

Dynamic Surface Antifouling Materials

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Abstract

The colonization of marine microorganisms, animals and plants on underwater surface forms marine biofouling. It has profound effects on marine industries. To solve the problem, we proposed a strategy of Dynamic Surface Antifouling (DSAF), i.e., continuously changing surfaces can effectively inhibit biofouling organisms landing and adhering, and developed degradable polymer based marine antifouling material. The degradation of polymer chain enables the surface dynamic or self-renewing even on static conditions. The final degradation products of these polymers are low molecular weight molecules, and do not produce marine microplastics. Meanwhile, the degradable polymers act as carriers and controlled release systems for antifoulants, further improving the antifouling efficiency. This article reviews the development of dynamic surface antifouling materials.

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What is the most favorite and original chemistry developed in your research group? Synthesis of marine anti-biofouling poly

Keywords

Marine biofouling | Antifouling | Biodegradable polymer | Hydrolysis | Synthesis design | Polymerization

Comprehensive Summary

The colonization of marine microorganisms, animals and plants on underwater surface forms marine biofouling. It has profo

Left to Right: Man Wang, Chunfeng Ma, Guangzhao Zhang **Man Wang completed his undergraduate programme**
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1. Introduction

Marine biofouling referring to the accumulation of marine microorganisms, animals, and plants has great adverse impacts on marine industries.^[1] Biofouling on ship increases its weight and navigation resistance, resulting in additional fuel consumption. It also accelerates the corrosion of metal, thereby shortening the service life of marine facility.^[2] Biofouling can block seawater pipelines of nuclear power plants, reducing the cooling efficiency or even slowing down the generators.^[3] In aquaculture, biofouling can block the mesh, decreasing the oxygen and nutrients in breeding cages, thereby lowering the production.^[4] On the other hand, fouling organisms on vessels can migrate from one sea area to another and affect the ecosystem.^[5] Anyhow, marine antifouling is of great economic and environmental importance. However, due to the wide variety of biofouling and complex marine environment, developing efficient and eco-friendly antifouling materials and techniques remains a challenge.

In the past decades, some antifouling approaches including coatings, mechanical treatment, electrolyzing seawater, and ultrasonic cleaning have been developed. Among them, using antifouling coatings is the most convenient, efficient and economic.^[6] The so-called self-polishing copolymer (SPC) coating containing tributyltin (TBT) can efficiently prevent the settlement and growth of biofouling. However, due to the toxicity to non-target creatures, it was banned by the International Marine Organization in 2008.^[7] Since then, development of eco-friendly and effective antifouling coatings has been an urgent task.

In recent years, cuprous oxide SPC coatings,^[8] protein-resistant polymers,^[9] amphiphilic polymers,^[10] and biomimetic polymers^[11] have been prepared. While they have some effectiveness in certain scenarios, they exhibit poor antifouling performance on static conditions with short service life. Moreover, they are unable to degrade and form marine microplastics once they are released into the ocean.^[12]

Based on a ten-year experience in marine antifouling, we put forward the strategy of Dynamic Surface Antifouling (DSAF), a changeable surface can renew itself in seawater and thus weaken the adhesion of fouling organism.^[13] Along this line, we developed high performance antifouling materials based on biodegradable polymers. Due to the degradation of the main polymer chain, the surface renewing is not driven by external force, so they still have good antifouling ability even under static conditions. They are also eco-friendly since such degradation yields low molecular weight molecules instead of microplastics. In this paper, we present the synthesis, structures and properties of DSAF polymers.

2. Dynamic Surface Antifouling (DSAF) Strategy

Biofouling formation on a submerged surface is a multi-step process involving the initial attachment of fouling organisms, secretion of biological adhesives, and subsequent growth. DSAF polymer can renew its surface and significantly reduce the contact time between microorganisms and coating surface, which is not conducive to the adhesion of biofouling.

We investigated the movement trajectory of bacteria by using digital holographic microscopy (DHM) to understand DSAF mechanism.^[14,15] DSAF surface was constructed by biodegradable copolymer (poly(CL-co-HL)) of ϵ -caprolactone (CL) and δ -hexalactone (HL). The degradation rate that characterizes the change of the coating surface was determined by quartz crystal microbalance with dissipation (QCM-D). Clearly, the degradation rate increased with HL content in the range we investigated.

