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Biodegradable Poly(ester-*co*-acrylate) with Antifoulant Pendant Groups for Marine Anti-Biofouling

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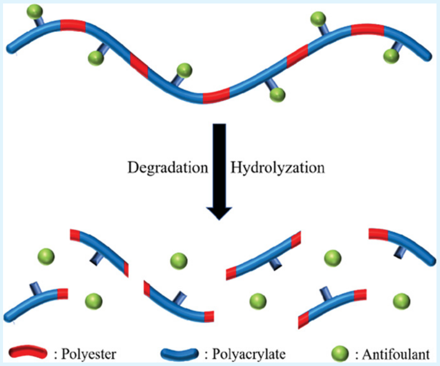
Supporting Information

ABSTRACT: Polymer resins are critical for marine anti-biofouling coatings. In this study, degradable poly(ester-*co*-acrylate) with antifoulant pendant groups has been prepared by the radical ring-opening polymerization of 2-methylene-1,3-dioxepane, methyl methacrylate, and *N*-methacryloyloxy methyl benzoisothiazolinone. Such a polymer containing main-chain esters can hydrolytically and enzymatically degrade. Both degradation rates increase with main-chain ester content. Moreover, since the antifoulant groups are chemically grafted to the degradable main chain, their release can be controlled by the degradation besides the hydrolysis of side groups. Our study shows that the copolymer coating is efficient in inhibiting the accumulation of marine bacterial biofilm of *Pseudomonas* sp. and diatom *Navicular incerta*. Marine field test reveals that the copolymer has excellent efficiency in preventing biofouling for more than 6 months.



KEYWORDS: *poly(ester-co-acrylate), polymeric antifoulant, degradation, radical ring-opening polymerization, marine anti-biofouling*

INTRODUCTION

Marine biofouling, the accumulation of diverse marine organisms on equipment surfaces under seawater, has detrimental impacts on marine economy.[1−3] Actually, marine anti-biofouling has been a worldwide problem. Ever since the global ban of coatings containing organic tin in 2008,[4] developing environment-friendly antifouling materials has become an urgent task. For this purpose, silyl, copper, or zinc acrylate-based self-polishing coatings,[5−7] fouling release coatings,[8−10] self-generated hydrogels,[11−13] slippery liquid-infused surfaces,[14,15] zwitterionic polymers,[16−18] amphiphilic polymers,[19,20] and antibacterial polymers[21,22] have been prepared. In parallel, screening environment-friendly antifoulants from agricultural pesticide and natural products have been developed.[23−26] Antifoulants are usually physically added to polymer to improve the antifouling performance and duration,[2,27,28] where the antifouling performance considerably depends on the release of antifoulants. Accordingly, the content of added antifoulant, the erosion of the polymer binder, and the compatibility between antifoulant and binder can considerably influence the release.[29] So far, the controlled release of antifoulant is still a challenge in that the antifoulant usually has a limited loading capacity and weak interactions with the polymer carrier.

Recently, we have developed degradable polymers that can form dynamic surface to combat marine biofouling.[30−36] Among them, poly(vinyl-*co*-ester)s, which were synthesized by radical ring-opening polymerization (RROP) of 2-methylene-1,3-dioxepane (MDO) and vinyl monomers, have degradable main chains and hydrolysable pendant groups.[34,35] Moreover, poly(vinyl-*co*-ester)s combining excellent film-forming ability of polyacrylate and degradability of polyester can be readily functionalized.[37,38] The above biodegradable polymers can act as a carrier of low-molecular weight organic antifoulants, and the release is well controlled because of their relatively strong interactions. On the other hand, covalently binding antifoulants to biodegradable polymer can improve the antifouling ability of such a system,[39] where its loading and release rate are tunable by adjusting the ratio between antifoulant group and main-chain ester. Actually, it was reported that polymeric prodrugs or polymers conjugation with biologically active components exhibit advantages over their low-molecular-weight precursors.[40−42] Low-molecular-weight drugs have a rapid release and thus a short half-life in blood stream, but active components conjugated with polymers are released in a controlled manner by the cleavage of linked group, so they can prolong pharmaceutical effect.[43,44] Similarly, antifoulants are chemically bonded to polymers to realize their controlled release. Pyridine−diphenylborane, glyphosate, or isothiazolinone have been grafted to polymer and the polymeric antifoulants exhibit prolonged antifouling effectiveness compared with the low-molecular-weight antifoulant and polymer mixture.[45−47] In such polymeric antifoulant systems, the main chain of the polymer is nondegradable. Therefore, the release of grafted antifoulant only relied on the hydrolysis of side groups, and the renewal of polymer surface needs the help of shear. In other words, the

