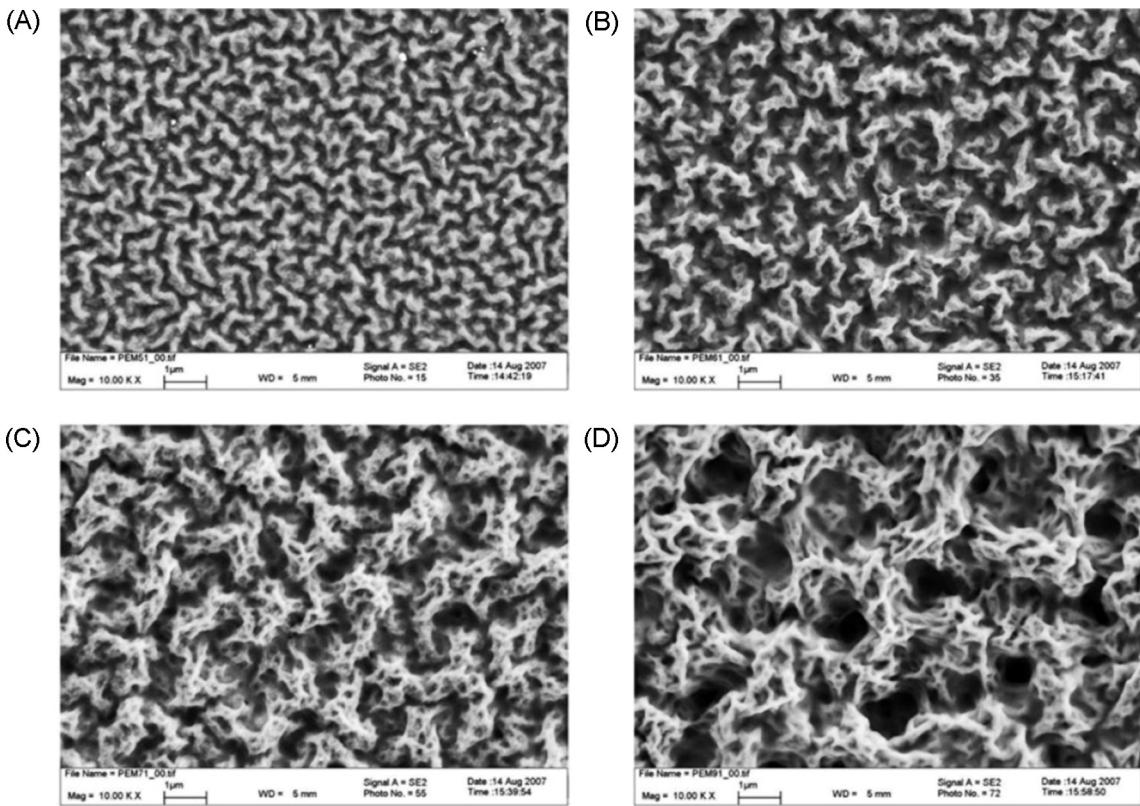
#### 5.4. Bioinspired micro- and nanostructured polymer surfaces

Surface topography plays an important role in the settlement of several marine species [52–58]. A variety of micro- and nanostructured surfaces, inspired by the naturally antifouling surfaces of the shells of invertebrate [185–187], skin of sharks [168,188–191] and lotus leaves [192], exhibit antifouling properties. 'The Sharklet' patterned surfaces have been shown to reduce spore settlement compared to smooth surfaces, regardless of the substrate used [193,194]. Inspired by skin of pilot whale *Globicephala melas*, a multilayer polymer coating with complex surface structure, as shown in Fig. 19, has been developed by layer-by-layer spray-coating deposition of oppositely charged PAA and PEI polyelectrolytes [195]. The texture size, which can be controlled by tuning the pH of PEI

solution, strongly influences the settlement of zoospores of *Ulva*. The settlement strength was reduced substantially on the sub-micrometer-sized surface with a morphological size of 600 nm. The capillary forces in the nanostructures bind water strongly and cannot be excluded by the adhesive of the spore. As for the settlement density, the lowest level of settlement was from the structures of the order of 2 μm, in a similar size class as that observed in the skin of *Globicephala melas* [195]. As a variety of organisms with different characteristics and settlement preferences are present in the marine environment, coating patterns with a single length scale will be unlikely to inhibit marine biofouling. Hierarchical surfaces [57,196] or micropatterned coatings with topographical features that are smaller than either dimension of marine organisms or the parts of organisms that explore the surface for settlement [197–199] may be promising as anti-biofouling coatings.



**Fig. 18.** (A) PDMS-QAS polymer coating and (B) semifluorinated-quaternized triblock copolymer.



**Fig. 19.** SEM topographic images of the PAA/PEI multilayer films prepared from polyelectrolyte solutions at different pH values: (A) PAA pH 2.89/PEI pH 5.0; (B) PAA pH 2.89/PEI pH 6.5; (C) PAA pH 2.89/PEI pH 7.5; (D) PAA pH 2.89/PEI pH 9.0. [195] Copyright 2010, Reproduced with permission from Wiley-VCH.

Examples for bio-inspiration may not need to come from the aquatic environment. Fouling-resistant and fouling release polymer coatings based on grafted poly(3-sulfopropyl methacrylate) (PSPMA) brushes have been prepared via SI-ATRP from the biomimetic structured surface of natural *Trifolium* leaf [200]. Settlement assays against two freshwater microalgae, *Chlorella* and *Nannochloropsis maritima*, indicated that both the biomimetic microstructures with self-cleaning property and surface chemical composition contributed greatly to fouling-resistant and fouling release properties.

## 6. Polymer coatings for combating marine biocorrosion

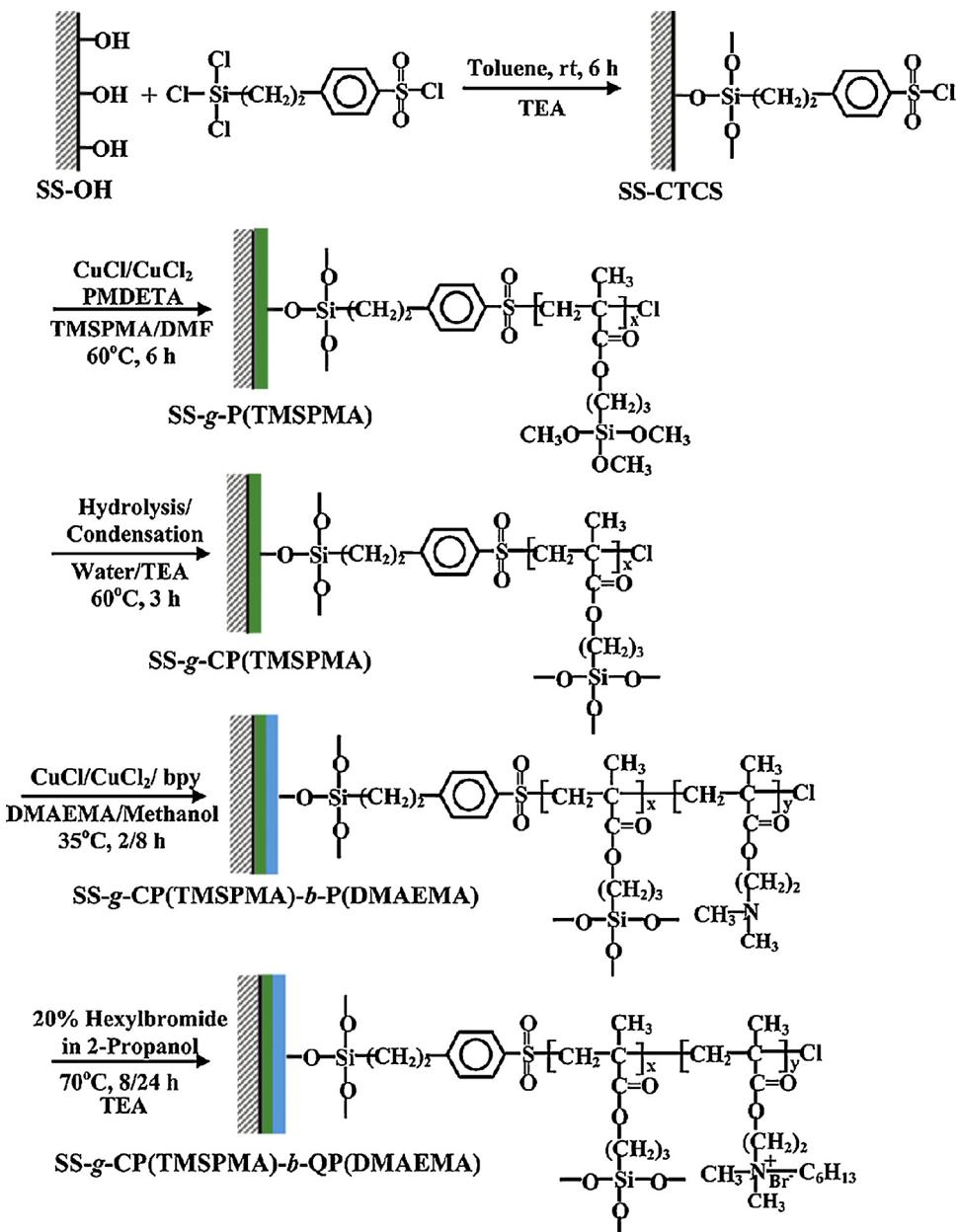
Microbiologically influenced corrosion (MIC), or biocorrosion, is the initiation and facilitation (or acceleration) of corrosion due to the activity of microbiological organisms, such as microorganism stimulated cathodic or anodic reaction and/or microorganisms promoted establishment of electrolytic environments [15,17]. It is a great concern for the aquatic and maritime industries, as about 20–30% corrosion is associated with microbial activity, resulting in a direct cost of 30–50 billion dollars per year worldwide [201].

