Synthesis and Biological Activity of Acrylate Copolymers Containing 3-Oxo-N-allyl-1,2-benzisothiazole-3(2*H*)-carboxamide Monomer as a Marine Antifouling Coating

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A type of grafted acrylate copolymer resins, containing 3-oxo-N-allyl-1,2-benzisothiazole-2(3*H*)-carboxamide monomer and heterocyclic monomers, was synthesized through the copolymerization of methyl methacrylate (MMA) and butyl acrylate (BA) with functional monomers. The structures of the monomers and copolymers were validated by infrared (IR) and ^{1}H nuclear magnetic resonance (NMR) spectroscopies. The inhibitory activities of the copolymers on algae, bacteria, and barnacle larvae were measured, and the antifouling potencies against marine macrofouling organisms were investigated. The results showed that the grafted resin had significant inhibitory effects on the growth of three marine algae (*Isochrysis galbana*, *Nannochloropsisoculata*, and *Chlorella pyrenoidosa*), and three bacteria (*Vibrio coralliilyticus*, *Staphylococcus aureus*,and *Vibrio parahaemolyticus*). The target copolymers also showed excellent inhibition of the survival of barnacle larvae. Additionally, the release rate of the antifoulant and the results of the marine field tests indicated that the grafted copolymers had outstanding antifouling potency against the attachment of marine macrofouling organisms.

1. Introduction

Marine macrofouling organisms that adhere and grow on the surface of ships or water facilities corrode the hull, increase friction, reduce navigational speed, and increase fuel consumption,[1–4] which can lead to serious property damage and pecuniary losses.[5–9] The use of antifouling coatings is an effective measure to prevent the attachment of undesirable marine fouling organisms.[10–12] In the early 1970s tin-based self-polishing coatings (TBT-SPC) were used to prevent and control marine biofouling. However, TBT-SPC could release large amounts of deleterious tributyltin into the marine environment, which was noxious to aquatic organisms;[13–15] thus, TBT-SPC was banned in 2008.[16]

The solution for this problem was to develop environment-friendly antifouling systems, usually including tin-free antifoulants[17–19] and biodegradable polymers.[20–23] The tin-free antifouling coating mainly involves detachment of biocide ingredients, such as Zn^{2+} or Cu^{+}, contained in the paint. Since the dissolved Zn^{2+} or Cu^{+} ions leaching from the resins do not provide a sufficient inhibitory efficiency, it is essential for these polymeric coatings to graft with biocides instead of TBT, thus endowing the coating with outstanding performance by controlling/regulating antifoulants.[24,25] Recently, the synthesis of copolymer-based antifouling coatings has emerged as an attractive research area, and multiple achievements have been reported in this field. The grafted acrylic copolymers bearing functional side chains can continuously release active substances into the seawater and the erosion process is associated with a gradual hydrolysis of ester groups, leading to a reduction in the coating thickness.[26]

In this study, a novel acrylate copolymer antifouling paint was prepared using 3-oxo-N-allyl-1,2-benzbeen reported in this field. The grafted acrylic copolymers bearing functional side chains can continuously release active substances into the seawater and the erosion process is associated with a gradual hydrolysis of ester groups, leading to a reduction in the coating thickness.[26] isothiazole-2(3*H*)-carboxamide and heterocyclic compounds as functional monomers, polymerized with methyl methacrylate (MMA) and butyl acrylate (BA) monomers. The bioactivities of the functional copolymer were tested against three marine algae (*Isochrysis galbana*, *Nannochloropsisoculata*, and *Chlorella pyrenoidosa*) and three bacteria (*Vibrio coralliilyticus*, *Staphylococcus aureus*, and *Vibrio parahaemolyticus*), and its preliminary marine anti-biofouling performance was also investigated.

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Table 1. The composition and characterization of the copolymers.

Samples	Composition [wt%]	Contact Angle [°]	Mn [kg/mol]	Mw [kg/mol]	Mz [kg/mol]	T_g [°C][a]
6a	5% NCM	79.1 ± 0.59	1.6	5.2	9.0	30.23 ± 0.19
6b	10% NCM	75.6 ± 0.46	1.5	4.8	8.2	58.88 ± 0.38
6c	15% NCM	64.7 ± 0.35	1.4	4.8	9.2	41.15 ± 0.44
6d	20% NCM	62.1 ± 0.29	1.4	4.8	8.6	47.88 ± 0.52
7a	20% NCM + 15% R_1	74.2 ± 0.25	1.4	4.8	8.6	49.90 ± 0.39
7b	20% NCM + 15% R_2	75.4 ± 0.33	1.4	4.7	8.5	47.63 ± 0.21
7c	20% NCM + 15% R_3	73.9 ± 0.38	1.5	4.7	8.3	44.94 ± 0.29
7d	20% NCM + 15% R_4	73.6 ± 0.49	1.4	4.6	8.3	31.57 ± 0.32
8a	20% NCM + 10% ZnBOH	70.0 ± 0.37	1.3	4.5	8.0	55.46 ± 0.42
8b	20% NCM + 15% ZnBOH	67.8 ± 0.39	1.3	4.4	8.0	56.25 ± 0.28
8c	20% NCM + 20% ZnBOH	57.4 ± 0.28	1.3	4.6	8.1	59.90 ± 0.37
KB	0% NCM	77.3 ± 0.42	1.4	4.5	8.2	45.85 ± 0.29

[a] Glass transition temperature.

2. Results and Discussion

2.1. Physical Properties

The molecular compositions and characterization of the copolymers are given in Table 1.The contact angles of the grafted acrylic resins were all smaller than 90°, indicating that the resin has a hydrophilic and wettable characteristic.The number-average molecular weight (M_n) was between 1.3 and 1.5 kg/mol and the weight-average molecular weight (M_w) was between 4.4 and 5.2 kg/mol, it is indicated that the relative molecular mass distribution of some synthetic resins is wider and indicates the presence of a significant amount of oligomers. The low molecular part of the resin sample affects the number average molecular weight, and the high molecular part affects the weight average molecular weight. The glass transition temperature was less than 60°C, indicating that the softening temperature of the resins was lower, and further increase of the molecular weight was needed (Table 1).

The structure of copolymer **6** was confirmed by FT-IR spectroscopy (Figure 1). Copolymer **6d** (containing 20% NCM) was selected as a representative to illustrate whether the copolymerization reaction was complete. No absorption is observed on the curve of 6d in the ranges 3100–3000 cm^{-1}, 1650–1680 cm^{-1}, and 990–910 cm^{-1} (red line), which are the characteristic peaks corresponding to the alkene double bond stretching vibration or relevant C–H bond bending vibration, indicating that C=C of the monomer is reacted completely. The absorptions at 1560 cm^{-1} and 1602 cm^{-1} reveal the existence of an aromatic ring in **6d** which does not appear in the control group (KB). The absorption peaks that newly appeared at 1730 and 1680 cm^{-1} imply the presence of an ester group. Except for the C=C bond, the functional groups of monomer are present in the copolymer. All the structural characterizations validated that the copolymerization reaction has been completed, and the monomer NCM participated in the polymerization.