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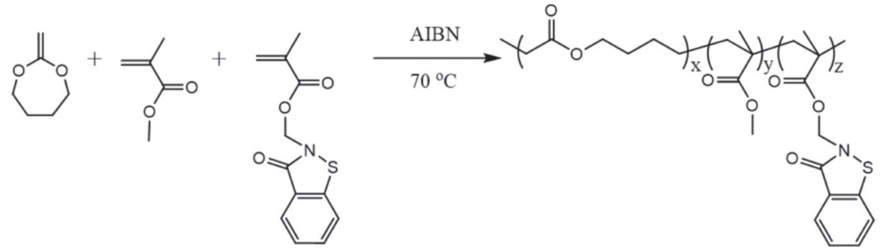
Scheme 1. Synthetic Route of PMxBy



release rate largely depends on the flow of water, and it will decrease under static conditions.

We herein report a novel degradable copolymer with antifoulant pendant groups by RROP of methyl methacrylate (MMA), MDO, and *N*-methacryloyloxy methyl benzoisothiazolinone (V-BIT), where both the side-group hydrolysis and main-chain degradation can decompose the polymer into small fragment whose dispersion into seawater is readily realized even under static immersion. Therefore, we can facilely adjust the release of antifoulant or its derivatives by changing the main-chain degradation as well as the side-group hydrolysis. BIT was chosen as the antifoulant group because it is a well-known environment-friendly antifoulant due to its high efficiency, broad-spectrum antimicrobial property, and biodegradation.[48,49] The polymer is capable of hydrolytically and enzymatically degrading in natural seawater, yielding a constantly renewed surface along with released antifoulants or its derivatives, so a synergetic effect can inhibit biofouling accumulation. We studied the enzymatic/hydrolytic degradation and anti-biofouling property of the copolymer with different compositions through laboratory and marine field tests. We aim to develop an environment-friendly and efficient antifouling material.

■ EXPERIMENTAL SECTION

Materials. 2-Methylene-1,3-dioxepane (MDO) was synthesized according to previous literature.[50] Methyl methacrylate (MMA, Aladdin) was distilled under reduced pressure prior to use. 1,2-Benzisothiazolin-3-one (BIT, Aladdin) was used as received. 2,2-Azobisisobutyronitrile (AIBN, Aladdin) was recrystallized twice from methanol before use. 1,4-Dioxane was purified by drying over calcium hydride and distillation. Artificial seawater (ASW) was prepared according to standard ASTM D1141-98 (2013).[51] Other reagents were directly used without purification.

Synthesis of *N*-Methacryloyloxy Methyl Benzoisothiazolinone (V-BIT). The synthesis of V-BIT is conducted as follows. BIT (0.1 mol), 15.10 g, and 15 mL of formaldehyde solution (0.15 mol) were dissolved in 100 mL methanol. The mixture was then allowed to react at 60 °C for 8 h with stirring by a magnetic bar. Afterward, the solvents were removed by evaporation and the obtained residue was filtered. Then, the solid product was rinsed with deionized water, followed by drying in a vacuum oven at 70 °C overnight, yielding the product BIT-OH. Then, 18.10 g of BIT-OH (0.1 mol) and 11.11 g of triethylamine (0.11 mol) in 100 mL dichloromethane were stirred at 0 °C and 11.44 g of methacryloyl chloride (0.11 mol) was added into the solution dropwise. The mixture was subsequently warmed to room temperature and allowed to react for 6 h with stirring, followed by washing with saturated $\mathrm{NaHCO_3}$ and NaCl for three times. The lower organic layer was dried with sodium sulfate and then filtered. The oily product was finally purified by column chromatography. ^{1}H NMR (600 MHz, DMSO-d_6, ppm): 8.00, 7.90, 7.75, 7.45 ($\mathrm{C_6H_4}$), 6.10, 5.80 ($\mathrm{C}H_2\mathrm{C(CH_3)CH_2}-$), 5.90 ($-\mathrm{NC}H_2\mathrm{O}-$), 1.90 ($\mathrm{CH_2C}$-$(\mathrm{C}H_3)\mathrm{CH_2}-$).

