

Poly(propylene carbonate) polyurethane self-polishing coating for marine antifouling application

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ABSTRACT: In this contribution, a series of environmentally friendly thermoplastic poly(propylene carbonate) polyurethane (PPCU) were prepared by two-step condensation polymerization and used to fabricate antifouling coatings. The poly(propylene carbonate) (PPC) segments served as degradable moieties. Quartz crystal microbalance with dissipation (QCM-D) measurements revealed that the polyurethane could degrade in the presence of enzyme and the degradation rate increases with the decrease of the molecular weight of the polyurethane. Investigation on the hydrolytic degradation behavior and the release rate test of the antifoulants in artificial seawater also demonstrated that the hydrolysis rate and the release rate increased as the molecular weight decreased, which makes the coating controllable at the hydrolysis rate range of 0.012–0.051 g/(m²d). Marine field tests and algae settlement assay tests revealed that the polyurethane coating possessed antibiofouling ability due to its self-renewal property and the release of antifoulants. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43667.

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INTRODUCTION

Marine biofouling derives from the undesired accumulation and growth of marine organisms such as microorganisms, barnacles, and seaweeds on submerged surfaces. It has adverse effects on maritime and aquatic industries.^{1–3} For instance, biofouling on ships leads to the increase of hydrodynamic drag. The fuel consumption increases by up to 40%.⁴ The overall cost increase by 77%.⁵ In addition, the release of adhered organisms from hull of foreign ship may cause biological threat to local species.⁶ Since 1970s, the biocidal coatings containing tributyltin proved to be very effective and widely used. However, later research suggested that toxic organic tin accumulated in marine organisms and further endanger human health through food chain, resulting in the global ban of tributyltin containing coatings.^{7,8} Now, less toxic biocides such as Cu₂O and some organic biocides are widely used, but their usage will be forbidden in the near future.^{9–11} In this context, several kinds of environment-friendly antifouling materials, such as low surface energy silicon elastomers,^{12–14} bioinspired textured surface,^{15,16} and natural antifoulants,^{17,18} have been developed. However,

whether these materials can withstand long term marine field test is still uncertain.

In principle, hydrolyzable and biodegradable polymers can be used to fabricate antibiofouling coatings with the self-polishing function and the controlled release of incorporated biocides if water penetration is slow compared to the erosion process, and the mass loss is confined to the surface layers.^{19,20} Till now, many efforts have been devoted to use biodegradable polyester to build antifouling coating system. For instance, Fay and coworkers prepared δ -valerolactone and L-lactide incorporated polycaprolactone to decrease the crystallinity and found that the release of biocides could be correlated with the degradation of polymer. Ma *et al.* prepared poly(caprolactone-co-glycolide) polyurethane coatings and the coating kept non-fouling up to 150 d with the aid of the environmentally friendly antifoulant of 4,5-dichloro-2-octyl-iso-thiazolone (DCOIT).²¹ Yu's investigation on hydrophobic polyhydroxyalkanoates suggested that the polymer could act as a self-polishing coating with a constant renewal rate in a water fluid field and the renewal rate could be adjusted by blending with other degradable polymers.²²

Poly(propylene carbonate) (PPC), the product of alternating copolymerization of carbon dioxide and propylene oxide, is an environmentally friendly polymer due to its biodegradability and hydrolytically degradability which makes it attractive for packaging purposes. To date, a great number of papers based on PPC have been reported. Y. Hwang *et al.* have reported for the first time that PPC reveals excellent enzymatic degradability toward *Rhizopus arrhizus* lipase, esterase/lipase Colonezyme A, and Proteinase K.²³ Other works demonstrated that the degradability increases in the order PCL \ll PLA < PPC as they were tested in strongly basic pH while show a slow degradation in moderate acidic and alkaline conditions.²⁴ They also explain the differences in strongly basic and moderate alkaline medium here.

In this work, we employed PPCdiol as starting material to prepare poly(propylene carbonate) polyurethane (PPCU). The PPCU coating with DCOIT was able to degrade in marine environment. The enzymatic degradation behavior was studied by Quartz crystal microbalance with dissipation (QCM-D) measurements. The hydrolytic degradation and antifouling performance of the polyurethane were also investigated. In this article, we mainly focus on the relations among the molecular weight, the degradation rate of the polyurethane and the antifouling performance of the PPCU coatings.