Among the diverse anti-biocorrosion techniques, which include the use of biocides, cathodic protection, beneficial

application of bacterial biofilms and application of protective coatings, the use of protective organic coatings has been the major strategy since the 1980s and accounts for 80% of the total cost for corrosion prevention [202]. Traditionally, polymers, such as polyurethane, silicones, epoxy resins, polyimides and fluorinated compounds, are used in protective coatings. Recently, functional polymer brushes, including antimicrobial polymers and electroactive polymers, have been employed as protective coatings to combat biocorrosion [84,85,203–207].

### 6.1. Antimicrobial polymers

Antimicrobial polymer brush coatings containing tertiary amino groups, such as quaternized poly(4-vinylpyridine) (P4VP) and poly(2-dimethylaminoethyl methacrylate) (PDMAEMA), have been prepared by SI-ATRP and quaternized with alkyl halides to impart the antibacterial property [85,203]. Furthermore, using antibacterial polymer brushes as the outer layer, inorganic-organic hybrid coatings with titanium oxide or polysilsesquioxane as inner layers were developed for inhibition of biocorrosion [84,204]. The well-defined hybrid polymer coating, poly(3-(trimethoxysilyl)propyl methacrylate)-block-poly(2-(dimethylamino)ethyl methacrylate) (PTMSPMA-*b*-PDMAEMA), prepared by consecutive SI-ATRP (Fig. 20), exhibited good antibacterial



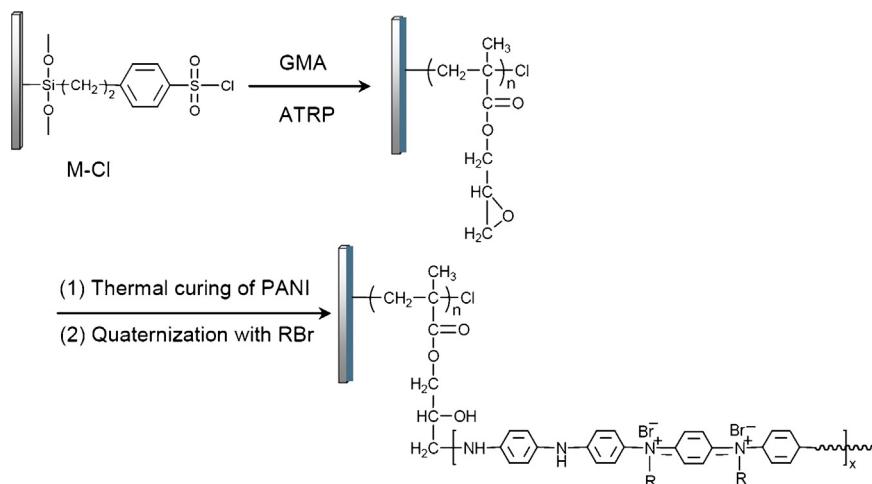
**Fig. 20.** Schematic illustration of the preparation of inorganic-organic hybrid coatings via SI-ATRP for combating biocorrosion [84]. Copyright 2010, Reproduced with permission from the American Chemical Society.

1062 effects and inhibited biocorrosion induced by sulfate-  
1063 reducing bacterial *Desulfovibrio desulfuricans* (*D.*  
1064 *desulfuricans*) [84]. The cross-linked polysilsesquioxane  
1065 as inner layer provided a durable and resistant coating  
1066 to electrolytes, while the pendant quaternary ammonium  
1067 cations produced the biocidal effects.

#### 1068 6.2. Electroactive polymers

1069 Conducting polymers have been proposed as a means  
1070 to provide corrosion protection, via anodic protection

1071 and mediation of oxygen reduction as well as serving  
1072 as barriers and inhibitors [208–210]. A bilayer polymer  
1073 coating consisting of poly(glycidyl methacrylate) (PGMA)  
1074 and polyaniline (PANI) was synthesized by SI-ATRP of  
1075 GMA, followed by thermal curing with PANI and quaternization  
1076 with alkyl halide (Fig. 21) [206]. PANI is the  
1077 most widely used conducting polymer for anticorrosion  
1078 coatings because of its environmental stability, low cost,  
1079 good process ability, ease of synthesis, and unique redox  
1080 properties [211,212]. The resulting cross-linked electro-  
1081 active coating exhibited good antibacterial effect against



**Fig. 21.** Schematic illustration of the preparation of poly(glycidyl methacrylate)-polyaniline bilayer coatings via SI-ATRP for combating biocorrosion [206].

*Pseudomonas* sp. and high biocorrosion inhibition efficiency (up to 95% reduction in corrosion current density from that of the control).

## 7. Conclusions and outlook

A wide variety of polymer brushes and coatings for inhibiting marine biofouling and biocorrosion have been developed in recent years. In comparison to biocide-releasing coatings, the polymer brush coatings described in this review combat marine biofouling (microfouling and macrofouling) via environment-safe mechanisms as they do not release biocides. The environmental impact of the coatings is further reduced through the use of biological and biomimetic coupling agents or anchors for the brush coatings. Fouling-resistant coatings based on hydrophilic polymer brush coatings have been demonstrated good success. Another strategy is by employing fouling release polymer coatings to reduce the adhesion strength between marine organisms and material surfaces, leading to an easy removal of biofoulants. Antimicrobial polymer brush coatings, cationic polymers in particular, are effective in reducing marine biofouling and preventing biocorrosion because of their good antimicrobial properties. Bioinspired micro- and nano-textures, such as complex topographies that mimic the skin of sharks and lotus leaves, can also inhibit biofouling and exhibit 'self-cleaning' property. Antimicrobial and electroactive polymers have been applied as effective anti-biocorrosion coatings through their bactericidal ability and anodic protection, respectively. Well-defined and multifunctional polymer coatings, possessing fouling-resistant, fouling release and antimicrobial properties, have been designed and synthesized via controlled radical polymerization and click chemistry. In particular, amphiphilic polymer coatings are effective in combating marine biofouling through a combination of combining fouling-resistant and fouling release properties.

However, major challenges lies ahead for the development of antifouling and anti-biocorrosion polymer coatings into viable commercial products. First of all, the antifouling

polymer coatings will require good stability and durability in long-term applications as conditions of use in the natural marine environment are harsh. The ocean contains a vast diversity of marine fouling organisms that use different ways to adhere to surfaces. It is difficult to define generalities as various fouling organisms respond differently to the different polymer coatings. A promising approach is to develop 'multifunctional coatings', combining synergistically fouling-resistance, fouling release and antimicrobial properties, for surfaces with specifically patterned topographies.

There remains also the problem that some polymer coatings, especially amphiphilic polymers, will reconstruct once immersed in aqueous media, resulting in changes in surface morphology (roughness) and composition. In this case, it is of great importance to keep the functional groups of the polymer coatings on the top/outer surface, rather than burying inside, for the coating to work effectively. Characterization of the surface structures of polymer coatings by atomic force microscopy and sum frequency generation vibrational spectroscopy [213] after immersing in an aqueous environment will be necessary. Besides, a good understanding of the interactions between marine organisms and polymer coatings will be very helpful when designing effective antifouling polymer coatings.

## Acknowledgement

The authors would like to acknowledge the financial support for this study from A\*STAR-SERC MIMO Program under grant no. 1123004048 (NUS WBS no. R279-000-356-305)

## References

- [1] Callow JA, Callow ME. Trends in the development of environmentally friendly fouling-resistant marine coatings. *Nat Commun* 2011;2, 244/1-10.
- [2] Magin CM, Cooper SP, Brennan AB. Non-toxic antifouling strategies. *Mater Today* 2010;13:36–44.