Polymer Synthesis. Scheme 1 shows the RROP route of copolymers consisting of MDO, MMA, and V-BIT. In a typical reaction, 5.00 g of MDO, 5.00 g of MMA, 2.50 g of V-BIT, and 0.05 g of AIBN and 10 mL of dioxane were introduced into a 100 mL Schlenk tube. Freeze−evacuate−thaw cycles were performed for three times to degas the mixture. The copolymerization was conducted in $\mathrm{N_2}$ atmosphere at 70 °C for 24 h. Then, the yielded copolymer was purified by precipitation and dried in a vacuum oven at 70 °C overnight. ^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$, ppm): 8.05, 7.65, 7.55, 7.4 ($\mathrm{C_6}H_4$), 5.85 ($-\mathrm{NC}H_2\mathrm{O}-$), 4.01 ($-\mathrm{CH_2COOC}H_2\mathrm{CH_2CH_2CH_2}-$), 3.63 ($-\mathrm{COOC}H_3$), 2.48 ($-\mathrm{C}H_2\mathrm{COOCH_2CH_2CH_2CH_2}-$), 1.2-1.7 ($-\mathrm{CH_2COOCH_2C}H_2\mathrm{C}H_2\mathrm{C}H_2-$), 1.0−1.2 ($-\mathrm{C}H_2\mathrm{C(CH_3)(COO-)}$-$\mathrm{CH_2}-$), 0.8−1 ($-\mathrm{CH_2C(C}H_3\mathrm{)(COO-)CH_2}-$). The copolymer is named as PMxBy for convenience, where *x* and *y* are the weight percentages of V-BIT and polyester, respectively, as calculated from ^{1}H NMR result.

Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR). ^{1}H NMR analysis was done on a Bruker AV600 NMR spectrometer. The sample was dissolved in $\mathrm{CDCl_3}$ or DMSO-d_6 with tetramethylsilane as the internal standard.

Gel Permeation Chromatography (GPC). The number-average molecular weight (M_n) and the polydispersity ($Đ_M$) of the polymer were determined by GPC (Agilent 1260 Infinity), which is equipped with ultraviolet and refractive index detectors. The eluent was THF (flow rate: 1.0 mL/min) and the test was performed at 35 °C with two identical PLgel columns (5 μm, MIXED-C). Calibration curve was determined by pretests on polystyrene standards (1.30×10^3 to 2.21×10^6 g/mol) with narrow polydispersity.

Adhesion Strength Test. A pull-off experiment was performed to measure the adhesion strength of PMxBy coating (dry thickness: ∼300 μm) to epoxy panel substrate. The PMxBy coating was prepared by applying polymer solution (30% w/v in xylene) on substrate and subsequently drying at room temperature. An automatic tester (PosiTest AT-A) was employed to conduct the test. The adhesion strength was gathered by detaching a glued aluminum dolly with the diameter of 20 mm at 25 °C, where the speed was controlled at 0.2 MPa/s. An average adhesion value reported was calculated from 5 different test point on each coating.

Differential Scanning Calorimeter (DSC). The glass-transition temperature (T_g) of the polymer was determined by DSC test (NETZSCH DSC 204F1) under a $\mathrm{N_2}$ flow of 50 mL/min. Thermal history of the polymer was eliminated by quickly heating it to 150 °C and equilibrating for 5 min, followed by cooling to −60 °C at a rate of 10 °C/min. Then, the polymer was heated to 150 °C at a rate of 10 °C/min. T_g was determined from the endothermic shift occurring in the second heating scan.