EXPERIMENTAL

Materials

1,4-Butanediol (1,4-BD, 99%, water \leq 500 ppm) was purchased from J&K Chemicals. Poly(propylene carbonate) (PPC, $M_w = 2000$ g/mol) was purchased from Jiangsu Zhongke Jinlong Chemical Co., Ltd. and dried under vacuum at 110 °C prior to use. 4,5-Dichloro-2-octyl-isothiazolone (DCOIT) was acquired from Xiya Reagent Co. Hexamethylene diisocyanate (HDI) and Tin 2-ethylhexanoate were obtained from Aladdin Chemical Co., China. *Chlorella* (Chlorophyta) was acquired from East China Sea and was grown in sterilized Guillard's *f/2* medium without Na_2SiO_3 . Tetrahydrofuran, methanol, glutaraldehyde, dimethyl formamide (DMF), and xylene were purchased from Sinopharm Chemical Reagent Co., Ltd. DMF was dried over CaH_2 and distilled under reduced pressure. All other reagents were used without further purification. Lipase PS obtained from Aldrich was purified by filtration and freeze-drying before use. Artificial seawater (ASW) was prepared according to ASTM D1141-98 (2013).

Measurements

^1H nuclear magnetic resonance spectroscopy (NMR) experiments were performed on a Varian Mercury plus 400 NMR spectrometer at 20 °C. The samples were dissolved with CDCl_3 and the solutions were measured with tetramethylsilane as an internal reference. Fourier transform infrared (FTIR) spectra were recorded on a PE Paragon 1000 spectrometer (KBr disk). Ultraviolet-Visible (UV-Vis) spectroscopic analysis was recorded on a Lambda 950 UV-Vis spectrophotometer. Gel permeation chromatography (GPC) was recorded on a Perkin Elmer HP 1100, using THF as the eluent at a flow rate of 1 mL min^{-1} , RI-WAT 150 CVt+ as the detector and linear polystyrene for calibration at 40 °C for characterization of apparent molecular weights. The adhesion strength value between coatings and epoxy resin panels were measured by portable pull-off adhesion testers using an epoxy adhesive (Loctite 907). The quantity of algae was counted using a dimension 3100v confocal laser

scanning microscope (CLSM) analysis system. The commercially available Quartz crystal microbalance (QCM) gold sensor chip was comprised of a bare gold surface (Q-sense SX-301, Q-SENSE, Sweden). The chip was rinsed with ethanol and dried under a gentle stream of high-purity N_2 gas, after which it was placed in a 1:1:5 mixtures of ammonia (28%), hydrogen peroxide (30%), and high-purity water, at 60 °C for 10 min. Subsequently, the chip was thoroughly rinsed with high-purity water and ethanol, and then dried under a steady stream of N_2 gas for further use.

Enzymatic Degradation

Detailed information of QCM-D measurements technique can be found elsewhere.^{25–28} Briefly, the mass of a thin layer on quartz crystal is related to the resonant frequency of the crystal and the viscoelastic properties of the additional layer influences the dissipation of the crystal. The changes in the frequency (Δf) and dissipation (ΔD) afford information about the mass variation and structural change of the film.

The dimethyl formamide (DMF) solution of PPCU was cast on the gold sensor chips and dried. The lipase PS solution (0.5 mg/mL) was streamed to the chip surfaces at a flow rate of $150 \mu\text{L/min}$, and deionized water was used as reference. The QCM-D experiments were performed at 25 °C. The increase of the oscillation frequency was indicative of the mass loss of the film on the QCM sensor surface. All the Δf and ΔD values were collected from the third overtone ($n = 3$). The values from the fundamental frequency were discarded because they were noise due to insufficient energy trapping.²⁹

Hydrolytic Degradation of PPCU in ASW

The neat PPCU coatings were prepared by solution casting. Glass slides ($25.4 \times 76.2 \text{ mm}$) were ultrasonically cleaned in acetone for 15 min and rinsed with deionized water. The DMF solution of PPCU (30 wt %) was cast on glass slides, and placed into a drying cabinet with ventilation for one day to evaporate the majority of DMF. Residual DMF was removed by vacuum drying for three days at 40 °C. The prepared coating samples were immersed in an ASW tank. ASW was renewed in every 2 weeks. In schedule times, the samples were taken out of ASW, rinsed by deionized water for three times and dried at 25 °C in a vacuum oven until constant weight (W_1) was gained. The initial weights of the samples were denoted as W_0 . Since the weight loss, ($W_0 - W_1$), was associated with the contact area, $[(W_0 - W_1)/\text{contact area}]$ was defined as the mass loss. Besides, the CA value was measured when the mass loss value was measured. For each sample, three coated panels were prepared and measured, and each data point was averaged over three successive and consistent measurements.