- [3] Lejars M, Margallan A, Bressy C. Fouling release coatings: a nontoxic alternative to biocidal antifouling coatings. *Chem Rev* 2012;112:4347–90.
- [4] Yebra DM, Kiil S, Dam-Johansen K. Antifouling technology – past, present and future steps towards efficient and environmentally friendly antifouling coatings. *Prog Org Coat* 2004;50: 75–104.
- [5] Chambers LD, Stokes KR, Walsh FC, Wood RJK. Modern approaches to marine antifouling coatings. *Surf Coat Technol* 2006;201:3642–52.
- [6] Almeida E, Diamantino TC, de Sousa O. Marine paints: the particular case of antifouling paints. *Prog Org Coat* 2007;59:2–20.
- [7] Krishnan S, Weinman CJ, Ober CK. Advances in polymers for anti-biofouling surfaces. *J Mater Chem* 2008;18:3405–13.
- [8] Groza CM, Walker GC. Approaches in designing non-toxic polymer surfaces to deter marine biofouling. *Soft Matter* 2009;5: 4088–100.
- [9] Finnie AA, Williams DN. Paint and coatings technology for the control of marine fouling. In: Durr S, Thomason JC, editors. *Biofouling*. Chichester: Wiley-Blackwell; 2010. p. 185–206.
- [10] Champ MA. A review of organotin regulatory strategies, pending actions, related costs and benefits. *Sci Total Environ* 2000;258:21–71.
- [11] Abbott A, Abel PD, Arnold DW, Milne A. Cost-benefit analysis of the use of TBT: the case for a treatment approach. *Sci Total Environ* 2000;258:5–19.
- [12] Schultz MP. Effects of coating roughness and biofouling on ship resistance and powering. *Biofouling* 2007;23:331–41.
- [13] Videla HA. Manual of biocorrosion. Boca Raton FL: CRC Press; 1996, 273 pp.
- [14] Rascio VJD. Antifouling coatings: where do we go from here. *Corros Rev* 2000;18:133–54.
- [15] Beech IB, Sunner JA, Hiraoka K. Microbe-surface interactions in bio-fouling and biocorrosion processes. *Int Microbiol* 2005;8:157–68.
- [16] Rao TS. Microbiologically influenced corrosion: basics and case studies. *Corros Rev* 2009;27:333–65.
- [17] Beech WB, Sunner J. Biocorrosion: towards understanding interactions between biofilms and metals. *Curr Opin Biotechnol* 2004;15:181–6.
- [18] Flemming HC, Heitz E, Sand W. Checklist. In: Heitz E, Flemming HC, Sand W, editors. *Microbially influenced corrosion of materials: scientific and engineering aspects*. Berlin: Springer-Verlag; 1996. p. 461–3.
- [19] Neoh KG, Kang ET. Combating bacterial colonization on metals via polymer coatings: relevance to marine and medical applications. *ACS Appl Mater Interfaces* 2011;3:2808–19.
- [20] Hellio C, Yebra DM. Introduction. In: Hellio C, Yebra DM, editors. *Advances in marine antifouling coatings and technologies*. Cambridge UK: Woodhead Publishing Ltd; 2009. p. 1–15.
- [21] Evans SM, Leksono T. The use of whelks and oysters as biological indicators of pollution from anti-fouling paints. *J Biol Educ* 1995;29:97–102.
- [22] Evans SM, Leksono T, McKinnell PD. Tributyltin pollution – a diminishing problem following legislation limiting the use of Tbt-based anti-fouling paints. *Mar Pollut Bull* 1995;30:14–21.
- [23] Voulvouli N, Scrimshaw MD, Lester JN. Alternative antifouling biocides. *Appl Organomet Chem* 1999;13:135–43.
- [24] Omae M. General aspects of tin-free antifouling paints. *Chem Rev* 2003;103:3431–48.
- [25] Matyjaszewski K, Tsarevsky NV. Nanostructured functional materials prepared by atom transfer radical polymerization. *Nat Chem* 2009;1:276–88.
- [26] Xu FJ, Neoh KG, Kang ET. Bioactive surfaces and biomaterials via atom transfer radical polymerization. *Prog Polym Sci* 2009;34:719–61.
- [27] Matyjaszewski K. Atom transfer radical polymerization (ATRP): current status and future perspectives. *Macromolecules* 2012;45:4015–39.
- [28] Kolb HC, Finn MG, Sharpless KB. Click chemistry: diverse chemical function from a few good reactions. *Angew Chem Int Ed* 2001;40:2004–21.
- [29] Lutz JF. 1,3-Dipolar cycloadditions of azides and alkynes: a universal ligation tool in polymer and materials science. *Angew Chem Int Ed* 2007;46:1018–25.
- [30] Hoyle CE, Lowe AB, Bowman CN. Thiol-click chemistry: a multi-faceted toolbox for small molecule and polymer synthesis. *Chem Soc Rev* 2010;39:1355–87.
- [31] Hoyle CE, Bowman CN. Thiol-ene click chemistry. *Angew Chem Int Ed* 2010;49:1540–73.
- [32] Duque L, Menges B, Borros S, Forch R. Immobilization of biomolecules to plasma polymerized pentafluorophenyl methacrylate. *Biomacromolecules* 2010;11:2818–23.
- [33] Deng XP, Eyster TW, Elkasaibi Y, Lahann J. Bio-orthogonal polymer coatings for co-presentation of biomolecules. *Macromol Rapid Commun* 2012;33:640–5.
- [34] Rittschof D. Research on environmentally benign antifouling coatings. In: Durr S, Thomason JC, editors. *Biofouling*. Chichester: Wiley-Blackwell; 2010. p. 396–409.
- [35] Clare AS, Rittschof D, Gerhart DJ, Maki JS. Molecular approaches to non-toxic antifouling. *Invertebrate Reprod Dev* 1992;22:67–76.
- [36] Baier RE, Shafrin EG, Zisman WA. Adhesion mechanisms that assist or impede it. *Science* 1968;162:1360–8.
- [37] Roberts D, Rittschof D, Holm E, Schmidt AR. Factors influencing initial larval settlement – temporal, spatial and surface molecular components. *J Exp Mar Biol Ecol* 1991;150:203–21.
- [38] Baier RE, Meyer AE. Surface analysis of fouling-resistant marine coatings. *Biofouling* 1992;6:165–80.
- [39] Gerhart DJ, Rittschof D, Hooper IR, Eisenman K, Mayer AE, Baier RE, Young C. Rapid and inexpensive quantification of the combined polar components of surface wettability: application to biofouling. *Biofouling* 1992;5:251–9.
- [40] Ista LK, Callow ME, Finlay JA, Coleman SE, Nolasco AC, Simons RH, Callow JA, Lopez GP. Effect of substratum surface chemistry and surface energy on attachment of marine bacteria and algal spores. *Appl Environ Microbiol* 2004;70:4151–7.
- [41] Bennett SM, Finlay JA, Gunari N, Wells DD, Meyer AE, Walker GC, Callow ME, Callow JA, Bright JV, Detty MR. The role of surface energy and water wettability in aminoalkyl/fluorocarbon/hydrocarbon-modified xerogel surfaces in the control of marine biofouling. *Biofouling* 2010;26:235–46.
- [42] Wu L, Jasinski J, Krishnan S. Carboxybaitaine, sulfobaitaine, and cationic block copolymer coatings: a comparison of the surface properties and antibiofouling behavior. *J Appl Polym Sci* 2012;124:2154–70.
- [43] Dahlstrom M, Jonsson H, Jonsson PR, Elwing H. Surface wettability as a determinant in the settlement of the barnacle *Balanus improvisus* (DARWIN). *J Exp Mar Biol Ecol* 2004;305:223–32.
- [44] Petrone L, Di Fino A, Aldred N, Sukkaew P, Ederth T, Clare AS, Liedberg B. Effects of surface charge and Gibbs surface energy on the settlement behaviour of barnacle cyprids (*Balanus amphitrite*). *Biofouling* 2011;27:1043–55.
- [45] Yang WJ, Neoh KG, Kang ET, Lee SSC, Teo SLM, Rittschof D. Functional polymer brushes via surface-initiated atom transfer radical graft polymerization for combating marine biofouling. *Biofouling* 2012;28:895–912.
- [46] Rasmussen K, Ostgaard K. Adhesion of the marine fouling diatom *Amphora coffeaeformis* to non-solid gel surfaces. *Biofouling* 2001;17:103–15.
- [47] Rasmussen K, Willemse PR, Ostgaard K. Barnacle settlement on hydrogels. *Biofouling* 2002;18:177–91.
- [48] Rasmussen K, Ostgaard K. Adhesion of the marine bacterium *Pseudomonas* sp NCIMB2021 to different hydrogel surfaces. *Water Res* 2003;37:519–24.
- [49] Evariste E, Gatley CM, Detty MR, Callow ME, Callow JA. The performance of aminoalkyl/fluorocarbon/hydrocarbon-modified xerogel coatings against the marine alga *Ectocarpus crouaniorum*; relative roles of surface energy and charge. *Biofouling* 2013;29:171–84.
- [50] Ueshima M, Tanaka S, Nakamura S, Yamashita K. Manipulation of bacterial adhesion and proliferation by surface charges of electrically polarized hydroxyapatite. *J Biomed Mater Res* 2002;60:578–84.
- [51] Zhao YH, Zhu XY, Wee KH, Bai RB. Achieving highly effective non-biofouling performance for polypropylene membranes modified by UV-induced surface graft polymerization of two oppositely charged monomers. *J Phys Chem B* 2010;114:2422–9.
- [52] Kirschner CM, Brennan AB. Bio-inspired antifouling strategies. In: Clarke DR, editor. *Annual review of materials research*, vol. 42. Palo Alto: Annual Reviews; 2012. p. 211–29.
- [53] Scardino AJ, de Nys R. Mini review: biomimetic models and bioinspired surfaces for fouling control. *Biofouling* 2011;27:73–86.
- [54] Bhushan B, Jung YC. Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction. *Prog Mater Sci* 2011;56:1–108.
- [55] Marmur A. Super-hydrophobicity fundamentals: implications to biofouling prevention. *Biofouling* 2006;22:107–15.
- [56] Salta M, Wharton JA, Stoodley P, Dennington SP, Goodes LR, Werwinski S, Mart U, Wood RJ, Stokes KR. Designing biomimetic antifouling surfaces. *Philos Trans R Soc A* 2010;368:4729–54.