Hydrolytic and Enzymatic Degradation. PMxBy on an epoxy thin panel with an area of 20 × 20 mm^2 was prepared as follows. PMxBy, 0.3 g, was dissolved in 1 mL of THF and applied on 3 parallel panels. Afterward, the coated panel was dried until the weight was constant. The initial weight of each panel, designated as W_p, and the initial weight of dry coating and its panel, designated as W_0, were recorded. The panel coated with polymer was immersed in ASW at 25 °C and freshly made ASW was used every 14 days. After certain immersion time, the panel was removed from ASW and carefully washed with deionized water and the dry weight was recorded (W_t). Different lipase concentration (0.1, 0.5, and 1.0 mg/L) in ASW was used for enzymatic degradation. The mass loss of coating was calculated by $(W_0 - W_t)/(W_0 - W_p)$. For each polymer, triplicate samples were tested in parallel to give an average mass loss.

The molecular weight and ^{1}H NMR spectra of the degraded product of PMxBy were investigated under accelerated condition. One hundred milligrams of PMxBy was dissolved in 2 mL of THF and subsequently mixed with 6 mL of 0.1 M potassium hydroxide methanol. The mixture was stirred at 25 °C. One milliliter of the mixture was taken and subsequently neutralized by hydrochloric acid after certain intervals. Then, the solvents were removed by evaporation and the obtained residues (oligomer and salt) were separated by a mixture of water and chloroform. Afterward, the organic layer was dried and analyzed with GPC and ^{1}H NMR.

Antibacterial Tests. Marine bacteria *Pseudomonas* sp. was chosen to study the antibacterial performance of PMxBy. The bacteria were cultured following the procedures detailed in previous paper.[16] One milliliter of bacteria suspension (10^8 cell/mL) was introduced to the well of 24-well microplate whose bottom had been coated with PMxBy, and noncoated polystyrene was the control. The bacterial biofilm was grown at 30 °C for 48 h. Afterward, the suspension was taken out and the well was gently washed 3 times to remove the unattached biofilm. The biofilm on the coating was fixed with methanol and stained with crystal violet (0.3 wt % aqueous solution). The excessive crystal violet was rinsed with ASW and the photos of the biofilm were captured by digital camera. Finally, the stain was extracted with acetic acid (33% in water) and optical density was tested at $\lambda = 589$ nm.

The values of minimal inhibit concentration (MIC) against *Pseudomonas* sp. for V-BIT and BIT-OH were evaluated to determine their toxicity. One milliliter of the suspension with 10^5 cell/mL was added with different concentrations of V-BIT or BIT-OH and subsequently cultivated at 150 rpm at 30 °C for 24 h. The optical density of the suspension was measured at $\lambda = 600$ nm and triplicate samples were tested to give an average value.

Anti-Diatom Tests. Diatom *Navicula incerta* was kindly offered by Xiamen University. The diatom was cultivated in F/2 culture medium under a 12:12 h light−dark cycle at 23 °C. One milliliter of *N. incerta* suspension with a chlorophyll value of 0.25 μg/mL was added to a 24-well microplate, which contains a silicon slide (1×1 cm^2) coated with PMxBy, and cultured for 24 h, and noncoated silicon slide was the control. Then, the silicon slides were taken out and gently rinsed with ASW to remove the unattached diatom. The attached diatom was observed with a microscope (Scope A1, Zeiss) and counts were made by 10 random fields of views of each silicon slide. Each sample was tested in triplicates.

Marine Field Tests. The test was conducted in East China Sea (Xiamen Bay, December 2017 to May 2018). The polymer coated on epoxy substrate with an area of 120×120 mm^2 was put in seawater (∼1 m deep). After certain interval, the sample was moved out from seawater, carefully rinsed, and photographed. After the inspection, it was immediately immersed again. A blank epoxy panel without coating as control was also tested. The antifouling performance of the coating was determined based on ASTM D6990-05 (2011).[52] Fouling rating (FR) essentially shows the nonfouled area, where a coating without fouling organisms attached is recorded as 100.

