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Polymer brush coatings for combating marine biofouling

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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 do not actively release 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.

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-vinylpridine); 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, polyethyleneimine; PFPE, penfluoropolyether; 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.

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Contents

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.