The adhesion of *Pseudomonas sp.* (*P. sp.*) or *Escherichia coli* (*E. coli.*) on the coating surface was monitored by recording and reconstructing bacterial behavior with DHM. Subdiffusive motion of the bacteria near the surface was observed before irreversible adhesion.^[16] The mean square displacement (MSD) of bacteria

indicated that a higher degradation rate diminished the bacterial coverage (10%-20%) and the probability of subdiffusive motion on coating surface (Figure 1a). Accordingly, a dynamic surface with a certain change rate can significantly hinder the adhesion of bacteria.

Atomic force microscopy (AFM) observation showed the adhesion force (γ) of bacteria on dynamic surface. We can see that γ significantly decreased as the surface self-renewal rate increased (Figure 1b). Clearly, the self-renewal surface based on degradable polymer can reduce adhesion strength of bacteria, thereby preventing bacteria from irreversible adhesion so that they had to escape from the surface (Figure 1c). DSAF surface can keep dynamic or changeable in seawater with the ongoing hydrolytic and enzymatic degradation.

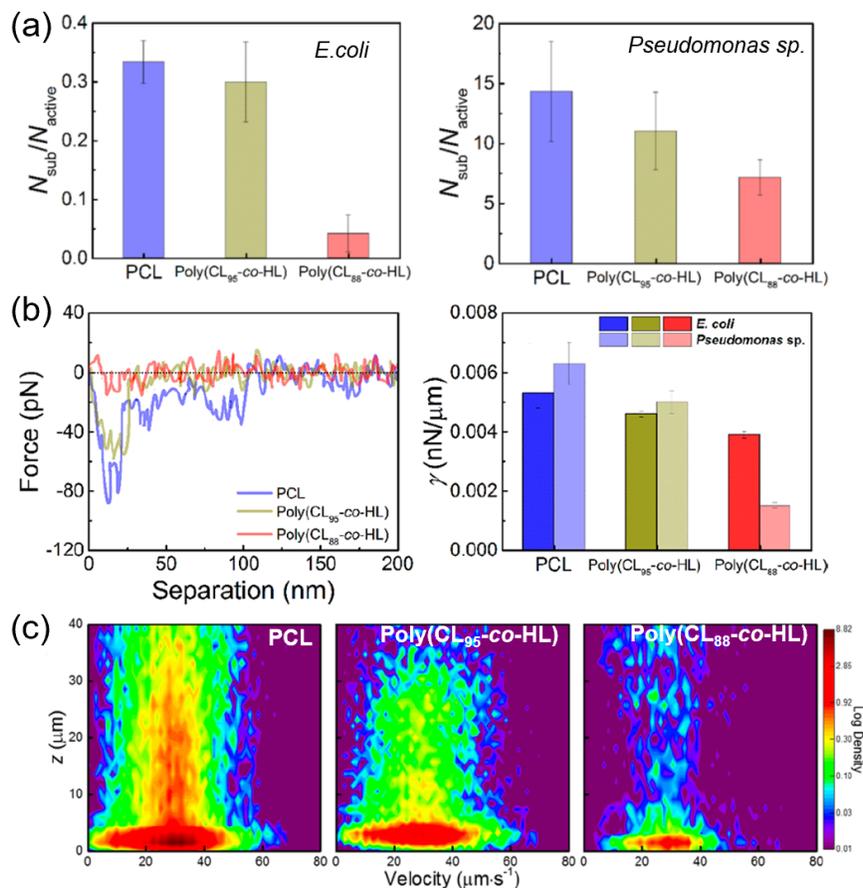


Figure 1 (a) The ratio of subdiffusive motion and active motion of both bacteria near the coating surfaces. (b) Force vs apparent separation curves of *P. sp.* and mean normalized adhesion force (γ) of both bacteria on the coating surfaces. (c) Density distribution of instantaneous 3D velocity and distance from the surface for *E. coli* on coating surfaces. Reproduced with permission.[14] Copyright 2017 American Chemical Society.

Polymer erosion usually results in mass loss of polymer and renewal of coating surface. It contains water intrusion and removals of polymers via main chain degradation and hydrolysis of lateral groups. The erosion including surface erosion and bulk erosion leads to a dynamic coating surface. Generally, the former occurs only on the surface with stable self-renewal rate, whereas the later occurs throughout the coating.