RESULTS AND DISCUSSION

Considering the service condition in the sea is harsh, we first studied the adhesion of PMxBy coating (Figure 1). All PMxBy samples have the same substrate failure mode. For PM49B0, the adhesion strength is 1.7 MPa. For PM35B14, PM23B28, PM11B41, and PM0B47, the adhesion strength is 1.8, 2.7, 2.8, and 3.0 MPa, respectively. Namely, the adhesion strength increases with the BIT content. The trend is understandable because the polar interaction of the copolymer and epoxy panel increases as the density of polar acrylate groups increases. Note that there is a sharp difference between PM49B0, PM35B14, and other three coatings. The reason is probably that T_g of PM49B0 or PM35B14 is lower than room temperature, whereas T_g of others is above (Table 1). Anyhow, all coatings have adhesion strength higher than 1.5 MPa, so they can fulfill the requirement for application in the complicated natural marine environment.

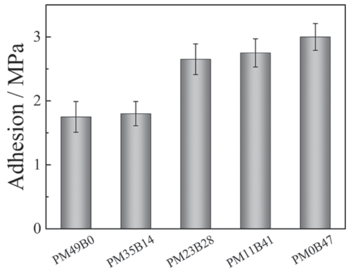


Figure 1. Adhesion of the PMxBy on epoxy substrate.

Then, we examined the degradation of the polymer coatings. Figure 2 shows the variation of mass loss of PMxBy in ASW. Regarding PM0B47, it starts to lose weight after immersion in ASW, and the percentage of weight loss gradually reaches 1.8% after 90 days. Note that the backbone of PM0B47 does not contain ester, so the mass loss comes from the hydrolysis of BIT pendant group. For PM11B41, PM23B28, PM35B14, and PM49B0, the percentage of mass loss reaches 2.1, 4.5, 5.8, and 7.3% after 90 days, respectively. As we know, the main-chain cleavage leads the copolymer surface to turn into small fragments whose dispersion in seawater is readily achieved. Actually, either the main-chain degradation or the side-group hydrolysis would contribute to the mass loss of PM11B41, PM23B28, and PM35B14. From PM0B47 to PM49B0 (Table 1), the content of the main-chain ester bonds increases, whereas the content of the BIT side groups decreases. Clearly, the former contributes more than the latter. Namely, hydrolytic degradation can be adjusted by changing the main-chain ester content. Actually, the hydrolysis rate of the antifoulant side group is lower than the degradation rate of the main chain because the former has a larger steric hindrance.[53] Thus, the final released products could include the antifoulant or the degraded fragments with antifoulant groups. The degraded fragments with antifoulant groups should have antifouling ability and can also serve as "antifoulants".[39] In other words, the degradation can control the release of antifoulant or its derivatives. Note that the glass-transition temperatures of these samples vary widely, which affects the overall properties such as the adhesion strength. However, for the mass loss, the difference of polymer degradation plays much more important role than the physical properties because PM49B0 and PM35B14 have similar glass-transition temperatures (6 and 7 °C, respectively) but totally different mass losses.

Various microorganisms can secrete enzymes that induce biodegradation of polymer in marine environment. We also tested the enzymatic degradation of PM23B28 in different lipase concentrations in ASW at 25 °C (Figure 3). Without lipase, the mass loss of PM23B28 after 28 days in ASW is about 3%. When it is in the lipase ASW solution, the mass loss rate is faster. At concentrations of 0.1, 0.5, and 1.0 mg/mL, the mass loss after 28 days is 6.8, 9.1, and 9.8% after 28 days, respectively. This indicates that the degradation rate of main-chain ester increases with enzyme concentration. Accordingly, the copolymer has a fouling pressure response.

Due to the slow degradation rate of PMxBy in ASW, we cannot determine the final degraded product in a short time.

Table 1. Composition, Molecular Weight, and Glass-Transition Temperature of PMxBy

entry	feed weight ratio MDO/MMA/V-BIT	polymer composition[a] polyester/MMA/V-BIT	M_n (kDa)[b]	$Đ_M$[b]	T_g (°C)[c]
PM49B0	66/34/0	49/51/0	37	2.4	6
PM35B14	60/32/8	35/51/14	37	2.3	7
PM23B28	40/40/20	23/49/28	43	2.1	32
PM11B41	19/45/36	11/48/41	42	2.3	56
PM0B47	0/50/50	0/53/47	41	1.9	116

[a] Weight percentage calculated from ^{1}H NMR. [b] Obtained from GPC. [c] Determined by DSC.