- [57] Efimenko K, Finlay J, Callow ME, Callow JA, Genzer J. Development and testing of hierarchically wrinkled coatings for marine antifouling. *ACS Appl Mater Interfaces* 2009;1:1031–40.
- [58] Aldred N, Clare AS. The adhesive strategies of cyprids and development of barnacle-resistant marine coatings. *Biofouling* 2008;24:351–63.
- [59] Zhao Q, Su XJ, Wang S, Zhang XL, Navabpour P, Teer D. Bacterial attachment and removal properties of silicon- and nitrogen-doped diamond-like carbon coatings. *Biofouling* 2009;25:377–85.
- [60] Baier RE. Surface behaviour of biomaterials: the theta surface for biocompatibility. *J Mater Sci Mater Med* 2006;17:1057–62.
- [61] Schultz MP, Kavanagh CJ, Swain GW. Hydrodynamic forces on barnacles: implications on detachment from fouling-release surfaces. *Biofouling* 1999;13:323–35.
- [62] Brady RF. Fouling-release coatings for warships. *Def Sci J* 2005;55:75–81.
- [63] Brady RF, Singer IL. Mechanical factors favoring release from fouling release coatings. *Biofouling* 2000;15:73–81.
- [64] Beigbeder A, Degée P, Conlan SL, Mutton RJ, Clare AS, Pettitt ME, Callow ME, Callow JA, Dubois P. Preparation and characterisation of silicone-based coatings filled with carbon nanotubes and natural sepiolite and their application as marine fouling-release coatings. *Biofouling* 2008;24:291–302.
- [65] Rittschof D, Orihuela B, Harder T, Stafsliden S, Chisholm B, Dickinson GH. Compounds from silicones alter enzyme activity in curing barnacle glue and model enzymes. *PLoS ONE* 2011;6, e16487/1–12.
- [66] Feng DQ, Rittschof D, Orihuela B, Kwok KWH, Stafsliden S, Chisholm B. The effects of model polysiloxane and fouling-release coatings on embryonic development of a sea urchin (*Arbacia punctulata*) and a fish (*Oryzias latipes*). *Aquat Toxicol* 2012;110:162–9.
- [67] Kingshott P, Thissen H, Griesser HJ. Effects of cloud-point grafting, chain length, and density of PEG layers on competitive adsorption of ocular proteins. *Biomaterials* 2002;23:2043–56.
- [68] Higuchi A, Sugiyama K, Yoon BO, Sakurai M, Hara M, Sumita M, Sugawara S, Shirai T. Serum protein adsorption and platelet adhesion on pluronic (TM)-adsorbed polysulfone membranes. *Biomaterials* 2003;24:3235–45.
- [69] Statz A, Finlay J, Dalsin J, Callow M, Callow JA, Messersmith PB. Algal antifouling and fouling-release properties of metal surfaces coated with a polymer inspired by marine mussels. *Biofouling* 2006;22:391–9.
- [70] Schilp S, Kueller A, Rosenhahn A, Grunze M, Pettitt ME, Callow ME, Callow JA. Settlement and adhesion of algal cells to hexa(ethylene glycol)-containing self-assembled monolayers with systematically changed wetting properties. *Biointerphases* 2007;2:143–50.
- [71] Schilp S, Rosenhahn A, Pettitt ME, Bowen J, Callow ME, Callow JA, Grunze M. Physicochemical properties of (ethylene glycol)-containing self-assembled monolayers relevant for protein and algal cell resistance. *Langmuir* 2009;25:10077–82.
- [72] Lee SB, Koepsel RR, Morley SW, Matyjaszewski K, Sun YJ, Russell AJ. Permanent, nonleaching antibacterial surfaces. 1. Synthesis by atom transfer radical polymerization. *Biomacromolecules* 2004;5:877–82.
- [73] Murata H, Koepsel RR, Matyjaszewski K, Russell AJ. Permanent, non-leaching antibacterial surfaces – 2: how high density cationic surfaces kill bacterial cells. *Biomaterials* 2007;28:4870–9.
- [74] Huang JY, Koepsel RR, Murata H, Wu W, Lee SB, Kowalewski T, Russell AJ, Matyjaszewski K. Nonleaching antibacterial glass surfaces via “Grafting Onto”: the effect of the number of quaternary ammonium groups on biocidal activity. *Langmuir* 2008;24:6785–95.
- [75] Li P, Poon YF, Li WF, Zhu HY, Yeap SH, Cao Y, Qi XB, Zhou CC, Lamrani M, Beuerman RW, Kang ET, Mu YG, Li CM, Chang MW, Leong SSJ, Chan-Park MB. A polycationic antimicrobial and biocompatible hydrogel with microbe membrane suctioning ability. *Nat Mater* 2011;10:149–56.
- [76] Palermo EF, Vemparala S, Kuroda K. Cationic spacer arm design strategy for control of antimicrobial activity and conformation of amphiphilic methacrylate random copolymers. *Biomacromolecules* 2012;13:1632–41.
- [77] Zhao B, Brittain WJ. Polymer brushes: surface-immobilized macromolecules. *Prog Polym Sci* 2000;25:677–710.
- [78] Edmondson S, Osborne VL, Huck WTS. Polymer brushes via surface-initiated polymerizations. *Chem Soc Rev* 2004;33:14–22.
- [79] Hansson S, Trouillet V, Tischer T, Goldmann AS, Carlmark A, Barner-Kowollik C, Malmström E. Grafting efficiency of synthetic polymers onto biomaterials: a comparative study of Grafting-from versus Grafting-to. *Biomacromolecules* 2013;14:64–74.