Both SPC and degradable polymers are DSAF materials because they can form a continuously changing surface in seawater. However, they are quite different from each other in structure and performance. SPC

has a hydrophobic and non-degradable backbone. The hydrolysis of the lateral groups is an equilibrium reaction, and a strong water flow is needed to remove the hydrolytic polymer chains. That is why SPC coating has poor antifouling performance under static conditions. SPC coatings generally do not exhibit linear thickness decrease over time, so the service life is difficult to control. Besides, SPC coating yields microplastics because of the non-degradable backbone.

In contrast, degradable polymer, e.g., degradable polyester undergo main chain cleavage spontaneously on surface in contact with seawater,^[17,18] yielding low molecular weight products which readily disperse into seawater, and they would eventually degrade into carbon dioxide and water. As a result, degradable polyester coating would have much less negative impact on ecology. On the other hand, the degradation of polyester backbone is non-equilibrium reaction, the removal of the degraded moieties on the coating surface does not need external force. Accordingly, the coating has good antifouling performance even on static conditions. The surface erosion exhibits linear kinetics, so the service life can be controlled by the coating thickness.

3. Degradable Polymers

3.1. Degradable Polyurethanes

Aliphatic polyesters such as PCL, poly(butylene succinate) (PBS) and poly(L-lactic acid) (PLA) can enzymatically or hydrolytically degrade with main chain cleavage, leading to a renewable surface.^[19,20] In principle, they can act as anti-biofouling materials. However, their low adhesion strength, low degradation rate, and poor film formation properties make it impossible. They must be chemically modified for this use.

We first synthesized PCL-based polyurethane (PU) with lysine ethyl ester diisocyanate and 1,4-butanediol. Yet, PCL-PU was highly crystallized and thus degraded slowly. To further lower crystallinity, we synthesized copolymer of CL and glycolide (GA) to use as the soft segment of PU.^[21] Differential scanning calorimetry (DSC) measurements showed that such a copolymer had lower crystallinity compared with PCL and PGA homopolymers. This is because the copolymerization destroys the regularity of molecular chains and hinder the crystallization. The increase of amorphous area makes it more possible that enzyme and water molecules can contact and react with the polymer chains, so the enzymatic and hydrolytic degradations of the copolymer happen. The increase of GA content can accelerate the degradation process of copolymer. The copolymer with 10 mol% GA exhibited best antifouling performance in a 3-month marine field test.

We introduced dihydroxy-terminated poly(ethylene adipate) (PEA), poly(1,4-butylene adipate) (PBA) or poly(1,6-hexamethylene adipate) (PHA) to regulate the surface renewal rate of degradable polyurethane.^[22] Our study demonstrated that when PU content was 80 wt%, the degradation rate and mass loss of PEA-PU is higher than that of PBA-PU and PHA-PU in artificial seawater (ASW) (Figure 2a). Namely, the probability of main chain cleavage increased with the ester density, so the degradability could be readily regulated. On the other hand, hydrogen bonding between the urethanes and polar substrate significantly improved the adhesion strength (4 MPa), which is favorable to long-term application in marine environments.

As we know, an antifouling system usually consists of antifoulants and polymer resin, where the latter serves as the carrier of the former. For a traditional system with polymer having non-degradable main chain, antifoulant usually is released quickly in the initial stage, but slows down thereafter. As a result, it has a short service time. In contrast, biodegradable polymer linearly degrades in seawater, so it can be well used as controllable release carrier for antifoulants. We have investigated the release of organic antifoulants carried by degradable polyurethane. PEA/PBA/PHA-based polyurethane were used to carry antifoulant 4,5-dichloro-2-octyl-isothiazolone (DCOIT), which can be released with a stable and sustainable release (Figure 2b). Anyhow, the combination of dynamic surface and stable release of antifoulants enable the coating to exhibit excellent antifouling performance in marine field test.