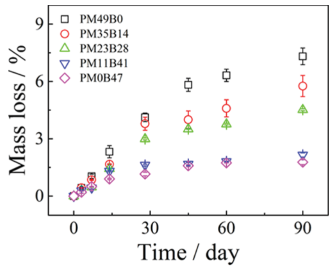


Figure 2. Variation of mass loss of PMxBy in ASW at 25 °C.

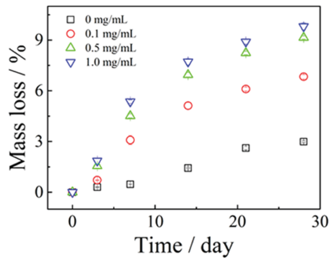


Figure 3. Variation of mass loss of PM23B28 in different concentrations of lipase in ASW at 25 °C.

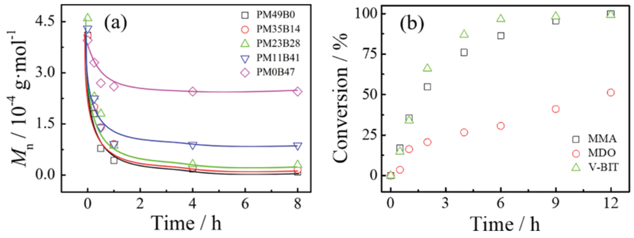


Figure 4. Variation of molecular weight of PMxBy in potassium hydroxide methanol solution at 25 °C (a). Variation of monomer conversion during MDO−MMA−V−BIT copolymerization, where the weight feed is 2/1/2 (b).

For instance, it could take more than 1200 days for PM49B0 coatings to totally degrade into small segment at the fastest degradation rate. Thus, we studied the degraded product of PMxBy in an accelerated process. As demonstrated by Figure 4a, the molecular weight of PM0B47 with no ester in its main chain decreases from 41 000 to 25 000 g/mol, which clearly indicates the hydrolysis of pendant group in a strong alkaline solution. We also used ^{1}H NMR to monitor the hydrolyzed residue. The disappearance of peak at 5.7 ppm (−COOCH_2N−) further suggests the hydrolysis of the antifoulant side groups (Figure S1). For PM11B41, PM23B28, PM35B14, and PM49B0, the molecular weight quickly decreases due to the cleavage of ester and gradually levels off, and the final degraded product has an average molecular weight of 1000−8700 g/mol, indicating all PMxBy samples can totally degrade into small fragments and the molecular weight of the final degraded product depends on the content of the main-chain ester. The molecular weight of the degraded fragments decreases as the main-chain ester content increases. Note that the decrease of the molecular weight is not proportional to the increase of the MDO monomer units. This is because the reactivities of MMA, V-BIT, and MDO monomers are not the same, as illustrated in Figure 4b. In such a system, MMA and V-BIT have higher reaction rates than MDO at the beginning of RROP, leading to an unevenly distributed polymer chains where some consecutive MMA and V-BIT repeating units are formed. In other words, some continuous nondegradable C−C main chains are present. Anyhow, the molecular weight of the final degraded product can be tuned by the MDO content and poses lower threat to marine organisms than that of traditional polyacrylate.[54]