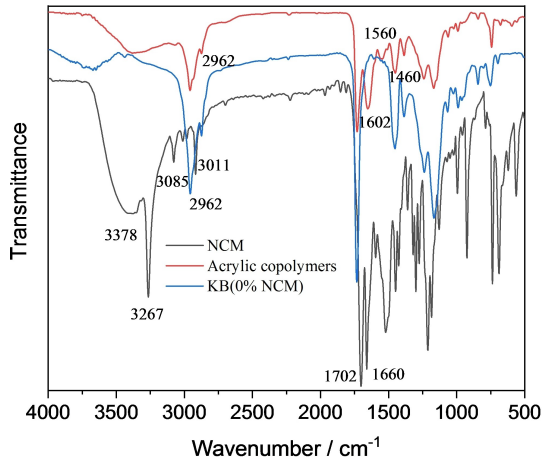


Figure 1. FT-IR of NCM, **6d**, and KB.

2.2. Inhibition on Marine Algae Growth

The corresponding algae concentration was calculated using the absorbance-concentration curve of the diluted solution. Setting the concentration of algal solution on the ordinate and the time on the abscissa (12 h, 24 h, 36 h, 48 h, 60 h, 72 h, 84 h, 96 h, 108 h, and 120 h), the inhibition effect of the copolymeric samples on the growth of three conventional marine algae (*Isochrysis galbana*, *Nannochloropsis oculata*, and *Chlorella pyrenoidosa*) was compared with that of the control group KB and Blank plates (Figure 2).

All the target polymer copolymers containing the NCM monomer were found to inhibit the growth of *Isochrysis galbana* effectively (Figure 2, (A)). In the first 24 h, *Isochrysis galbana* showed a small growth rate, which along with the prolonging of the culture, enabled most of the copolymers to exhibit an obvious inhibition effect on the growth of *Isochrysis galbana*. After 48 h, all the copolymers exhibited better inhibitory activities on *Isochrysis galbana* than the control groups KB and Blank and completely inhibited the growth of the algae.

Among copolymers **6**, it was shown that, as the content of the BIT monomer **NCM** in the resin increased, the inhibitory rate on *Isochrysis galbana* increased (Table 2). When the BIT

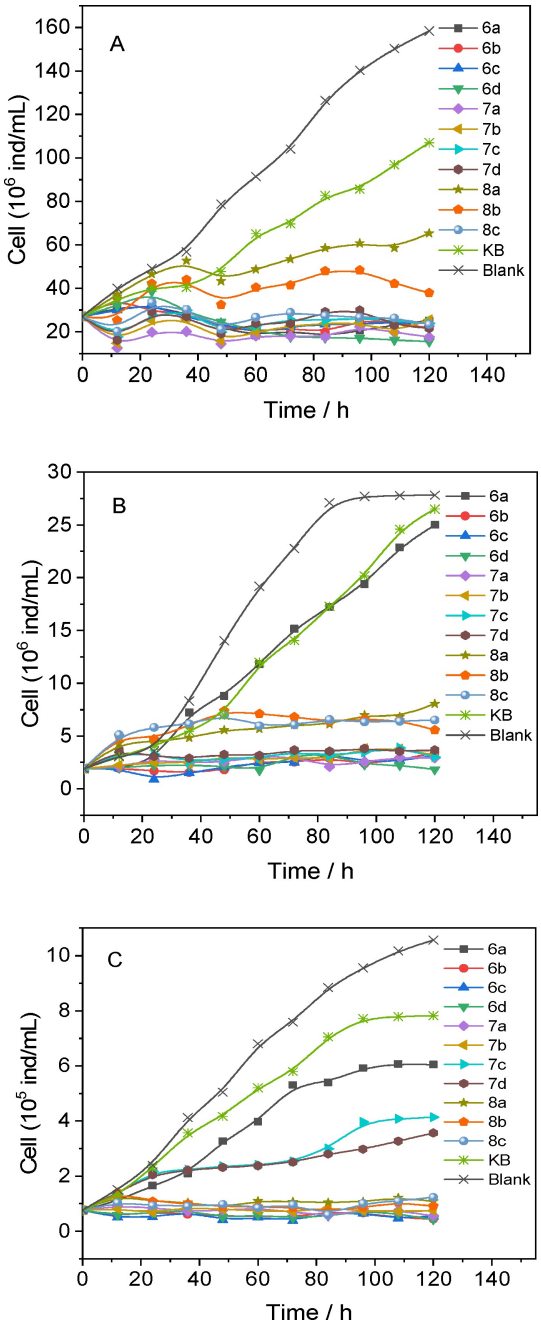


Figure 2. Inhibition of Isochrysis galbana(A), Nannochloropsis oculata(B) and Chlorella pyrenoidosa(C).

monomer was 5% (**6a**), the inhibitory rate was 11.35% at 12 h and 29.52% at 36 h. When the BIT monomer was 20% (**6d**), the inhibitory rate increased to 18.26% at 12 h and 29.52% at 36 h. The addition of the heterocyclic monomer HCM can improve the inhibitory rate on *Isochrysis galbana* dramatically. For copolymers **7**, copolymerized with 20% BIT monomer and 15% heterocyclic monomer simultaneously, the inhibitory rate of **7a** was 32.63% at 12 h and 59.12% at 36 h and the inhibitory rate of **7d** was 45.71% at 12 h and 53.09% at 36 h.

Additionally, it was found that introducing zinc basic benzoate (ZnBOH) in the resin, which is generally considered to increase the self-polishing properties, could also increase the inhibition of the growth of *Isochrysis galbana*. However, when the ZnBOH content was 10% (**8a**), the inhibitory rate was 4.06% at 12 h and 7.98% at 36 h, and when the ZnBOH content was 15% (**8b**), the inhibitory rate was 7.27% at 12 h and 18.77% at 36 h. Further increase in the ZnBOH content to 20% (**8c**) increased the inhibitory rate to 28.35% at 12 h and 45.05% at 36 h, which was better than that of **6d**.

The target copolymers showed favorable inhibitory activities on *Nannochloropsis oculata*in Figure 2(B). In the first 24 h, no obvious reproduction was observed and the concentration of algae remained almost unchanged. The inhibitory effect was not obvious, indicating that, in the short term, the algae themselves had some small tolerance and adaptability. Besides prolonging the culture procedure, the copolymers had apparent inhibition effects on *Nannochloropsis oculata*. The concentration of the BIT monomer NCM in the resin influenced the inhibition of the copolymers **6**. The resin containing 5% BIT monomer did not directly inhibit the growth of the algae. When the BIT monomer content was increased to 20%, the resin had a significant inhibitory effect on the growth of *Nannochloropsis oculata*.

The inhibitory rates of the target copolymers on *Nannochloropsis oculata* are shown in Table 3. When the BIT monomer content was 5% (**6a**), the inhibitory rate was 14.92% at 12 h and 20.98% at 36 h. When the BIT monomer content was 20% (**6d**), the inhibitory rate increased to 34.92% at 12 h and 68.96% at 36 h. Unfortunately, the addition of the heterocyclic monomer HCM cannot improve the inhibitory rate of *Nannochloropsis oculata* compared to **6d**. For copolymers **7**, copolymerized with 20% BIT monomer and 15% heterocyclic monomer simultaneously, the inhibitory rate of **7a** was 31.32% at 12 h and 54.94% at 36 h and the inhibitory rate of **7d** was 20.39% at 12 h and 46.09% at 36 h. Additionally, the copolymer **7a** had a slightly better inhibitory effect than other copolymers containing HCM monomers.