Release of DCOIT in ASW

A series of different concentrations of DCOIT in xylene solutions was examined by means of UV-Vis spectroscopy³⁰ and the results were presented in Figure 1. The maximum absorbance of the solution (A) in a certain range was proportional to the concentration of DCOIT (c). The samples were prepared in the same way as the above processing showed in the hydrolytic degradation of PPCU part. The only difference was that all the coatings contained 10 wt % of DCOIT in them. The samples were immersed in individual ASW tanks (50 mL). In schedule times, the samples were taken off and the residual DCOIT on the sample surface were rinsed by

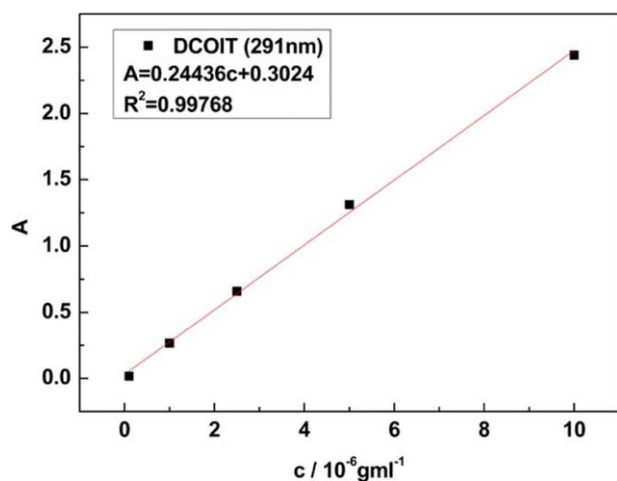


Figure 1. Effect of concentration (c) of DCOIT in xylene solution on standard absorbance (A) curve. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

deionized water for three times. The DCOIT was extracted by 20 mL of xylene for each aqueous solution and analyzed by UV-Vis spectroscopy. The concentration value of DCOIT was calculated by the equation: $A = 0.22436c + 0.03024$. Thus, the release rate of DCOIT in PPCU coatings could be gained.

Biofouling Test

The field biofouling tests were conducted for 134 days in the seawater (Zhoushan Bay, China) which had an average temperature of 22.9 °C with a maximum of 26.0 °C and a minimum of 17.3 °C. The salinity ranges from 20.8% to 24.8%, and the pH is from 7.96 to 8.14. The glass fiber reinforced epoxy resin panels (200 × 100 × 3 mm) were used as substrates after being rubbed with sandpapers. The coating was painted on each panel by a paintbrush to gain a film (about 400 μm in thickness). The coating samples were placed into seawater at a depth of 1.5 m. After a certain period of time, the panels were taken out of the sea, softly washed with seawater and photographed (120 × 90 mm of each panel in the photos were

Table I. GPC Results for the Prepared PPCUs under Different Reaction Times

Sample	Time/h	M_n (k)	M_w (k)	PDI ^a
PPCU-1	0.5	4.5	12.2	2.71
PPCU-2	1	8.6	17.8	2.09
PPCU-3	4	9.7	29.6	3.05
PPCU-4	8	10.3	43.0	4.27
PPCU-5	12	12.1	52.8	4.37

^aPolydispersity index (M_w/M_n).

used to avoid the influence caused by the bracket), and then placed back into the sea to continue the test.