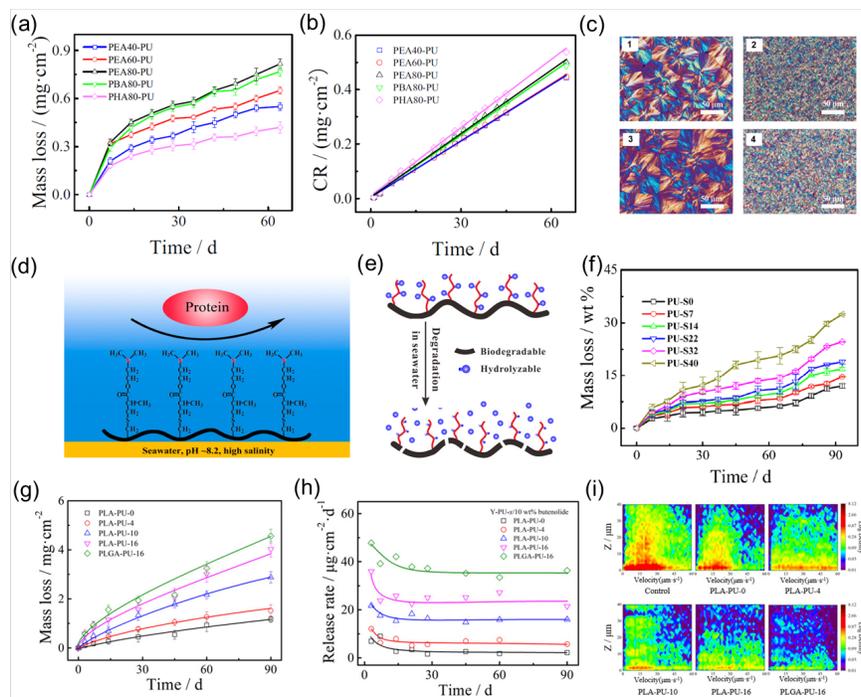


Figure 2 (a) The mass loss of the PU coatings as a function of immersion time in ASW at 25 °C. (b) Time dependence of the cumulative release of DCOIT from the PU coatings. Reproduced with permission.[22] Copyright 2017 Elsevier. (c) The POM images of pure PCL and PCL/clay (1. PCL; 2. PCL/clay; 3. PCL/DCOIT; 4. PCL/clay/DCOIT). Reproduced with permission.[26] Copyright 2014 Royal Society of Chemistry. (d) Illustration of the antiprotein mechanism of PCL-PU-DEM coatings. Reproduced with permission.[29] Copyright 2015 American Chemical Society. (e) Schematic diagram of degradation of PU-S_x coatings. (f) Mass loss of PU-S_x coatings as a function of immersion time in ASW at 25 °C. Reproduced with permission.[30] Copyright 2014 American Chemical Society. (g) Mass loss of PLA-PU coatings as a function of immersion time in ASW at 25 °C. (h) Release rate of butanolide from PLA-PU-*x* as a function of soaking time in ASW at 25 °C. (i) Density distribution of instantaneous 3D velocity on PLA-PU-*x* coating surface for *P. sp.*. Reproduced with permission.[32] Copyright 2020 American Chemical Society

Butanolide is a natural compound and highly effective antifoulant with low toxicity.^[23,24] We used degradable PCL-PU80 to carry butanolide. QCM-D measurements showed that PCL-PU80 degraded much faster in natural seawater (NSW) than in ASW, indicating enzymes secreted by marine microorganisms can improve the degradation rate. With the butanolide content above 5 wt%, PCL-PU80 coating can effectively inhibit bacterial adhesion. However, because the self-renewal rate was slower, the release of butanolide decreased. The coating surface was covered by biofouling in 3 months. Introduction of rosin to PCL-PU80 can reduce the crystallinity and accelerate its erosion. For the same content (5 wt%) of butanolide, PCL-PU80 with rosin had better antifouling performance than that without rosin since the former has a higher and stable release rate. Clearly, both the dynamic surface and release of butanolide play critical roles in antibiofouling. On the other hand, as the seawater temperature rises, the release rate of butanolide increased. This is understandable because the mobility of butanolide ($T_m=23\text{ °C}$) would increase with temperature. Note that biofouling accumulation also accelerates with temperature yielding more enzymes. So, the system is enzyme and temperature responsive. We also used degradable PU to carry other natural antifoulants of fungal isolates from the depths of South China Sea.^[25] PCL-PU coating with *Aspergillus westerdijkiae* had excellent antifouling performance after 4-month immersion in seawater.