- [80] Barbey R, Lavanant L, Paripovic D, Schuewer N, Sagnaux C, Tugulu S, Klok HA. Polymer brushes via surface-initiated controlled radical polymerization: synthesis, characterization, properties, and applications. *Chem Rev* 2009;109:5437–527.
- [81] Gentsch R, Pippig F, Nilles K, Theato P, Kikkeri R, Maglinao M, Lepenies B, Seeger PH, Borner HG. Modular approach toward bioactive fiber meshes carrying oligosaccharides. *Macromolecules* 2010;43:9239–47.
- [82] Guenay KA, Theato P, Klok HA. Standing on the shoulders of hermann staudinger: post-polymerization modification from past to present. *J Polym Sci A: Polym Chem* 2013;51:1–28.
- [83] Guenay KA, Schuewer N, Klok HA. Synthesis and post-polymerization modification of poly(pentafluorophenyl methacrylate) brushes. *Polym Chem* 2012;3:2186–92.
- [84] Yuan SJ, Pehkonen SO, Ting YP, Neoh KG, Kang ET. Antibacterial inorganic–organic hybrid coatings on stainless steel via consecutive surface-initiated atom transfer radical polymerization for biocorrosion prevention. *Langmuir* 2010;26:6728–36.
- [85] Yuan SJ, Xu FJ, Pehkonen SO, Ting YP, Neoh KG, Kang ET. Grafting of antibacterial polymers on stainless steel via surface-initiated atom transfer radical polymerization for inhibiting biocorrosion by *Desulfovibrio desulfuricans*. *Biotechnol Bioeng* 2009;103:268–81.
- [86] Yang W, Chen SF, Cheng G, Vaisocherova H, Xue H, Li W, Zhang JL, Jiang SY. Film thickness dependence of protein adsorption from blood serum and plasma onto poly(sulfobetaine)-grafted surfaces. *Langmuir* 2008;24:9211–4.
- [87] Aldred N, Li GZ, Gao Y, Clare AS, Jiang SY. Modulation of barnacle (*Balanus amphitrite* Darwin) cyprid settlement behavior by sulfobetaine and carboxybetaine methacrylate polymer coatings. *Biofouling* 2010;26:673–83.
- [88] Zhang Z, Finlay JA, Wang LF, Gao Y, Callow JA, Callow ME, Jiang SY. Polysulfobetaine-grafted surfaces as environmentally benign ultralow fouling marine coatings. *Langmuir* 2009;25:13516–21.
- [89] Fan XW, Lin LJ, Dalsin JL, Messersmith PB. Biomimetic anchor for surface-initiated polymerization from metal substrates. *J Am Chem Soc* 2005;127:15843–7.
- [90] Yah WO, Xu H, Soejima H, Ma W, Lvov Y, Takahara A. Biomimetic dopamine derivative for selective polymer modification of halloysite nanotube lumen. *J Am Chem Soc* 2012;134:12134–7.
- [91] Yuan SJ, Wan D, Liang B, Pehkonen SO, Ting YP, Neoh KG, Kang ET. Lysozyme-coupled poly(poly(ethylene glycol) methacrylate)-stainless steel hybrids and their antifouling and antibacterial surfaces. *Langmuir* 2011;27:2761–74.
- [92] Li CY, Wang WC, Xu FJ, Zhang LQ, Yang WT. Preparation of pH-sensitive membranes via dopamine-initiated atom transfer radical polymerization. *J Membr Sci* 2011;367:7–13.
- [93] Liu Y, Tan TTY, Yuan SJ, Choong C. Multifunctional P(PEGMA)-REDV conjugated titanium surfaces for improved endothelial cell selectivity and hemocompatibility. *J Mater Chem B* 2013;1:157–67.
- [94] Faure E, Falentin-Daudre C, Jerome C, Lyskawa J, Fournier D, Woisel P, Detrembleur C. Catechols as versatile platforms in polymer chemistry. *Prog Polym Sci* 2013;38:236–70.
- [95] Xu LQ, Jiang H, Neoh KG, Kang ET, Fu GD. Poly(dopamine acrylamide)-co-poly(propargyl acrylamide)-modified titanium surfaces for ‘click’ functionalization. *Polym Chem* 2012;3:920–7.
- [96] Yang WJ, Cai T, Neoh KG, Kang ET, Dickinson GH, Teo SLM, Rittschof D. Biomimetic anchors for antifouling and antibacterial polymer brushes on stainless steel. *Langmuir* 2011;27:7065–76.
- [97] Yang WJ, Cai T, Neoh KG, Kang ET, Teo SLM, Rittschof D. Barnacle cement as surface anchor for “clicking” of antifouling and antimicrobial polymer brushes on stainless steel. *Biomacromolecules* 2013;14:2041–51.
- [98] Harder P, Grunze M, Dahint R, Whitesides GM, Laibinis PE. Molecular conformation in oligo(ethylene glycol)-terminated self-assembled monolayers on gold and silver surfaces determines their ability to resist protein adsorption. *J Phys Chem B* 1998;102:426–36.
- [99] Ostuni E, Chapman RG, Holmlin RE, Takayama S, Whitesides GM. A survey of structure–property relationships of surfaces that resist the adsorption of protein. *Langmuir* 2001;17:5605–20.
- [100] Muroski T, Ahmed N, Gong JP. Antifouling properties of hydrogels. *Sci Technol Adv Mater* 2011;12:064706.
- [101] Lundberg P, Bruin A, Klijnstra JW, Nyström AM, Johansson M, Malkoch M, Hult A. Poly(ethylene glycol)-based thiol-ene hydrogel coatings—curing chemistry, aqueous stability, and potential marine antifouling applications. *ACS Appl Mater Interfaces* 2010;2:903–12.
- [102] Ekblad T, Bergstrom G, Ederth T, Conlan SL, Mutton R, Clare AS, Wang S, Liu YL, Zhao Q, D’Souza F, Donnelly CT, Willemsen PR, Pettitt ME, Callow ME, Callow JA, Liedberg B. Poly(ethylene glycol)-containing hydrogel surfaces for antifouling applications