The inhibitory activities of the grafted BIT copolymers on the growth of *Chlorella pyrenoidosa* are shown in Figure 2(C). In the first 12 h, the algae exhibited resistance and there were no obvious differences in algae concentration between the samples and the control group. As the cultivating process continued, most of the target copolymers had significant inhibition effect on the tested algae and prevented their reproduction completely after 24 h.

The inhibitory rates of the target copolymers on *Chlorella pyrenoidosa* are shown in Table 4. With increasing content of the BIT monomer **NCM** in the resin, the inhibitory rate increased accordingly. When the BIT monomer content was 5% (**6a**), the inhibitory rate was 15.90% at 12 h and 27.87% at 24 h. When the BIT monomer content was 20% (**6d**), the inhibitory rate increased to 55.09% at 12 h and 70.59% at 24 h. However, the addition of the heterocyclic monomer HCM did not cause any obviously difference in inhibitory rate on *Chlorella pyrenoidosa* between **6a** and **7**. For copolymers **7**, copolymerized with 20% BIT monomer and 15% heterocyclic monomer simultaneously, the inhibitory rate of **7a** (copolymerized with 15% benzothiazole)was 30.46% at 12 hand 62.94% at 24 h and the

Table 2. Inhibitory rate of resin on *Isochrysis galbana*.

Time (h)	Compounds								
	6a	6b	6c	6d	7a	7b	7c	7d	8a	8b	8c
12	11.35 ± 0.22	12.02 ± 0.24	14.45 ± 0.19	18.26 ± 0.27	32.63 ± 0.33	34.57 ± 0.18	39.48 ± 0.11	45.71 ± 0.18	4.06 ± 0.11	7.27 ± 0.31	28.35 ± 0.33
24	21.47 ± 0.18	28.62 ± 0.21	18.79 ± 0.33	24.48 ± 0.41	50.00 ± 0.33	46.84 ± 0.25	40.70 ± 0.38	47.73 ± 0.17	4.91 ± 0.13	14.39 ± 0.22	43.67 ± 0.11
36	29.52 ± 0.26	28.62 ± 0.31	34.88 ± 0.22	38.62 ± 0.29	59.12 ± 0.22	49.09 ± 0.24	45.44 ± 0.36	53.09 ± 0.27	7.98 ± 0.11	18.77 ± 0.22	45.05 ± 0.21
48	54.62 ± 0.32	53.86 ± 0.38	50.07 ± 0.44	48.55 ± 0.57	69.80 ± 0.33	60.67 ± 0.38	58.42 ± 0.48	59.93 ± 0.33	9.10 ± 0.14	31.86 ± 0.19	55.38 ± 0.39
60	71.74 ± 0.31	68.96 ± 0.51	70.07 ± 0.36	68.4 ± 0.18	72.30 ± 0.49	68.68 ± 0.59	65.07 ± 0.33	63.40 ± 0.49	25.02 ± 0.19	37.82 ± 0.23	58.95 ± 0.11
72	70.53 ± 0.31	68.98 ± 0.19	67.94 ± 0.15	74.68 ± 0.33	74.17 ± 0.43	67.42 ± 0.32	63.27 ± 0.11	65.87 ± 0.22	23.34 ± 0.23	40.45 ± 0.24	58.60 ± 0.15
84	78.23 ± 0.29	76.04 ± 0.38	71.67 ± 0.41	79.10 ± 0.35	78.67 ± 0.22	70.56 ± 0.33	69.49 ± 0.19	64.68 ± 0.33	29.28 ± 0.38	41.95 ± 0.41	66.87 ± 0.28
96	76.01 ± 0.28	70.52 ± 0.35	72.63 ± 0.26	79.98 ± 0.47	73.90 ± 0.22	71.79 ± 0.38	69.25 ± 0.55	69.03 ± 0.59	29.14 ± 0.39	53.50 ± 0.16	68.83 ± 0.33
108	76.17 ± 0.55	74.68 ± 0.46	76.68 ± 0.59	84.27 ± 0.33	79.53 ± 0.55	79.53 ± 0.38	76.31 ± 0.44	78.17 ± 0.49	39.58 ± 0.49	64.38 ± 0.57	72.81 ± 0.58
120	76.40 ± 0.19	79.78 ± 0.31	77.75 ± 0.41	85.53 ± 0.57	83.50 ± 0.61	79.06 ± 0.59	77.75 ± 0.49	79.78 ± 0.58	38.88 ± 0.22	64.57 ± 0.28	73.09 ± 0.52

Data are expressed in mean ± SD. Inhibitory rate [%].

inhibitory rate of **7b** (copolymerized with 15% thiazole) was 38.29% at 12 h and 70.59% at 24 h. After being cultured for 84 h, the algae inhibition rates of most copolymers **7** was up to 90%.

2.3. Inhibition on Bacterial Growth

The antibacterial rate of the target resin on *Vibrio coralliilyticus*is shown in Figure 3(A). All the resins had significant inhibition and the extension of the culture time caused the antibacterial

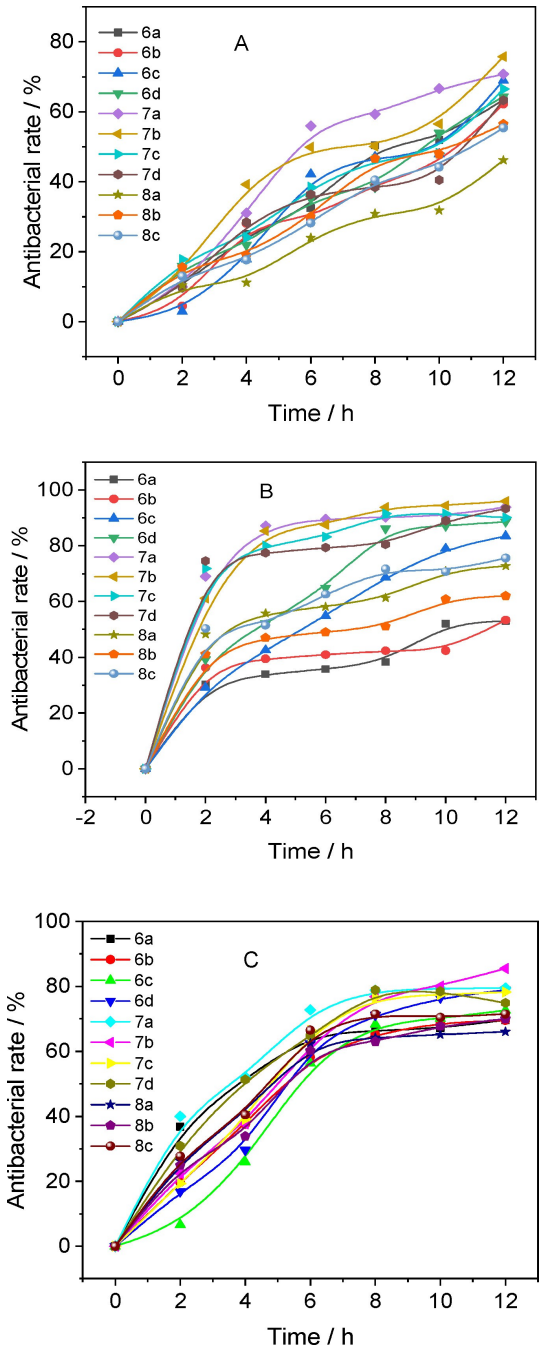


Figure 3. Antibacterial activity against Vibrio coralliilyticus (A), Staphylococcus aureus (B) and Vibrio parahaemolyticusl (C).