Besides crystallinity, spherulite size also influences the degradation rate. We developed PCL/clay composite

coating via solution mixing process.^[26] DSC measurements showed that the crystallinity of composite was close to that of PCL without clay, which makes sure that the coating had enough mechanical strength. We observed smaller spherulites in the composite compared to pure PCL by using polarizing optical microscope (POM) (Figure 2c), which accelerates enzymatic and hydrolytic degradation. We added DCOIT to the composite to further improve its antifouling performance, which was released along with PCL degradation. The combination of dynamic surface and stable release rate of DCOIT enables the composite to have good antifouling performance for up to 10 months in seawater.

Another approach to reduce spherulite size is to blend different biodegradable polymers together. We prepared PCL/PBS blend by mixing them in solution.^[27] Because they inhibit each other in crystal growth, the blend had spherulite notably smaller than those of the two homopolymers. Namely, it had increased amorphous interfacial area. After a 4-month immersion in ASW, the mass loss of blend coating is higher than that of pure PCL. The blend was also used as controlled release system of DCOIT with a stable release rate in ASW (correlation coefficient >0.99).

Grafting antifouling groups to degradable polymer can improve its antifouling performance. Through click reaction and polymerization, we synthesized PCL-PU with N-(2,4,6-trichlorophenyl) maleimide (TCPM) as lateral chains.^[28] Due to the large phenyl groups, TCPM reduced the crystallinity of polymer and accelerated degradation process in ASW, which is beneficial for surface renewal and resisting marine organisms. In addition, we also grafted 2-(dimethylamino) ethyl methacrylate (DEM), an acrylate monomer with fouling resistant group, to PCL-PU to regulate its crystallinity (Figure 2d).^[29] The crystallinity of PCL-PU decreased with DEM content. Due to the hydrophilic nature and full deprotonation of DEM in seawater, the anti-adhesion properties against marine bacteria increased with DEM content. Therefore, we can adjust the surface renewal rate of degradable PU by changing the structure of backbone and lateral groups to meet different application requirements.

We synthesized triisopropylsilyl acrylate (PTIPSA) oligomers with two hydroxyls at one end and grafted them onto PCL-PU so that the hydrolyzable side chains were introduced to degradable main chain (Figure 2e).^[30,31] As PTIPSA content increased, the water contact angle (WCA) after immersion decreased significantly. The mass loss of copolymer also increased with PTIPSA content, so it is related to the surface renewal or antifouling ability (Figure 2f). We used scanning electron microscopy (SEM) to investigate the effect of PTIPSA hydrolysis on coating surface morphology. As the soaking time increased, the coating surface roughness slightly varied, so its effect could be neglected. PU-S40 (contain 40 wt% of PTIPSA) exhibited excellent antifouling performance in a 3-month marine field test even without antifoulants. After carrying DCOIT, it exhibited better antifouling performance and longer service life. Polyurethanes with various polyester (PLA, PEA) segments and different length of PTIPSA side chains were also examined. The degradation rate increased with density of ester bonds no matter whether they were in the main chain or lateral chains.

We prepared PLA-PU containing hydrolyzable TIPSA side groups via thiol-ene click reaction.^[32] Since polyurethane has excellent mechanical properties, PLA-PU showed a high adhesion strength on flexible substrate surface. We adjusted the degradation rate by changing the structure of soft segment and TIPSA content (Figure 2g), and used it as a carrier of butanolide. By regulating the degradation rate, we achieved controlled release of butanolide (Figure 2h). The system could have a long-term antifouling performance. We observed and recorded the movement trajectory of *P. sp.* on the coating surface by DHM. The PLA-PU-0 without butanolide was used as the control sample. The adhered number (N_b) of *P. sp.* on control sample was higher than that on PLA-PU-0 with butanolide. For the same butanolide content, as TIPSA content increased, N_b of *P. sp.* decreased, further indicating that both dynamic surface and release of antifoulants would affect antifouling performance (Figure 2i).