- in marine and freshwater environments. *Biomacromolecules* 2008;9:2775–83.
- [103] Yoshikawa C, Goto A, Tsujii Y, Fukuda T, Kimura T, Yamamoto K, Kishida A. Protein repellency of well-defined, concentrated poly(2-hydroxyethyl methacrylate) brushes by the size-exclusion effect. *Macromolecules* 2006;39:2284–90.
- [104] Murosaki T, Noguchi T, Kakugo A, Putra A, Kurokawa T, Furukawa H, Osada Y, Gong JP, Nogata Y, Matsumura K, Yoshimura E, Fusetani N. Antifouling activity of synthetic polymer gels against cyprids of the barnacle (*Balanus amphitrite*) in vitro. *Biofouling* 2009;25: 313–20.
- [105] Murosaki T, Noguchi T, Hashimoto K, Kakugo A, Kurokawa T, Saito J, Chen YM, Furukawa H, Gong JP. Antifouling properties of tough gels against barnacles in a long-term marine environment experiment. *Biofouling* 2009;25:657–66.
- [106] Jiang SY, Cao ZQ. Ultralow-fouling, functionalizable, and hydrolyzable zwitterionic materials and their derivatives for biological applications. *Adv Mater* 2010;22:920–32.
- [107] Chen SF, Zheng J, Li LY, Jiang SY. Strong resistance of phosphorylcholine self-assembled monolayers to protein adsorption: insights into nonfouling properties of zwitterionic materials. *J Am Chem Soc* 2005;127:14473–8.
- [108] He Y, Hower J, Chen SF, Bernards MT, Chang Y, Jiang SY. Molecular simulation studies of protein interactions with zwitterionic phosphorylcholine self-assembled monolayers in the presence of water. *Langmuir* 2008;24:10358–64.
- [109] Li Y, Liu CM, Yang JY, Gao YH, Li XS, Que GH, Lu JR. Anti-biofouling properties of amphiphilic phosphorylcholine polymer films. *Colloids Surf B* 2011;85:125–30.
- [110] Morra M, Cassinelli C. Non-fouling properties of polysaccharide-coated surfaces. *J Biomater Sci Polym Ed* 1999;10:1107–24.
- [111] Morra M, Cassinelli C. Surface studies on a model cell-resistant system. *Langmuir* 1999;15:4658–63.
- [112] Morra M. Engineering of biomaterials surfaces by hyaluronan. *Biomacromolecules* 2005;6:1205–23.
- [113] Cao XY, Pettitt ME, Conlan SL, Wagner W, Ho AD, Clare AS, Callow JA, Callow ME, Grunze M, Rosenhahn A. Resistance of polysaccharide coatings to proteins, hematopoietic cells, and marine organisms. *Biomacromolecules* 2009;10:907–15.
- [114] Ederth T, Ekblad T, Pettitt ME, Conlan SL, Du CX, Callow ME, Callow JA, Mutton R, Clare AS, D'Souza F, Donnelly G, Bruun A, Willemsen PR, Su XJ, Wang S, Zhao Q, Hederos M, Konradsson P, Liedberg B. Resistance of galactoside-terminated alkanethiol self-assembled monolayers to marine fouling organisms. *ACS Appl Mater Interfaces* 2011;3:3890–901.
- [115] Fyrner T, Lee HH, Mangone A, Ekblad T, Pettitt ME, Callow ME, Callow JA, Conlan SL, Mutton R, Clare AS, Konradsson P, Liedberg B, Ederth T. Saccharide-functionalized alkanethiols for fouling-resistant self-assembled monolayers: synthesis, monolayer properties, and antifouling behavior. *Langmuir* 2011;27:15034–47.
- [116] De Kerchove AJ, Elimelch M. Calcium and magnesium cations enhance the adhesion of motile and nonmotile *Seadomonas aeruginosa* to alginate films. *Langmuir* 2008;24:3392–9.
- [117] Patwardhan SV, Taori VP, Hassan M, Agashe NR, Franklin JE, Beaugage G, Mark JE, Clarson SJ. An investigation of the properties of poly(dimethylsiloxane)-bioinspired silica hybrids. *Eur Polym J* 2006;42:167–78.
- [118] Stein J, Truby K, Wood CD, Stein J, Gardner M, Swain G, Kavanagh C, Kovach B, Schultz M, Wiebe D, Holm E, Montemarano J, Wendt D, Smith C, Meyer A. Silicone foul release coatings: effect of the interaction of oil and coating functionalities on the magnitude of macrofouling attachment strengths. *Biofouling* 2003;19:71–82.
- [119] Brady RF. A fracture mechanical analysis of fouling release from nontoxic antifouling coatings. *Prog Org Coat* 2001;43:188–92.
- [120] Marabotti I, Morelli A, Orsini LM, Martinelli E, Galli G, Chiellini E, Lien EM, Pettitt ME, Callow ME, Callow JA, Conlan SL, Mutton RJ, Clare AS, Kocjan A, Donik C, Jenko M. Fluorinated/siloxane copolymer blends for fouling release: chemical characterisation and biological evaluation with algae and barnacles. *Biofouling* 2009;25:481–93.
- [121] Martinelli E, Sarvothaman MK, Alderighi M, Galli G, Mielczarski E, Mielczarski JA. PDMS network blends of amphiphilic acrylic copolymers with poly(ethylene glycol)-fluoroalkyl side chains for fouling-release coatings. I. Chemistry and stability of the film surface. *J Polym Sci A: Polym Chem* 2012;50:2677–86.
- [122] Martinelli E, Sarvothaman MK, Galli G, Pettitt ME, Callow ME, Callow JA, Conlan SL, Clare AS, Sugiharto AB, Davies C, Williams D. Poly(dimethyl siloxane) (PDMS) network blends of amphiphilic acrylic copolymers with poly(ethylene glycol)-fluoroalkyl side chains for fouling-release coatings. II. Laboratory assays and field immersion trials. *Biofouling* 2012;28:571–82.
- [123] Martinelli E, Suffredini M, Galli G, Glisenti A, Pettitt ME, Callow ME, Callow JA, Williams D, Lyall G. Amphiphilic block copolymer/poly(dimethylsiloxane) (PDMS) blends and nanocomposites for improved fouling-release. *Biofouling* 2011;27:529–41.
- [124] Beigbeder A, Mincheva R, Pettitt ME, Callow ME, Callow JA, Clae M, Dubois P. Marine fouling release silicone/carbon nanotube nanocomposite coatings: on the importance of the nanotube dispersion state. *J Nanosci Nanotechnol* 2010;10:2972–8.
- [125] Beigbeder A, Labruyere C, Viville P, Pettitt ME, Callow ME, Callow JA, Bonnau L, Lazzaroni R, Dubois P. Surface and fouling-release properties of silicone/organomodified montmorillonite coatings. *J Adhes Sci Technol* 2011;25:1689–700.
- [126] Ekin A, Webster DC. Combinatorial and high-throughput screening of the effect of siloxane composition on the surface properties of crosslinked siloxane-polyurethane coatings. *J Comb Chem* 2007;9:178–88.
- [127] Ekin A, Webster DC, Daniels JW, Stafslien SJ, Casse F, Callow JA, Callow ME. Synthesis, formulation, and characterization of siloxane-polyurethane coatings for underwater marine applications using combinatorial high-throughput experimentation. *J Coat Technol Res* 2007;4:435–51.
- [128] Sommer S, Ekin A, Webster DC, Stafslien SJ, Daniels J, VanderWal LJ, Thompson SEM, Callow ME, Callow JA. A preliminary study on the properties and fouling-release performance of siloxane-polyurethane coatings prepared from poly(dimethylsiloxane) (PDMS) macromers. *Biofouling* 2010;26:961–72.
- [129] Fang J, Kelarakis A, Wang DY, Giannelis EP, Finlay JA, Callow ME, Callow JA. Fouling release nanostructured coatings based on PDMS-polyurea segmented copolymers. *Polymer* 2010;51:2636–42.
- [130] Youngblood JP, Andruzzi L, Ober CK, Hexemer A, Kramer Ej, Callow JA, Finlay JA, Callow ME. Coatings based on side-chain ether-linked poly(ethylene glycol) and fluorocarbon polymers for the control of marine biofouling. *Biofouling* 2003;19:91–8.
- [131] Krishnan S, Wang N, Ober CK, Finlay JA, Callow ME, Callow JA, Hexemer A, Sohn KE, Kramer Ej, Fischer DA. Comparison of the fouling release properties of hydrophobic fluorinated and hydrophilic PEGylated block copolymer surfaces: attachment strength of the diatom *Navicula* and the green alga *Ulva*. *Biomacromolecules* 2006;7:1449–62.
- [132] Krishnan S, Ayothi R, Hexemer A, Finlay JA, Sohn KE, Perry R, Ober CK, Kramer Ej, Callow ME, Callow JA, Fischer DA. Anti-biofouling properties of comblike block copolymers with amphiphilic side chains. *Langmuir* 2006;22:5075–86.
- [133] Shivapooja P, Wang Q, Orihuela B, Rittschof D, Lopez GP, Zhao X. Bioinspired surfaces with dynamic topography for active control of biofouling. *Adv Mater* 2013;25:1430–4.
- [134] Fuchs AD, Tiller JC. Contact-active antimicrobial coatings derived from aqueous suspensions. *Angew Chem Int Ed* 2006;45:6759–62.
- [135] Kristensen JB, Meyer RL, Laursen BS, Shipovskov S, Besenbacher F, Poulsen CH. Antifouling enzymes and the biochemistry of marine settlement. *Biotechnol Adv* 2008;26:471–81.
- [136] Cordeiro AL, Werner C. Enzymes for antifouling strategies. *J Adhes Sci Technol* 2011;25:2317–44.
- [137] Dong YH, Zhang LH. Quorum sensing and quorum-quenching enzymes. *J Microbiol* 2005;43:101–9.
- [138] Tasso M, Conlan SL, Clare AS, Werner C. Active enzyme nanocoatings affect settlement of *Balanus amphitrite* barnacle cyprids. *Adv Funct Mater* 2012;22:39–47.
- [139] Tasso M, Pettitt ME, Cordeiro AL, Callow ME, Callow JA, Werner C. Antifouling potential of Subtilisin A immobilized onto maleic anhydride copolymer thin films. *Biofouling* 2009;25:505–16.
- [140] Pettitt ME, Henry SL, Callow ME, Callow JA, Clare AS. Activity of commercial enzymes on settlement and adhesion of cypris larvae of the barnacle *Balanus amphitrite*, spores of the green alga *Ulva linza*, and the diatom *Navicula permixta*. *Biofouling* 2004;20: 299–311.
- [141] Aldred N, Phang IY, Conlan SL, Clare AS, Vancso GJ. The effects of a serine protease, Alcalase (R), on the adhesives of barnacle cyprids (*Balanus amphitrite*). *Biofouling* 2008;24:97–107.
- [142] Rawlings ND, Barrett AJ. Families of serine peptidases. *Methods Enzymol* 1994;244:19–61.
- [143] Tasso M, Cordeiro AL, Salchert K, Werner C. Covalent immobilization of Subtilisin A onto thin films of maleic anhydride copolymers. *Macromol Biosci* 2009;9:922–9.
- [144] Rittschof D, Costlow JD. Bryozoan and barnacle settlement in relation to initial surface wettability: a comparison of laboratory and field studies. *Sci Mar* 1989;53:411–6.