Table 3. Inhibitory rate of resin on *Nannochloropsis oculata*.

Time (h)	Compounds									
	6a	**6b**	**6c**	**6d**	**7a**	**7b**	**7c**	**7d**	**8a**	**8b**	**8c**
12	14.92 ± 0.51	36.12 ± 0.22	36.12 ± 0.11	34.92 ± 0.33	31.32 ± 0.16	26.52 ± 0.22	15.77 ± 0.43	20.39 ± 0.32	10.79 ± 0.19	17.98 ± 0.29	19.98 ± 0.22
24	15.31 ± 0.38	48.01 ± 0.27	48.98 ± 0.38	44.39 ± 0.26	47.78 ± 0.23	40.04 ± 0.31	18.98 ± 0.19	23.51 ± 0.33	11.08 ± 0.29	18.90 ± 0.39	20.59 ± 0.25
36	20.98 ± 0.21	71.69 ± 0.22	72.36 ± 0.39	68.96 ± 0.39	54.94 ± 0.44	54.94 ± 0.24	52.26 ± 0.46	46.90 ± 0.38	11.39 ± 0.33	22.89 ± 0.28	30.91 ± 0.55
48	33.99 ± 0.24	74.26 ± 0.31	75.60 ± 0.23	79.55 ± 0.33	63.28 ± 0.11	56.49 ± 0.43	59.62 ± 0.37	53.35 ± 0.33	20.43 ± 0.22	38.90 ± 0.18	49.9 ± 0.18
60	41.54 ± 0.37	78.29 ± 0.23	79.51 ± 0.37	79.93 ± 0.35	74.64 ± 0.41	77.08 ± 0.55	75.25 ± 0.39	73.73 ± 0.41	32.71 ± 0.22	40.83 ± 0.28	50.27 ± 0.33
72	51.68 ± 0.39	81.98 ± 0.49	82.24 ± 0.37	80.04 ± 0.35	78.34 ± 0.22	78.86 ± 0.28	75.21 ± 0.33	73.91 ± 0.51	34.02 ± 0.39	41.54 ± 0.29	56.74 ± 0.33
84	60.41 ± 0.49	83.25 ± 0.62	80.71 ± 0.59	81.14 ± 0.44	87.90 ± 0.33	83.46 ± 0.61	81.77 ± 0.57	79.45 ± 0.58	40.65 ± 0.55	50.17 ± 0.56	62.12 ± 0.49
96	63.83 ± 0.49	88.16 ± 0.37	87.26 ± 0.18	88.53 ± 0.22	87.26 ± 0.66	81.09 ± 0.58	82.72 ± 0.44	81.09 ± 0.33	53.31 ± 0.55	59.31 ± 0.66	68.58 ± 0.39
108	66.98 ± 0.33	88.80 ± 0.38	89.25 ± 0.44	90.89 ± 0.33	87.91 ± 0.33	84.64 ± 0.39	84.19 ± 0.59	85.53 ± 0.67	57.29 ± 0.18	61.63 ± 0.28	73.93 ± 0.11
120	67.64 ± 0.61	87.12 ± 0.44	88.09 ± 0.55	92.06 ± 0.69	88.92 ± 0.44	85.95 ± 0.58	85.64 ± 0.44	86.15 ± 0.35	58.58 ± 0.22	62.97 ± 0.47	74.38 ± 0.55

Data are expressed in mean ± SD. Inhibitory rate [%].

rate to steadily increase as well. The resin grafted with benzothiazole (**7a**) or thiazole (**7b**) had higher inhibitory activity than other resins, with antibacterial rates of 70.78% or 75.79%, respectively, at 12 h, and the resin grafted with 10% ZnBOH (**8a**) had lower inhibitory activity than other resins, with an antibacterial rate of 46.13% at 12 h.

The antibacterial rate of the grafted resin against *Staphylococcus aureus*is shown in Figure 3(B). All the samples had obvious inhibitory effects and the antibacterial rate increased rapidly with the extension of the culture time.

As the content of the BIT monomer **NCM** increased, the inhibition increased accordingly. Among copolymers **6**, when the BIT monomer content was 5% (**6a**), the antibacterial rate was 35. 71% at 6 h and 53.00% at 12 h, respectively. When the BIT monomer content was 20% (**6d**), the antibacterial rate increased to 64.83% at 6 h and 88.61% at 12 h, respectively. Particularly, the resins containing heterocyclic compounds had an obvious antibacterial activity. Samples **7a** grafted with benzothiazole, **7b** grafted with thiazole, and **7d** grafted with 5-methyl-2-pyridine, all had outstanding inhibitory activities compared to other resins, with antibacterial rates of 93.48%, 95.95%, and 93.28% at 12 h, respectively. However, the resin grafted with 10% ZnBOH (**8a**) had a lower inhibitory activity than other resins, with an antibacterial rate of 72.76% at 12 h.

The antibacterial rate of the grafted resin against *Vibrio parahaemolyticus*is shown in Figure 3(C). All the resin samples had obvious inhibitory properties and the antibacterial rate increased significantly with the extension of the culture time. As thecontent of the BIT monomer increased, the antibacterial rate increased accordingly. For copolymers **6**, when the BIT monomer was at 5% (**6a**), the antibacterial rate was 65.38% at 6 h and 69.66% at 12 h, respectively. When the BIT monomer content was 20% (**6d**), the antibacterial rate increased to 62.40% at 6 h and 78.90% at 12 h. Interestingly, the resins containing heterocyclic monomers had a marked antibacterial activity. Samples **7a** grafted with benzothiazole, **7b** grafted with thiazole, and **7d** grafted with 5-methyl-2-pyridine had outstanding inhibitory activities, with antibacterial rates of 79.53%, 85.53%, and 74.91%, respectively, at 12 h. However, the resin grafted with ZnBOH can also affect the inhibitory activity, with the antibacterial rate of the resin increasing gradually with the increase in ZnBOH content. The resin **8a**, grafted with 10%ZnBOH,has an antibacterial rate of 66.04% at 12 h, and the resin **8c**, grafted with 20%ZnBOH had an antibacterial rate of 71.53% at 12 h.

2.4. Inhibition of Barnacle Larvae

The biotoxicity effects of the grafted acrylic copolymers on barnacle larvae at 24 h are summarized in Figure 4. The inhibitory activities of all the resins were higher than that of the control group with no active monomer in the structure, and the mortalities of the barnacle larvae were increased with increasing content of the NCM monomers. For the copolymer **6a**, grafted with 5% NCM, the mortality rate of the barnacle larvae was 71%. In contrast, the copolymer **6d**, grafted with 20%

Table 4. Inhibitory rate of resin on *Chlorella pyrenoidosa*.