Hyperbranched polymers with three-dimensional random structures are a homologue of dendritic macromolecules. Due to their special branched molecular structure and abundant terminal groups, they usually exhibit high solubility, chemical reactivity and excellent film-forming properties, which enables them to be used in antifouling coatings. Compared with linear degradable polymers, hyperbranched polymer can degrade in its main chain and branching points, leading to lower molecular weight degradation products. Thus, degradable

hyperbranched polymers are more eco-friendly.

We prepared hyperbranched PCL (h-PCL) by using CL, glycidol and 3-isocyanatopropyltriethoxysilane.^[33] The degradable PCL segments in h-PCL lead to dynamic surface to inhibit the attachment of fouling organisms, whereas the siloxane endows h-PCL with fouling release ability. To further improve the antifouling performance of h-PCL coating, we introduced an amphiphilic triblock copolymer as crosslinking agent.^[34] The anti-adhesion performance to bacteria and diatom markedly increased with the amphiphilic triblock copolymer content.

3.2. Degradable Polyacrylates

Polyacrylates have found wide applications in adhesives and coatings. Traditional antifouling coating is composed of polyacrylate with hydrolyzable side groups in seawater. However, only hydrolysis cannot enable the antifouling ability enough, especially on static conditions. Polyacrylate with degradable main chain and hydrolysable side groups is expected to have excellent antifouling ability, but its synthesis is a challenge. This is because it is synthesized via copolymerization of cyclic monomers and vinyl monomers, which generally does not happen. In 2012, our group found anionic hybrid copolymerization of cyclic monomers and vinyl monomers in the presence of organic catalyst phosphazene base (*t*-BuP₄)^[35,36], making the synthesis of degradable polyacrylates possible. We synthesized random copolymer of CL and MMA^[37], hyperbranched PCL with glycidyl methacrylate as branching agent^[38] and poly(CL-co-methacrylic acid)^[39]. To enhance the fouling resistance, we combined LA with 2-(2-methoxyethoxy) ethyl methacrylate (MEO2MA) to synthesize a random copolymer that has good enzymatic degradation and antifouling performance.^[40]

We prepared poly(ester-co-acrylate) with low crystallinity and good degradability by using radical ring opening polymerization (RROP) of cyclic ketene acetals (CKA) and vinyl monomers. For example, we synthesized amorphous polymer of methylene-1,3-dioxepane (MDO) and MMA by RROP.^[41] It exhibited excellent film-forming properties and mechanical properties. The antifouling ability of the copolymer increased with the ester density. Acting as a controlled release carrier for DCOIT, it showed good antifouling performance with long service life.

We synthesized poly(ester-co-acrylate) via RROP of MDO, MMA and tributylsilyl methacrylate (TBSM),^[42] which has degradable backbone and hydrolyzable lateral base. The degradable backbone accelerated the erosion process of copolymer and decreased the swelling degree, which ensured a stable release rate when it was used as DCOIT carrier in ASW. Even under the static immersion in seawater, the copolymer coating had good antifouling performance.

As regarding these copolymers, the ratio of polyester to silyl methacrylate plays a crucial role in optimizing polymer properties. To understand the effect of the silyl methacrylate group on coating properties, we synthesized degradable copolymers by reacting MDO with various silyl acrylates (bis(trimethylsiloxy)methylsilyl methacrylate (MATM2), triisopropylsilyl methacrylate (TIPSM), and TBSM).^[43] Our study showed that the hydrolysis rate of silyl methacrylate decreased with the steric hindrance. After 7-week immersion in ASW, MDO-MATM2 and MDO-TBSM exhibited a significant reduction of weight (90% and 86%), whereas MDO-TIPSM held its weight. Actually, the rapid hydrolysis of silyl methacrylate groups enabled the surface more hydrophilic with higher water absorption, promoting the breaking of the polymer backbone. By adjusting the molecular structure, we can also regulate the degradability and hydrolysability of polymer.

We have made attempts to improve the antifouling ability of degradable polyacrylates. N-methacryloyloxymethyl benzisothiazolinone (BIT) monomer with antifouling function was introduced by copolymerizing with MDO and MMA (Figure 3a).^[44] After a 90-day immersion in ASW, the PM49B0 coating (with 49 wt% ester units) showed pronounced mass loss. In the laboratory tests, the PM0B47 coating (with 47 wt% BIT) has the best anti-adhesion performance in relation. However, marine field test shows that the PM23B28 (with 28 wt% BIT) coating has much better antifouling performance. The facts further indicate that both surface self-renewal and BIT release play critical roles in anti-biofouling.