- [145] Schmidt AR, Rittschof D, Hooper IR, Gerhart DJ, Hill L, Bonaventura J, Costlow JD. Wettability affects settlement of barnacles and bryozoans in the field. *Am Zool* 1987;27:A42-A.
- [146] Tang Y, Finlay JA, Kowalke GL, Meyer AE, Bright FV, Callow ME, Callow JA, Wendt DE, Detty MR. Hybrid xerogel films as novel coatings for antifouling and fouling release. *Biofouling* 2005;21:59-71.
- [147] McMaster D, Bennett S, Tang Y, Finlay J, Kowalke G, Nedved B, Bright F, Callow M, Callow J, Wendt D, Hadfield M, Detty M. Antifouling character of 'active' hybrid xerogel coatings with sequestered catalysts for the activation of hydrogen peroxide. *Biofouling* 2009;25:21-33.
- [148] Finlay JA, Bennett SM, Brewer LH, Sokolova A, Clay G, Gunari N, Meyer AE, Walker GC, Wendt DE, Callow ME, Callow JA, Detty MR. Barnacle settlement and the adhesion of protein and diatom micro-fouling to xerogel films with varying surface energy and water wettability. *Biofouling* 2010;26:657-66.
- [149] Gunari N, Brewer LH, Bennett SM, Sokolova A, Kraut ND, Finlay JA, Meyer AE, Walker GC, Wendt DE, Callow ME, Callow JA, Bright FV, Detty MR. The control of marine biofouling on xerogel surfaces with nanometer-scale topography. *Biofouling* 2011;27:137-49.
- [150] Sokolova A, Bailey JJ, Waltz GT, Brewer LH, Finlay JA, Fornalik J, Wendt DE, Callow ME, Callow JA, Bright FV, Detty MR. Spontaneous multiscale phase separation within fluorinated xerogel coatings for fouling-release surfaces. *Biofouling* 2012;28:143-57.
- [151] Yarbrough JC, Rolland JP, DeSimone JM, Callow ME, Finlay JA, Callow JA. Contact angle analysis, surface dynamics, and biofouling characteristics of cross-linkable, random perfluoropolyether-based graft terpolymers. *Macromolecules* 2006;39:2521-8.
- [152] Hu ZK, Finlay JA, Chen L, Betts DE, Hillmyer MA, Callow ME, Callow JA, DeSimone JM. Photochemically cross-linked perfluoropolyether-based elastomers: synthesis, physical characterization, and biofouling evaluation. *Macromolecules* 2009;42:6999-7007.
- [153] Weinman CJ, Finlay JA, Park D, Paik MY, Krishnan S, Sundaram HS, Dimitriou M, Sohn KE, Callow ME, Callow JA, Handlin DL, Willis CL, Kramer EJ, Ober CK. ABC triblock surface active block copolymer with grafted ethoxylated fluoroalkyl amphiphilic side chains for marine antifouling/fouling-release applications. *Langmuir* 2009;25:12266-74.
- [154] Wang YP, Betts DE, Finlay JA, Brewer LH, Callow ME, Callow JA, Wendt DE, DeSimone JM. Photocurable amphiphilic perfluoropolyether/poly(ethylene glycol) networks for fouling-release coatings. *Macromolecules* 2011;44:878-85.
- [155] Wang YP, Finlay JA, Betts DE, Merkel TJ, Luft JC, Callow ME, Callow JA, DeSimone JM. Amphiphilic co-networks with moisture-induced surface segregation for high-performance nonfouling coatings. *Langmuir* 2011;27:10365-9.
- [156] Wang YP, Pitet LM, Finlay JA, Brewer LH, Cone G, Betts DE, Callow ME, Callow JA, Wendt DE, Hillmyer MA, DeSimone JM. Investigation of the role of hydrophilic chain length in amphiphilic perfluoropolyether/poly(ethylene glycol) networks: towards high-performance antifouling coatings. *Biofouling* 2011;27:1139-50.
- [157] Imbesi PM, Finlay JA, Aldred N, Eller MJ, Felder SE, Pollack KA, Lonnecker AT, Raymond JE, Mackay ME, Schweikert EA, Clare AS, Callow JA, Callow ME, Wooley KL. Targeted surface nanocomplexity: two-dimensional control over the composition, physical properties and anti-biofouling performance of hyperbranched fluoropolymer-poly(ethylene glycol) amphiphilic crosslinked networks. *Polym Chem* 2012;3:3121-31.
- [158] Imbesi PM, Gohad NV, Eller MJ, Orihuela B, Rittschof D, Schweikert EA, Mount AS, Wooley KL. Noradrenaline-functionalized hyperbranched fluoropolymer-poly(ethylene glycol) cross-linked networks as dual-mode, anti-biofouling coatings. *ACS Nano* 2012;6:1503-12.
- [159] Gudipati CS, Finlay JA, Callow JA, Callow ME, Wooley KL. The antifouling and fouling-release performance of hyperbranched fluoropolymer (HBFP)-poly(ethylene glycol) (PEG) composite coatings evaluated by adsorption of biomacromolecules and the green fouling alga *Ulva*. *Langmuir* 2005;21:3044-53.
- [160] Park D, Weinman CJ, Finlay JA, Fletcher BR, Paik MY, Sundaram HS, Dimitriou MD, Sohn KE, Callow ME, Callow JA, Handlin DL, Willis CL, Fischer DA, Kramer EJ, Ober CK. Amphiphilic surface active triblock copolymers with mixed hydrophobic and hydrophilic side chains for tuned marine fouling-release properties. *Langmuir* 2010;26:9772-81.
- [161] Dimitriou MD, Zhou ZL, Yoo HS, Killops KL, Finlay JA, Cone G, Sundaram HS, Lynd NA, Barreau KP, Campos LM, Fischer DA, Callow ME, Callow JA, Ober CK, Hawker CJ, Kramer EJ. A general approach to controlling the surface composition of poly(ethylene oxide)-based block copolymers for antifouling coatings. *Langmuir* 2011;27:13762-72.
- [162] Sundaram HS, Cho YJ, Dimitriou MD, Finlay JA, Cone G, Williams S, Handlin D, Gatto J, Callow ME, Callow JA, Kramer EJ, Ober CK. Fluorinated amphiphilic polymers and their blends for fouling-release applications: the benefits of a triblock copolymer surface. *ACS Appl Mater Interfaces* 2011;3:3366-74.
- [163] Tan BH, Hussain H, Chaw KC, Dickinson GH, Gudipati CS, Birch WR, Teo SLM, He CB, Liu Y, Davis TP. Barnacle repellent nanostructured surfaces formed by the self-assembly of amphiphilic block copolymers. *Polym Chem* 2010;1:276-9.
- [164] Cho YJ, Sundaram HS, Weinman CJ, Paik MY, Dimitriou MD, Finlay JA, Callow ME, Callow JA, Kramer EJ, Ober CK. Triblock copolymers with grafted fluorine-free, amphiphilic, non-ionic side chains for antifouling and fouling-release applications. *Macromolecules* 2011;44:4783-92.
- [165] Grozea CM, Gunari N, Finlay JA, Grozea D, Callow ME, Callow JA, Lu ZH, Walker GC. Water-stable diblock polystyrene-block-poly(2-vinyl pyridine) and diblock polystyrene-block-poly(methyl methacrylate) cylindrical patterned surfaces inhibit settlement of zoospores of the green alga *Ulva*. *Biomacromolecules* 2009;10:1004-12.
- [166] Gohad NV, Shah NM, Metters AT, Mount AS. Noradrenaline deters marine invertebrate biofouling when covalently bound in polymeric coatings. *J Exp Mar Biol Ecol* 2010;394:63-73.
- [167] Hexemer A, Sivanian E, Kramer EJ, Xiang M, Li X, Fischer A, Ober CK. Managing polymer surface structure using surface active block copolymers in block copolymer mixtures. *J Polym Sci B: Polym Phys* 2004;42:411-20.
- [168] Schumacher JF, Aldred N, Callow ME, Finlay JA, Callow JA, Clare AS, Brennan AB. Species-specific engineered antifouling topographies: correlations between the settlement of algal zoospores and barnacle cyprids. *Biofouling* 2007;23:307-17.
- [169] Sundaram HS, Cho YJ, Dimitriou MD, Weinman CJ, Finlay JA, Cone G, Callow ME, Callow JA, Kramer EJ, Ober CK. Fluorine-free mixed amphiphilic polymers based on PDMS and PEG side chains for fouling release applications. *Biofouling* 2011;27:589-601.
- [170] Cho Y, Sundaram HS, Finlay JA, Dimitriou MD, Callow ME, Callow JA, Kramer EJ, Ober CK. Reconstruction of surfaces from mixed hydrocarbon and PEG components in water: responsive surfaces aid fouling release. *Biomacromolecules* 2012;13:1864-74.
- [171] Bartels JW, Imbesi PM, Finlay JA, Fidge C, Ma J, Seppala JE, Nystrom AM, Mackay ME, Callow JA, Callow ME, Wooley KL. Antibiofouling hybrid dendritic bolton/star PEG thiol-ene cross-linked networks. *ACS Appl Mater Interfaces* 2011;3:2118-29.
- [172] Martinelli E, Agostini S, Galli G, Chiellini E, Glisenti A, Pettitt ME, Callow ME, Callow JA, Graf K, Bartels FW. Nanostructured films of amphiphilic fluorinated block copolymers for fouling release application. *Langmuir* 2008;24:13138-47.
- [173] Beveridge CM, Parr ACS, Smith MJ, Kerr A, Cowling MJ, Hodgkiss T. The effect of benzalkonium chloride concentration on nine species of marine diatom. *Environ Pollut* 1998;103:31-6.
- [174] Parr ACS, Smith MJ, Beveridge CM, Kerr A, Cowling MJ, Hodgkiss T. Optical assessment of a fouling-resistant surface (PHEMA benzalkonium chloride) after exposure to a marine environment. *Adv Mater Opt Electron* 1998;8:187-93.
- [175] Cowling MJ, Hodgkiss T, Parr ACS, Smith MJ, Marrs SJ. An alternative approach to antifouling based on analogues of natural processes. *Sci Total Environ* 2000;258:129-37.
- [176] Smith MJ, Adam G, Duncan HJ, Cowling MJ. The effects of cationic surfactants on marine biofilm growth on hydrogels. *Estuarine Coast Shelf Sci* 2002;55:361-7.
- [177] Cowie PR, Smith MJ, Hannah F, Cowling MJ, Hodgkiss T. The prevention of microfouling and macrofouling on hydrogels impregnated with either Arquad 2C-75 (R) or benzalkonium chloride. *Biofouling* 2006;22:173-85.
- [178] Yang WJ, Pranantyo D, Neoh KG, Kang ET, Teo SLM, Rittschof D. Layer-by-layer click deposition of functional polymer coatings for combating marine biofouling. *Biomacromolecules* 2012;13:2769-80.
- [179] Majumdar P, Lee P, Patel N, Ward K, Stafsliden SJ, Daniels J, Chisholm BJ, Boudjouk P, Callow ME, Callow JA, Thompson SEM. Combinatorial materials research applied to the development of new surface coatings IX: an investigation of novel antifouling/fouling-release coatings containing quaternary ammonium salt groups. *Biofouling* 2008;24:185-200.
- [180] Ye SJ, Majumdar P, Chisholm B, Stafsliden S, Chen Z. Antifouling and antimicrobial mechanism of tethered quaternary ammonium salts in a cross-linked poly(dimethylsiloxane) matrix studied using