Time (h)	Compounds											
	6a	**6b**	**6c**	**6d**	**7a**	**7b**	**7c**	**7d**	**8a**	**8b**	**8c**
12	15.90 ± 0.20	57.33 ± 0.21	61.81 ± 0.30	55.09 ± 0.18	30.46 ± 0.35	38.29 ± 0.39	3.13 ± 0.20	6.49 ± 0.25	1.35 ± 0.31	7.61 ± 0.10	20.38 ± 0.23
24	27.87 ± 0.15	69.32 ± 0.12	77.61 ± 0.13	70.59 ± 0.11	62.94 ± 0.13	70.59 ± 0.19	5.55 ± 0.40	10.65 ± 0.22	52.74 ± 0.18	52.74 ± 0.33	59.11 ± 0.11
36	31.20 ± 0.31	82.7 ± 0.22	80.23 ± 0.17	79.00 ± 0.10	79.82 ± 0.40	75.71 ± 0.20	37.51 ± 0.21	37.92 ± 0.17	70.78 ± 0.18	72.02 ± 0.19	74.48 ± 0.2
48	41.52 ± 0.18	86.59 ± 0.19	90.11 ± 0.25	87.65 ± 0.11	81.67 ± 0.24	80.97 ± 0.31	43.33 ± 0.27	44.39 ± 0.29	79.21 ± 0.15	78.5 ± 0.22	76.39 ± 0.36
60	53.68 ± 0.27	89.55 ± 0.33	90.4 ± 0.31	88.71 ± 0.23	83.92 ± 0.16	85.61 ± 0.19	53.8 ± 0.26	54.36 ± 0.18	78.85 ± 0.11	82.8 ± 0.29	83.64 ± 0.29
72	58.43 ± 0.22	91.12 ± 0.21	93.4 ± 0.22	91.63 ± 0.18	88.09 ± 0.25	87.83 ± 0.15	56.22 ± 0.18	56.73 ± 0.25	81.51 ± 0.26	85.3 ± 0.19	83.28 ± 0.33
84	63.53 ± 0.21	90.00 ± 0.55	90.63 ± 0.44	92.08 ± 0.39	91.87 ± 0.16	87.93 ± 0.21	57.6 ± 0.11	60.3 ± 0.16	85.23 ± 0.33	89.59 ± 0.19	91.46 ± 0.25
96	63.53 ± 0.55	91.43 ± 0.43	91.62 ± 0.56	90.48 ± 0.39	90.10 ± 0.22	90.48 ± 0.59	58.68 ± 0.45	61.41 ± 0.51	86.11 ± 0.33	88.77 ± 0.29	86.87 ± 0.39
108	65.03 ± 0.58	93.58 ± 0.63	93.95 ± 0.48	91.88 ± 0.39	90.38 ± 0.28	90.75 ± 0.58	59.64 ± 0.39	62.99 ± 0.51	84.35 ± 0.52	86.61 ± 0.61	85.86 ± 0.39
120	66.07 ± 0.26	94.35 ± 0.27	93.04 ± 0.31	94.54 ± 0.17	92.85 ± 0.33	90.41 ± 0.58	60.09 ± 0.39	63.14 ± 0.47	86.1 ± 0.28	88.35 ± 0.33	84.22 ± 0.51

Data are expressed in mean ± SD. Inhibitory rate [%].

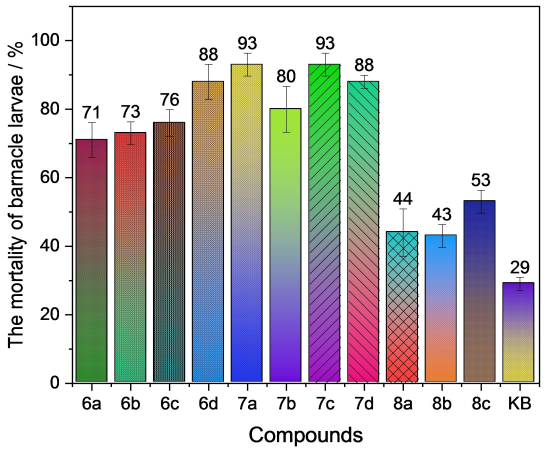


Figure 4. Barnacle larvae mortality at 24 h.

NCM, showed higher inhibitory activity than **6a**, with the mortality rate of the barnacle larvae increasing to 88%.

Additionally, the introduction of the heterocyclic monomer HCM considerably enhanced the mortality rate; the copolymers **7a**, grafted with benzothiazole, **7c**, grafted with 2-pyridine, and **7c**, grafted with 5-methyl-2-pyridine, had mortality rates of 93%, 93%, and 88% at 24 h, respectively, and all the barnacle larvae died. The resin grafted with ZnBOH**8**decreased the inhibitory activities compared to **6d**, with lower mortality rate ranging from 43% to 53% at 24 h.

2.5. Release Rate of Antifoulant

The controlled release of the antifoulant determined the duration and antifouling performance of the antifouling system (Figure 5). The hydrolysis release rate of the antifoulant BIT derivatives in the copolymers was tested and calculated from day 1 to day 45, with immersion time plotted on the abscissa and release rate on the ordinate. Figure 5 shows that each copolymer has a relatively high release rate in the early stage and, as time passes, the release rate decreases. However, the

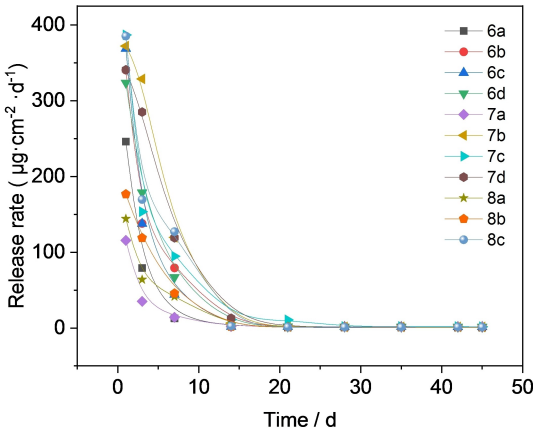


Figure 5. BIT actives release rate.

release rates increased with increasing monomer content in the resins. Before 14 days, all the samples had higher release rate due to the massive oligomers release from the surface layer. After immersion in seawater for 14 d, the release rates were stable in the range of 0.6–1.9 $\mu g\,cm^{-2}\,d^{-1}$.

The leaching out is expressed as decrement of thickness in the resin (Figure 6). The leached thickness rate of the polymers tends to be stable in the range of 0.2–0.4 $\mu m\,d^{-1}$from 20 d to 50 d as shown in figure 6. Relatively fast leaching out during the first 10 d may have been caused by the release of oligomers in the films, which means that the leached thickness rates after 2 weeks are stable.

2.6. Application on Antifouling Coatings

To further investigate the inhibitory performance of the grafting copolymers on marine macrofouling organisms, the short-term antifouling performance of the coatings with 20% BIT monomer

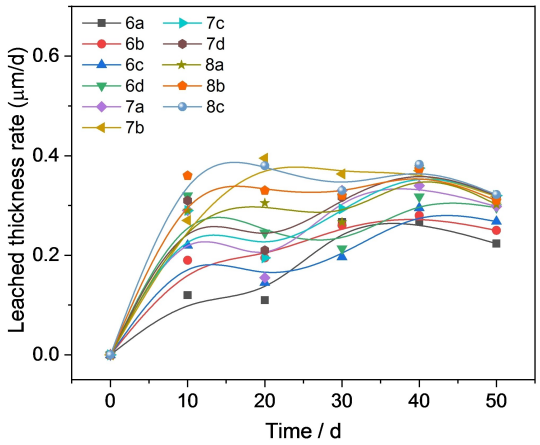


Figure 6. Leached thickness rate of the resins.