In principle, zwitterionic polymers can be used in antifouling. However, the high hydrophilicity enables

them to absorb water and swell readily in seawater, lowering their mechanical strength. Their high polarity also limits their copolymerization with non-polar monomers, so they are difficult to chemically modified. Particularly, non-degradable zwitterionic polymers have limited antifouling ability. To improve the properties, we synthesized tertiary carboxybetaine ester (TCB) which can convert into hydrophilic zwitterions after hydrolysis.^[45] Then, we prepared poly(ester-co-acrylate) with TCB and MDO via RROP. The ester bonds in the copolymer can degrade in seawater to form a dynamic surface. As the surface is renewed, the side groups are continuously hydrolyzed to generate zwitterions, so that the copolymer coating has a long-term antifouling ability. To regulate the generation rate of zwitterions, tertiary carboxybetaine triisopropylsilyl ester ethyl acrylate (TCBSA), a hydrolysis-induced zwitterions monomer, was used to synthesize a degradable polymer with self-generating zwitterionic (Figure 3b).^[46] The resulting polymer coating can generate hydrophilic zwitterionic in seawater with good mechanical strength, indicating that the hydrolysis only occurred on the surface. The roughness and mass loss increased with TCBSA content. Because of the self-generating zwitterionic, the copolymer could effectively restrain the attachment and growth of biofouling.

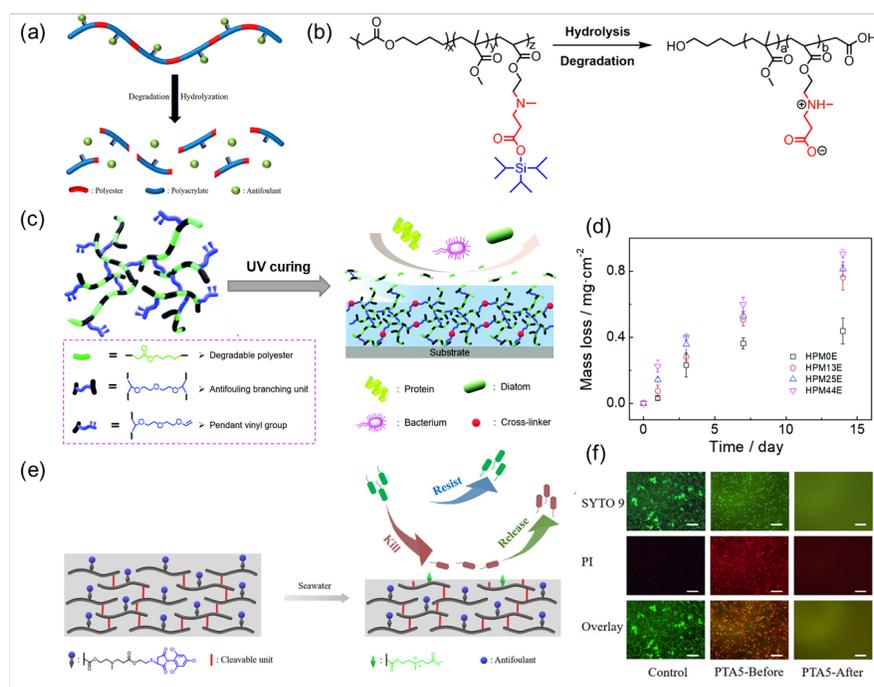


Figure 3 (a) Schematic diagram of degradation and hydrolysis of PM_x By. Reproduced with permission.^[44] Copyright 2019 American Chemical Society. (b) Hydrolysis and degradation of copolymer. Reproduced with permission.^[46] Copyright 2019 American Chemical Society. (c) Schematic diagram of the preparation and degradation process of HPM_xE. (d) Mass loss of HPM_xE after immersion in ASW at 25 °C. Reproduced with permission.^[47] Copyright 2021 Royal Society of Chemistry. (e) Schematic diagram of degradation and hydrolysis of PTA_x. (f) Fluorescence images of *P. sp.* on PTA5 surface with and without a 3-day pre-hydrolysis. Reproduced with permission.^[51] Copyright 2021 American Chemical Society.