- sum frequency generation vibrational spectroscopy. *Langmuir* 2010;26:16455–62.
- [181] Majumdar P, Crowley E, Htet M, Stafslie SJ, Daniels J, Van der Wal L, Chisholm BJ. Combinatorial materials research applied to the development of new surface coatings XV: an investigation of polysiloxane anti-fouling/fouling-release coatings containing tethered quaternary ammonium salt groups. *ACS Comb Sci* 2011;13:298–309.
- [182] Liu Y, Leng C, Chisholm B, Stafslie S, Majumdar P, Chen Z. Surface structures of PDMS incorporated with quaternary ammonium salts designed for antifouling and fouling release applications. *Langmuir* 2013;29:2897–905.
- [183] Park D, Finlay JA, Ward RJ, Weinman CJ, Krishnan S, Paik M, Sohn KE, Callow ME, Callow JA, Handlin DL, Willis CL, Fischer DA, Angert ER, Kramer EJ, Ober CK. Antimicrobial behavior of semi fluorinated quaternary triblock copolymers against airborne and marine microorganisms. *ACS Appl Mater Interfaces* 2010;2:703–11.
- [184] Liu T, Yin B, He T, Guo N, Dong LH, Yin YS. Complementary effects of nanosilver and superhydrophobic coatings on the prevention of marine bacterial adhesion. *ACS Appl Mater Interfaces* 2012;4:4683–90.
- [185] Bers AV, Wahl M. The influence of natural surface microtopographies on fouling. *Biofouling* 2004;20:43–51.
- [186] Scardino A, De Nys R, Ison O, O'Connor W, Steinberg P. Microtopography and antifouling properties of the shell surface of the bivalve molluscs *Mytilus galloprovincialis* and *Pinctada imbricata*. *Biofouling* 2003;19:221–30.
- [187] Bers AV, Diaz ER, da Gama BAP, Vieira-Silva F, Dobretsov S, Valdivia N, Thiel M, Scardino AJ, McQuaid CD, Sudgen HE, Thomason JC, Wahl M. Relevance of mytilid shell microtopographies for fouling defence – a global comparison. *Biofouling* 2010;26:367–77.
- [188] Schumacher JF, Long CJ, Callow ME, Finlay JA, Callow JA, Brennan AB. Engineered nanoforce gradients for inhibition of settlement (attachment) of swimming algal spores. *Langmuir* 2008;24:4931–7.
- [189] Carman ML, Estes TG, Feinberg AW, Schumacher JF, Wilkerson W, Wilson LH, Callow ME, Callow JA, Brennan AB. Engineered antifouling microtopographies: correlating wettability with cell attachment. *Biofouling* 2006;22:11–21.
- [190] Magin CM, Long CJ, Cooper SP, Ista LK, Lopez GP, Brennan AB. Engineered antifouling microtopographies: the role of Reynolds number in a model that predicts attachment of zoospores of *Ulva* and cells of *Cobetia marina*. *Biofouling* 2010;26:719–27.
- [191] Long CJ, Schumacher JF, Robinson PAC, Finlay JA, Callow ME, Callow JA, Brennan AB. A model that predicts the attachment behavior of *Ulva linza* zoospores on surface topography. *Biofouling* 2010;26:411–9.
- [192] Bhushan B, Jung YC, Koch K. Micro-, nano- and hierarchical structures for superhydrophobicity, self-cleaning and low adhesion. *Philos Trans R Soc A* 2009;367:1631–72.
- [193] Hage W, Bechert DW, Bruse M. Artificial shark skin on its way to technical application. In: Gyr A, Koumoutsakos PD, Burr U, editors. *Science and art symposium 2000*. Dordrecht: Kluwer Academic Publishers; 2000. p. 169–75.
- [194] Bechert DW, Bruse M, Hage W. Experiments with three-dimensional riblets as an idealized model of shark skin. *Exp Fluids* 2000;28:403–12.
- [195] Cao XY, Pettitt ME, Wode F, Sanct MPA, Fu JH, Ji JA, Callow ME, Callow JA, Rosenhahn A, Grunze M. Interaction of zoospores of the green alga *Ulva* with bioinspired micro- and nanostructured surfaces prepared by polyelectrolyte layer-by-layer self-assembly. *Adv Funct Mater* 2010;20:1984–93.
- [196] Nosonovsky M, Bhushan B. Multiscale effects and capillary interactions in functional biomimetic surfaces for energy conversion and green engineering. *Philos Trans R Soc A* 2009;367:1511–39.
- [197] Banerjee I, Pangule RC, Kane RS. Antifouling coatings: recent developments in the design of surfaces that prevent fouling by proteins, bacteria, and marine organisms. *Adv Mater* 2011;23:690–718.
- [198] Scardino AJ, Guenther J, de Nys R. Attachment point theory revisited: the fouling response to a microtextured matrix. *Biofouling* 2008;24:45–53.
- [199] Scardino AJ, Harvey E, De Nys R. Testing attachment point theory: diatom attachment on microtextured polyimide biomimics. *Biofouling* 2006;22:55–60.
- [200] Wan F, Pei XW, Yu B, Ye Q, Zhou F, Xue QJ. Grafting polymer brushes on biomimetic structural surfaces for anti-algae fouling and foul release. *ACS Appl Mater Interfaces* 2012;4:4557–65.
- [201] Flemming HC. Economical and technical overview. In: Flemming HC, Heitz E, Sand W, editors. *Microbially influenced corrosion of materials: scientific and engineering aspects*. New York: Springer-Verlag; 1996. p. 5–14.
- [202] Koch GH, Brongers MPH, Thompson NG, Virmani YP, Payer JH. Corrosion costs and preventive strategies in the United States. In: *Report FHWA-RD-01-156*. Springfield, VA: National Technical Information Service; 2002. p. 12.
- [203] Yuan SJ, Liu CK, Pehkonen SO, Bai RB, Neoh KG, Ting YP, Kang ET. Surface functionalization of Cu-Ni alloys via grafting of a bactericidal polymer for inhibiting biocorrosion by *Desulfovibrio desulfuricans* in anaerobic seawater. *Biofouling* 2009;25:109–25.
- [204] Yuan SJ, Pehkonen SO, Ting YP, Neoh KG, Kang ET. Inorganic-organic hybrid coatings on stainless steel by layer-by-layer deposition and surface-initiated atom transfer radical polymerization for combating biocorrosion. *ACS Appl Mater Interfaces* 2009;1:640–52.
- [205] Yuan SJ, Xu FJ, Kang ET, Pehkonen SO. Modification of surface-oxidized copper alloy by coupling of viologens for inhibiting microbiologically influenced corrosion. *J Electrochem Soc* 2007;154:C645–57.
- [206] Wan D, Yuan SJ, Neoh KG, Kang ET. Poly(glycidyl methacrylate)-polyaniline bilayer-modified mild steel for combating biocorrosion in seawater. *J Electrochem Soc* 2009;156:C266–74.
- [207] Wan D, Yuan SJ, Neoh KG, Kang ET. Surface functionalization of copper via oxidative graft polymerization of 2,2'-bithiophene and immobilization of silver nanoparticles for combating biocorrosion. *ACS Appl Mater Interfaces* 2010;2:1653–62.
- [208] Redondo MI, Breslin CB. Polypyrrole electrodeposited on copper from an aqueous phosphate solution: corrosion protection properties. *Corros Sci* 2007;49:1765–76.
- [209] Mirmohseni A, Oladegaragoze A. Anti-corrosive properties of polyaniline coating on iron. *Synth Met* 2000;114:105–8.
- [210] Zarras P, Anderson N, Webber C, Irvin DJ, Irvin JA, Guenther A, Stenger-Smith JD. Progress in using conductive polymers as corrosion-inhibiting coatings. *Radiat Phys Chem* 2003;68:387–94.
- [211] Mengoli G, Munari MT, Bianco P, Musiani MM. Anodic synthesis of polyaniline coatings onto Fe sheets. *J Appl Polym Sci* 1981;26:4247–57.
- [212] Kang ET, Neoh KG, Tan KL. Polyaniline: a polymer with many interesting intrinsic redox states. *Prog Polym Sci* 1998;23:277–324.
- [213] Chen Z. Investigating buried polymer interfaces using sum frequency generation vibrational spectroscopy. *Prog Polym Sci* 2010;35:1376–402.