NCM was evaluated by a marine field test. The typical images of the tested panels after immersion in seawater for 30–90 d were recorded and are shown in Figure 7.

The antifouling effect of the target resin was apparent compared to the blank panel. After 30 days, all the tested samples were very clean, with only a little sludge covered and a small amount of barnacles attached to the control group. After 60 days, some lime bugs were found attached on the surface of the tested panels, but the blank panels were fouled significantly by various marine organisms. After 90 days, only a small amount of barnacles was found adhered to the surface of the experimental groups, and a large number of barnacles and mussels was found attached to the control group.

Among these, panel **7**,which contained 15% HCM and 20% NCM, was found to have only a small amount barnacles, sludge, and algae attached to them after being immersed in seawater for 3 months. Interestingly, for sample **8c**, grafted with 20% ZnBOH, which led to the erosion of the zinc-based coatings and gradual release of the antifouling biocides, the surface was very smooth and there were hardly any organisms attached to it. In contrast, after a field exposure period of 3 months, the Blank control group was nearly completely covered by all types of fouling organisms, with an excessive amount of fouling organisms, such as mussels, lime bugs, barnacles, attached to the surface.

3. Conclusion

A type of graft copolymer resins was prepared by copolymerization of 1,2-benzo[d]isothiazol-3(2H)-one monomer, a heterocyclic monomer, and an acrylate monomer. The inhibitory effect of the resin on marine algae, bacteria, and barnacle larvae was investigated, and the release rate of the actives along with a marine field test environment was also evaluated. The findings of this study showed that the resin can effectively inhibit

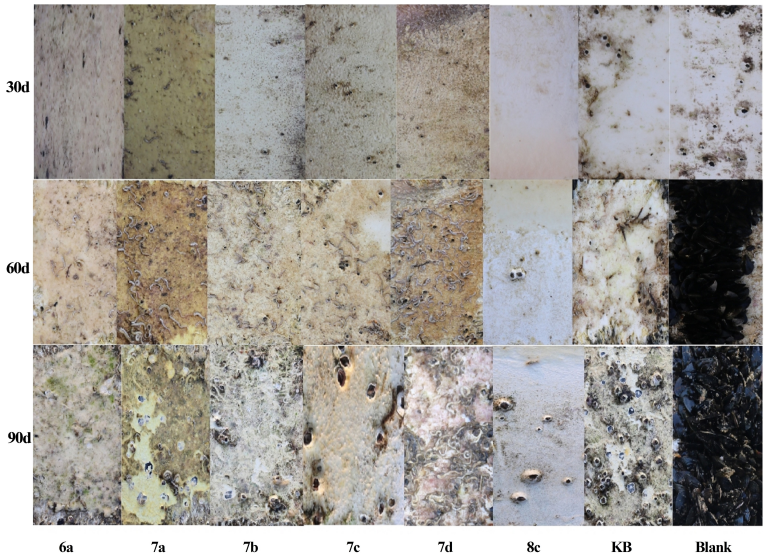


Figure 7. Antifouling performance of the resin immersion in seawater.

microbial adhesion, which indicated that the copolymer could be used as a potential marine antifouling coating.

Experimental Section

Materials

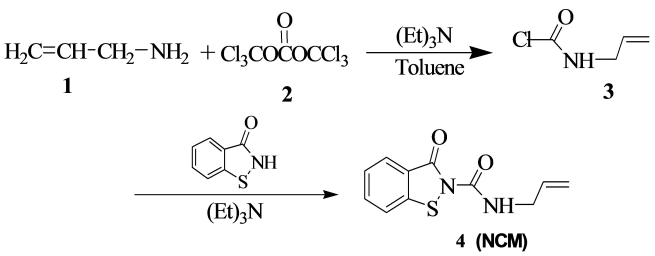
1,2-Benzisothiazolin-3-one (BIT), allylamine, trimethylamine (Et_3N), triphosgene (BTC), MMA, acrylic acid (AA), BA, zinc dibenzoate, 2,2-azobisisobutyronitrile (AIBN), N,N-dimethylformamide (DMF), methylbenzene, acryloyl chloride, dichloromethane (DCM), and tetrahydrofuran (THF) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd, and were used without further purification. Flash column chromatography was performed on gel (100–200 mesh, Qingdao Haiyang Chemical Co. Ltd). Thin layer chromatography (TLC) analysis was conducted on GF254 plates using ethyl acetate and petroleum ether mixtures as eluent. The seawater was collected from the coast near the Yingbin Peninsula in Hainan Province, then filtered, boiled, and disinfected before use.

Physical Properties

Hydrogen nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a 400-MHz Bruker spectrometer using tetramethylsilane (TMS) as the internal standard. FT-IR spectra were recorded at room temperature in the frequency range of 4000–400 cm^{-1} on a PerkinElmer spectrum 100 FT-IR spectrometer using KBr pellets. The average molecular weight and molecular weight distribution were obtained by gel permeation chromatography (Waters 2414). The experiment was conducted in tetrahydrofuran (THF) at 35 °C using a WAT044225 column (7.8×300 mm) at a flow rate of 1.0 mL/min. The instrument was calibrated using polystyrene (PS) standards. The glass transition temperature (T_g) was determined using differential scanning calorimetry (DSC, Q20, TA instrument). A hermetic aluminum pan was used for loading samples to prevent overflow during the heating process and the heating rate was 10 °C/min under a nitrogen flow of 50 mL/min.

N-allyl (1,2-Benzo[d]isothiazol-3(2H)-one) Carboxamide Monomer (NCM) Synthesis

As shown in Scheme 1, BTC 2 and allylamine **1** were reacted in toluene in the presence of Et_3N to produce N-allyl-carbamic chloride **3**. Then, intermediate 3 reacted with BIT to afford N-allyl-(1,2-Benzo[d] isothiazol-3(2H)-one) carboxamide 4. Precisely, 9.9 g BTC (0.033 mol) and 90 mL toluene were mixed in a 250-mL three-neck flask equipped with a stirrer and a thermometer, and cooled to 0–5 °C in an ice-water bath until BTC 2 dissolved completely. Furthermore, 8.6 g (0.15 mol) allylamine were mixed with 10 mL toluene and a small amount of triethylamine (4–5 d), and the mixture was added dropwise to the flask with vigorous stirring for 1 h and then stirred for 2 h until the end of adding the mixture. Subsequently, 8.6 g (0.057 mol) BIT was added to the above mixture and refluxed for 2 h. The mixture was then cooled to room temperature and washed twice with deionized water, and the pH was adjusted to neutral with a 10% sodium bicarbonate solution. The organic phase was separated and dried overnight with magnesium sulfate anhydrous, and filtered under vacuum. After the removal of the solvent, the products were purified by flash column chromatography on silica gel, eluting with mixtures of ethyl acetate and petroleum ether. Yield: 80%. ^{1}H NMR(400 MHz, $CDCl_3$), δ: 9.0(s, 1H, NH); 8.03(d, J=8.0 Hz, 1H); 7.70(t, J=8.0 Hz, 1H); 7.58(d, J=8.0 Hz, 1H); 7.43(t, J=8.0 Hz, 1H); 5.89–5.99 (m, 1H, -CH=); 5.31(dd, J=16.8, 1.2 Hz, 1H); 5.21(dd, J=10.4, 1.2 Hz, 1H); 4.07–4.10(m, 2H). IR (KBr): ν(cm^{-1}): 1660 (C=C), 3011 (=C–H), 3085 (=CH_2); 1702 (C=O); 3378, 1660 (–CONH–).