We synthesized hyperbranched degradable copolymer (HPM_xE) with via RROP of MDO, vinyl acetate (VAc) and diethylene glycol divinyl ether (DEGDVE) (Figure 3c).^[47] Since the vinyl monomers and MDO are close in reactivity ester bonds can randomly distribute along polymer chain, so that the degradation happens everywhere on the surface. The coating had high adhesion strength after crosslinking under UV. Figure 3d shows that mass loss of the coating increased with the ester units. The coating with 44 mol% ester units had the highest mass loss after a 14-day immersion in ASW, much higher than the coating without ester units (0.4 mg·cm⁻²). The final degradation product could dissolve in seawater, so it has limited impact

on the marine environment. Antibacterial assay demonstrates that the copolymers with 50 mol% DEGDVE had good antibacterial ability. That is due to the presence of DEGDVE, forming a hydration layer with water and hindering bacterial adhesion.

We also prepared a hyperbranched copolymer via reversible addition fragmentation chain transfer (RAFT) polymerization of MMA, TCB and divinyl-functional PCL (PCL-vi2).^[48] Owing to the hyperbranched structure, the hyperbranched PCL had a crystallinity lower than linear PCL. The fragmentation of branching points would make the final degradation product smaller. The existence of TCB further improved the hydrophilicity, self-renewal capacity and effectively inhibited the adhesion of fouling organism. Thanks to the continuous degradation of PCL and the hydrolysis of TCB, the self-renewal performance and long-term antifouling ability of coating were guaranteed even in static marine environments.

We studied the effect of branching points structure on self-renewal and antifouling properties of hyperbranched copolymer. Three kind of divinyl monomers including methacrylic anhydride (MAAH), N, N'-adipic bis(diacetone acrylamide hydrazone) (DAA₂H), and ethylene glycol dimethacrylate (EGDMA) were used.^[49] It shows the degradation rate and mass loss of the polymer increased with the branching point content. For the same branching point content, the more breakable sites in branching points, the greater the mass loss (EGDMA < MAAH < DAA₂H). Namely, the degradation rate of the hyperbranched copolymer can be regulated by varying the content or structure of branching points. Antibacterial and anti-diatom assays demonstrate that the coatings have excellent antifouling performance due to branching points degradation and zwitterions produced by hydrolysis. We synthesized vinyl-functional 4-bromo-2-(4-chlorophenyl)-5-trifluoromethyl-1H-pyrrole-3-carbonitrile (*Econea*-vi) as antifouling group, and introduced it to hyperbranched polymer via RAFT polymerization.^[50] With the function of contact killing, the grafted *Econea* could effectively inhibit biofouling. On the other hand, *Econea* could be released and degrade in seawater through the breaking the copolymer chain.

Based on previous research, we proposed a strategy called the "kill-resist-renew-trinity".^[51] For this purpose, we synthesized a dual-functional monomer with TCB and TCPM, and copolymerized it with MAAH to prepared a hyperbranched polymer (PTA_x) with fouling killing, resisting and releasing functions (Figure 3e). Even before hydrolysis, TCPM with contact killing property provided the coating antibacterial ability. After hydrolysis, TCPM was released from the coating to further improve antifouling performance. Meanwhile, it generated zwitterion inhibiting the adhesion of bacteria. The dynamic surface could remove the dead bacteria attached to the surface. As shown in Figure 3f, the hyperbranched polymer with fouling killing, resisting and releasing functions had excellent anti-biofouling performance. Moreover, the hyperbranched copolymer would eventually degrade into small molecules without formation of microplastics.

4. Conclusions

In conclusion, Dynamic Surface Antifouling (DSAF) provides a general strategy to defeat marine biofouling. We have developed main chain degradable polymer based antifouling materials. They exhibit good anti-biofouling performances and mechanical properties both on static and dynamic conditions. The surface erosion of degradable polymers has linear kinetics, the service life can be regulated by the coating thickness, and the release of the antifoulants can be well controlled. The main chain degradation yields low molecular weight molecules instead of microplastics, so the polymer materials are relatively eco-friendly. By adjusting the molecular structure of the polymer, the antifouling performance, service life and the mechanical properties can be regulated. DSAF materials are promising in marine antifouling.

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