To prove that antifoulant groups are distributed on the coating surface, we examined its surface wettability (Figure S2). The water contact angle increases from 76 to 94° with the BIT content, since BIT group is hydrophobic. Then, we studied their ability to inhibit marine bacterial biofilm of *Pseudomonas* sp. (Figure 5a). The biofilm is stained with crystal violet and the absorbance value is proportional to the amount of biofilm on the coating. On the PS control surface, the biofilm grows well with an absorbance of 2.5, whereas the biofilm on PM49B0 has an absorbance of 2.5, indicating that poly(ester-*co*-acrylate) without an antifoulant group is not able to resist biofilm formation. In comparison, significantly less biofilm accumulates on PM35B14 with an absorption of 1.0, indicating that the grafted antifoulant plays a critical part in preventing biofilm formation. Moreover, PM23B28, PM11B41, and PM0B47 exhibit excellent antibacterial ability with absorbance of 0.8, 0.5, and 0.4, respectively. As discussed above, the surface renewal rate from PM49B0 to PM0B47 decreases as the main-chain ester content decreases, whereas the antibacterial ability increases. The result indicates the grafted antifoulant plays an important role by inhibiting the growth of marine bacteria. To determine the antifouling activity or toxicity of leachates is important. However, as mentioned above, the slow release rate and uncertain structure of leachates make it difficult. We have tried to collect the leachates of PM0B47 by immersion in ASW for 7 days, but we cannot get enough samples to determine it. Actually, the toxicity of BIT and its derivatives has been extensively reported and the values of minimal inhibit concentration (MIC) ranges from 15 to 20 mg/L depending on the species of bacteria.[55] We also evaluated that the values of MIC against *Pseudomonas* sp. for V-BIT and BIT-OH are ~16 and ~8 mg/L, respectively (Figure S3). Considering that the time scale in the antibacteria experiment is very short and the hydrolysis is so slow that the excellent antifouling ability is mainly attributed to contact-kill

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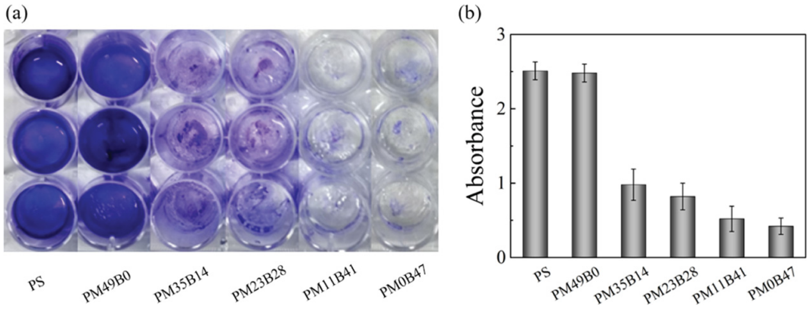

Figure 5. *Pseudomonas* sp. biofilm grown on the PMxBy coatings stained with crystal violet (a) and the absorbance of crystal violet from optical density test (b).

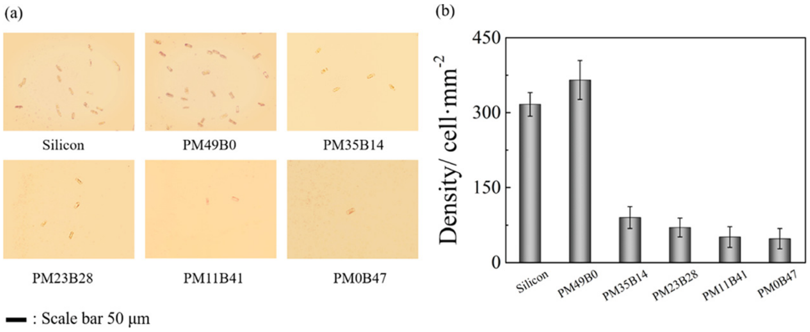

Figure 6. Images (a) and density (b) of diatom *N. incerta* on the PMxBy coatings after immersion in diatom *N. incerta* suspension for 24 h.

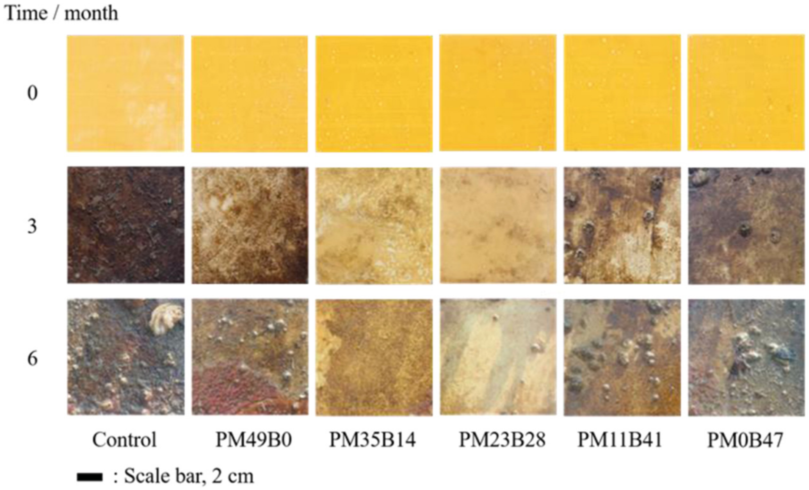

Figure 7. Images of PMxBy coatings after immersion in seawater (December 2017 to May 2018, Xiamen Bay, China).