Scheme 1. Synthesis of 3-oxo-N-allyl-1,2-benzisothiazole-2(3H)-carboxamide monomers.

Heterocyclic Monomers (HCM) Synthesis

As shown in Scheme 2, 0.02 mol heterocyclic compound and 50 mL dichloromethane were mixed in a 100-mL three-neck flask equipped with a stirrer and a thermometer and cooled to 0–5 °C using an ice-water bath. Then, 0.02 mol triethylamine was added as an acid acceptor. Acryloyl chloride (0.024 mol) was added dropwise to the flask in an ice bath with vigorous stirring for 1 h at 0–5 °C and then stirred for 2 h at room temperature.

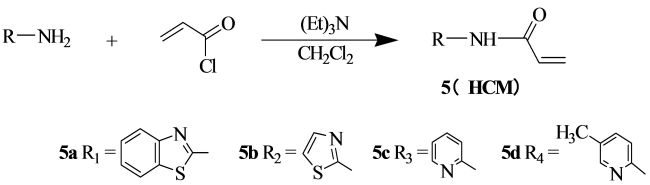
The mixture was extracted with 20 mL ethyl acetate, washed first with 20 mL saturated salt water, and then washed twice with 20 mL deionized water. The organic phase was separated and dried over anhydrous magnesium sulfate overnight and filtered under vacuum. After the removal of the solvent, the products were purified by flash column chromatography on silica gel eluting with a 10:1 petroleum ether:ethyl acetate mixture.

N-(benzo[d]thiazol-2-yl)acrylamide (**5a**), Yield: 75%. ^{1}H-NMR (400 MHz, DMSO-d6), δ 12.63(s, 1H, NH); 8.02 (d, J=8.0 Hz, 1H); 7.79 (d, J=8.0 Hz, 1H); 7.47 (t, J=7.6 Hz, 1H); 7.34 (t, J=7.6 Hz, 1H); 6.62 (dd, J=17.2, 10.0 Hz, 1H); 6.48 (dd, J=17.2, 2.0 Hz, 1H); 5.99 (dd, J=10.0, 2.0 Hz, 1H). IR (KBr): ν(cm^{-1}): 3438, 1586 (–CONH–), 1713 (C=O), 1610 (C=C).

N-(thiazol-2-yl)acrylamide (**5b**), Yield: 80%. ^{1}H-NMR (400 MHz, DMSO-d6), δ 12.38 (s, 1H, NH); 7.53 (d, J=3.2 Hz, 1H); 7.27(d, J=3.2 Hz, 1H); 6.56 (dd, J=17.2, 10.0 Hz, 1H); 6.42 (dd, J=17.2, 2.0 Hz, 1H); 5.92 (dd, J=10.0, 2.0 Hz, 1H). IR (KBr): ν(cm^{-1}): 3316, 1487 (–CONH–), 1710 (C=O), 1642 (C=C).

N-(pyridin-2-yl)acrylamide (**5c**), Yield: 97%. ^{1}H-NMR (400 MHz, DMSO-d6), δ 10.74 (s, 1H, NH); 8.35 (d, J=4.8 Hz, 1H); 8.23 (d, J=8.4 Hz, 1H); 7.80 (t, J=7.6 Hz, 1H); 7.10–7.13 (m, 1H); 6.65 (dd, J=16.8, 10.0 Hz, 1H); 6.34 (dd, J=16.8, 2.0 Hz, 1H); 5.79 (dd, J=10.0, 2.0 Hz, 1H). IR (KBr): ν(cm^{-1}): 3442, 1490 (–CONH–), 1712 (C=O), 1500 (C=C).

N-(5-methylpyridin-2-yl)acrylamide (**5d**), Yield: 92%. ^{1}H-NMR (400 MHz, DMSO-d6), δ 10.65 (s, 1H, NH); 8.17 (d, J=2.0 Hz, 1H); 8.11 (d, J=8.4 Hz, 1H); 7.62 (dd, J=8.4, 2.0 Hz, 1H); 6.3 (dd, J=16.8,



Scheme 2. Synthesis of N-heterocyclic acrylamide monomers.

10.0 Hz, 1H); 6.32 (dd, J = 16.8, 2.0 Hz, 1H); 5.77 (dd, J = 10.0, 2.0 Hz, 1H); 2.25 (s, 3H). IR (KBr): ν(cm^{-1}): 3310, 1510 (–CONH–), 1705 (C=O), 1535 (C=C), 1382 (–CH_3).

Copolymers Synthesis

Acrylic random copolymers **6** were synthesized by free radical polymerization as follows. AIBN (1.6 g, 0.01 mol), NCM (3.0 g, 0.013 mol), MMA (8.5 g, 0.08 mol), and BA (8.5 g, 0.06 mol), along with 4.0 mL butyl alcohol and 16 mL xylene, were added successively in a 100-mL three necked flask equipped with a reflux condenser, a thermometer, and a mechanical stirrer. The reaction mixture was heated slowly to 85 °C and maintained at this temperature for 6 h. Then, the solvent was partially evaporated at reduced pressure and 60 °C; the mixture was then cooled to room temperature to obtain the modified copolymer **6**.

Acrylic random copolymers **7** were synthesized by free radical polymerization as follows. AIBN (1.6 g, 0.01 mol), NCM (10 g, 0.043 mol), MMA (16.3 g, 0.163 mol), BA (16.3 g, 0.127 mol), 7.5 g HCM, 10 mL butyl alcohol, and 40 mL xylene were added in turn in a 250-mL three necked flask equipped with a reflux condenser, a thermometer, and a mechanical stirrer. The reaction mixture was slowly heated to 85 °C and this temperature was maintained for 8 h. Then, the solvent was partially evaporated at reduced pressure and 60 °C; the mixture was then cooled to room temperature to obtain the modified copolymers **7**.

Zinc acrylate copolymers **8** were synthesized by radical polymerization. Briefly, 15.0 g MMA (0.15 mol), 15.0 g BA (0.117 mol), 10.0 g AA (0.14 mol), and 2.25 g AIBN (0.014 mol) were added successively to a 100-mL three-neck flask equipped with a stirrer and a thermometer, and 10.0 g NCM (0.043 mol) was dissolved in xylenes/butyl alcohol (4:1) mixture and added to the same flask. The solution was stirred at 85 °C for 10 h and an acrylic prepolymer was obtained; subsequently, 30.4 g of zinc basic benzoate (ZnBOH) was added to the flask and the solution was stirred at 85 °C for another 5 h to obtain zinc acrylate resin **8** (Scheme 3).

As is well known,[27–28] the selection of monomer and polymerization technique has a significant effect on the properties of the polymeric coating. Therefore, the copolymeric resin was synthesized by introducing several functional monomers (NCM, HCM, and ZnBOH) in varying combinations into the copolymerization structure (Scheme 3). For copolymers **6**, the N-allyl-BIT monomer NCM was grafted at different percentages of 5%, 10%, 15%, and 20% of total weight and the weight ratio of [MMA]:[BA] was about 1:1. For copolymers **7**, the percentage of N-allyl-BIT monomer NCM contained in the resin was 20%, the heterocyclic monomer HCM was 15% of the total weight of the resin, and the weight ratio of [MMA]:[BA] was also 1:1. For copolymers 8, the ratio of [MMA]/[BA]/[AA]/[NCM] was 1.5/1.5/1/1, and ZnBA was introduced to the resin structure at 10%, 15%, and 20%. All the solid raw materials, including AIBN, were dissolved in xylene/butyl alcohol (4:1) mixed solvent and stirred at 85 °C for 10 h.

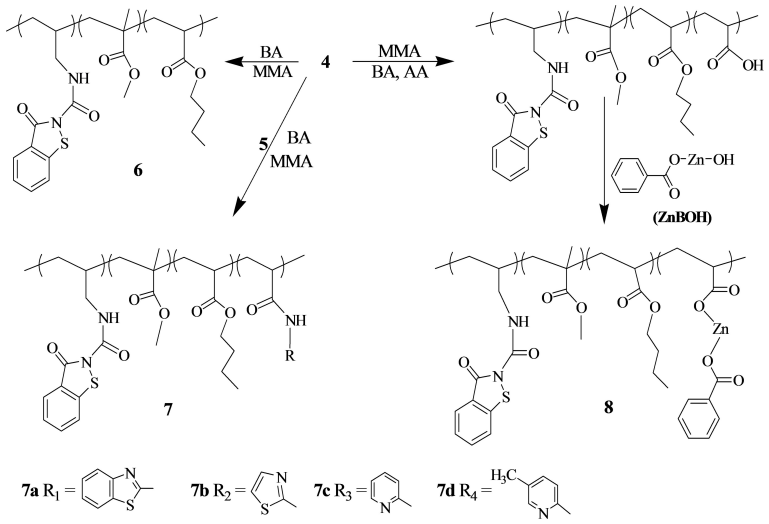
Biological Activity

Growth Inhibition of Marine Algae

The algae liquid was obtained from the Ocean College of Hainan University. The maximum absorption wavelengths of *Isochrysis galbana*, *Nannochloropsis oculata*, and *Chlorella pyrenoidosa* were 428 nm, 440 nm, and 680 nm, respectively, as obtained by ultraviolet wavelength scanning on a UV-vis spectrophotometer. The absorption value of each dilution was measured at the maximum absorption wavelength and each sample was measured three times to obtain an average concentration of the algae solution. The standard curve was drawn with the absorption value as the abscissa and the concentration of the marine algae as the ordinate.

The algae liquid, cultured to the exponential growth period, was diluted to a certain concentration with the nutrient solution, such that the absorption was between 0.05 and 0.10. The synthesized acrylic resin diluted with xylene/n-butanol (4:1) was coated on a glass sheet (76 mm × 25 mm × 1.2 mm), dried naturally in air, and immersed in 200 mL algal solution in conical bottles. Each sample was measured every 12 h and the absorbance was recorded using commercial acrylic polyester (non-grafted acrylic resin, named KB) and blank board (no resin coated on the surface of the glass sheet, named Blank) as the control groups. The algae inhibition rate of the corresponding compound is calculated from the concentration of the algae solution, according the following equation:

$$I = \frac{C_0 - C_i}{C_0} \quad (1)$$



Scheme 3. Grafted copolymers synthesis.

where I is the inhibition rate of algae, C_0 is the concentration of algae solution on non-grafted acrylic resin, and C_i is the concentration of algae liquid in the experimental group.

Bacteriostatic Activity

The target acrylic resin was coated on the surface of a 96-well microplate with commercial acrylic resin as the control group, and the antibacterial tests were conducted in an incubator under normal sunlight and suitable humidity. Prior to testing, the resin-coated cell culture plates were UV-sterilized for 1–2 h, 5 mL of the culture medium liquid was added to each well, and 120 μL of the culture solution, cultured to the logarithmic growth phase, was cultured in an incubator at 37 °C. Then, 90 μL of the bacterial solution was transferred to a 96-hole plate and tested every 2 h. The absorbance was measured at 600 nm after 2 h, 4 h, 6 h, 8 h, 10 h, and 12 h using an enzyme-labeled instrument. Each sample was measured three times in parallel and averaged. The inhibition curve was drawn with time on the abscissa and antibacterial rate on the ordinate.

Biological Activity Against Barnacle Larvae

Barnacles were collected from the shore of Haikou Bay near Haikou City. Each resin was evenly coated on the surface of petri dishes respectivelyand allowed to dry. Thirty barnacle larvae were kept in each dish. The survival of the barnacle larvae was observed under a stereomicroscope after 12 h and 24 h, and the number of deaths of barnacle larvae was recorded. To ensure the accuracy of the experiment, the dead larvae were taken out in-time. In each group, the experiments were repeated three times.

Antifoulant Release Rate

The surface of each frosted glass plate (30 mm × 90 mm) was cleaned with ethanol. The sample coatings were painted on the surface of the glass plate. After the coating dried naturally, the glass plates were immersed in natural seawater.

The samples were soaked for 1, 3, 7, 14, 21, 28, 35, 42, and 45 days while automatic oscillator for 2 hdaily for the antifoulant release. On the specified day, the plates were taken out and transferred to an individual container filled with 250 mL of fresh natural seawater. After one day of immersion, 100 mL of sea water was taken out from the container and extracted with ethyl acetate, and the ethyl acetate fraction was dried over anhydrous magnesium sulfate. After the removal of the solvent on a rotary evaporator, the extract was diluted with 5 mL methanol and analyzed by HPLC using a reversed-phase system (Agilent 1100 with ZORBAX SB–C18 column, 4.6 mm × 250 mm, 5 μm) and an UV detector at 254 nm. The BIT derivatives peak was determined at the retention time and its concentration was calculated from the established standard curves. The release rate of the BIT derivatives was calculated with the following equation:[29–30]

$$R = C \times 20/(T \times S) \quad (2)$$

where R is the antifoulant release rate ($\mu g\,cm^{-2}\,d^{-1}$), C is the concentration of the BIT derivatives in methanol ($\mu g\,mL^{-1}$) calculated based on HPLC data, T is the duration for which the specimens were immersed in the individual measuring container (d), and S is the surface area of the coated film (27.00 cm^2).

Marine Field Tests

The field tests were performed from July to October 2019 at a fish farm in Haikou Bay (110°11′38.39″E, 20°02′45.97″N), China, where the temperature of the surface water ranges from 25 °C to 28 °C and the salinity ranges from 33‰ to 35‰. The resin samples for the antifouling test in the sea were painted onto 150 mm × 200 mm × 3 mm steel panels, and phenolic epoxy resin is painted on the surface (as primer), after the primer is cured, two coats of laboratory-obtained acrylic resin antifouling was painted by brush coating, the solvent is xylene/n-butanol (4:1), and it is naturally dried at room temperature for later use. Commercial acrylic acid polymers (KB) and blank samples (only coated phenolic epoxy resin on the steel panel, named Blank) were used as the control groups. The sample panels were lowered into the seawater at a depth of 0.5–1.0 m. After a certain period, the panels were taken out of the seawater, carefully washed with seawater and photographed, and then placed back into the seawater to continue the test.[31]

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: acrylate copolymers · antifouling coatings · biological activity · copolymerization reactions · FT-IR spectroscopy

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