mechanism.[56] In other words, the coating surfaces are active by contact.

Figure 6 demonstrates the adhesion of diatom *Navicula incerta* on PMxBy surface. A large amount of Navicula colonize on the PM49B0 surface with a diatom density of ~350 cells/mm^2, slightly higher than the silicon control, indicating that PM49B0 is not able to resist diatom adhesion. There is a notably lower density of diatom (~90 cells/mm^2) on the PM35B14 surface, indicating that the antifoulant groups on the surface can effectively inhibit diatom. The density is about 70, 50, and 40 cells/mm^2 on PM23B28, PM11B41, and PM0B47 surfaces, respectively. Namely, the antiadhesion ability is enhanced with BIT content. In other words, the grafted antifoulants play a key part in preventing the adhesion and growth of bacteria and diatom.

The long-term antifouling performance of PMxBy was tested in natural seawater. Figure 7 shows the typical images of PMxBy after immersion in seawater, and Figure 8 shows the

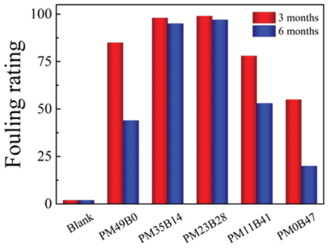

Figure 8. Fouling rating of PMxBy coatings after immersion in seawater (December 2017 to May 2018, Xiamen Bay, China).

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corresponding fouling rating. Various fouling species adhere and accumulate on the epoxy control after immersion, which indicates that the fouling pressure is high during immersion. For PM49B0, it does not effectively inhibit biofouling, although its surface renewal is the fastest. On the other hand, PM0B47 and PM11B41 also exhibit poor antifouling ability. In contrast, PM35B14 and PM23B28 have significantly better antifouling performance. This is distinct from the results of laboratory bioassays, where the samples containing high amounts of antifoulant exhibit enhanced antifouling efficiency. The possible reason is that the surface is renewed so slowly in seawater that the sea mud or marine organisms can cover it, which screens the function of the antifoulant groups. Actually, we also observed the erosion of the coatings in field tests and the surface erosion increases from PM0B47 to PM49B0, which is similar to the result from mass loss in laboratory assay. Therefore, considering that the hydrolyzed side groups or the degraded fragments with pendant antifoulant groups can inhibit biofouling, the present results that either PM0B47 with the highest content of antifoulant or PM49B0 with the fastest degradation exhibits poor AF performances, whereas PM35B14 or PM23B28 has good antifouling performance clearly indicates the in situ AF performances of PM35B14 and PM23B28 are due to a synergetic effect of surface renewal and release of antifoulant. In other words, both degradation and antifoulant group are critical for durable antifouling efficacy in natural seawater.

■ CONCLUSIONS

We have prepared biodegradable copolymer with antifoulant pendant groups by means of facile radical ring-opening polymerization. The copolymer exhibits not only tunable enzymatic and hydrolytic degradation but also high antifouling efficacy against marine bacteria *Pseudomonas* sp. and marine diatom *Navicula incerta*. Marine field tests demonstrate that the copolymer has good antifouling efficacy for more than 6 months due to the synergetic effect of surface renewal and release of antifoulant and its derivatives. This polymer has promising future as a high-performance antifouling material.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b01247.

> ^{1}H NMR spectra of PM0B47 and hydrolyzed residue, water contact angle of PMxBy coatings, and minimal inhibit concentration test result of V-BIT or BIT-OH (PDF)

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Notes

The authors declare no competing financial interest.

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