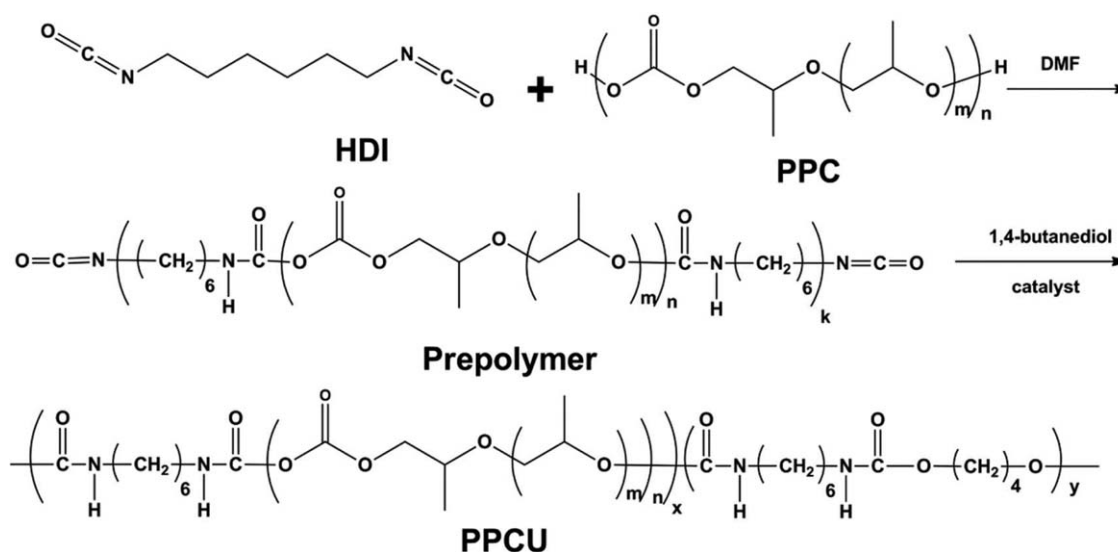
Algae Settlement Assay

Chlorella settlement assays were conducted with the glass fiber reinforced epoxy resin panels (20 × 20 × 3 mm) painted with prepared coatings. First, each sample was immersed in the tank filled with 100 mL of ASW and 100 mL of algae culture suspension separately. The cell density of culture suspension of Chlorella was approximately 3×10^7 cells mL⁻¹, and each treatment was repeated in triplicate. Then, the algae were left to statically settle for 7 days in a biochemical incubator. The culture was maintained at 22 °C under 25–37.5 μmol photons PAR m⁻² s⁻¹ of cool white fluorescent light under a 12 h light:12 h dark photoperiod. Finally, all the samples were rinsed by dipping into a new beaker of ASW for three times to remove the unattached Chlorella and set in a 2% glutaraldehyde seawater mixture for 15 min before sequential washing by ASW, 50% ASW, and distilled water.³¹ The quantity of algae was acquired through the CLSM analysis system. The fluorescence microscopy images of algae attached on the sample surfaces were recorded in 10 random fields of view per 0.16 mm² area on each sample.

RESULTS AND DISCUSSION

Synthesis of PPCU Polymer from PPC

HDI and PPC were mixed in 100 mL of DMF in a 500 mL necked flask equipped with a mechanical stirrer. The reaction was carried



Scheme 1. Synthetic route for PPCU from HDI, PPC and 1,4-butanediol.

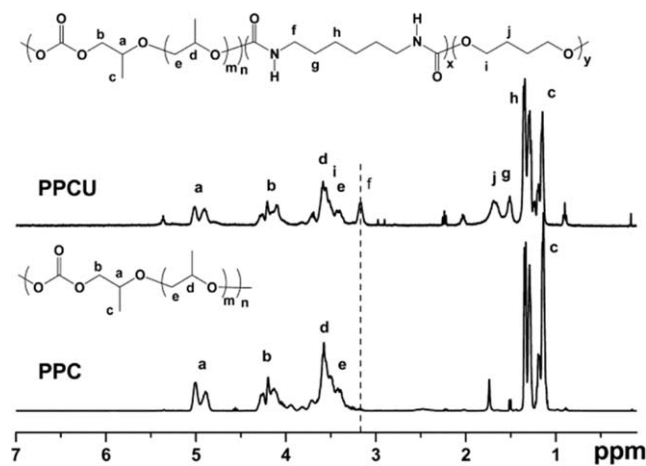


Figure 2. ^1H NMR spectra of PPCU and PPC.

out at 80°C for 1 h to prepare prepolymer. 1,4-butanediol and stannous octoate were mixed and added dropwise to the reaction mixture after cooling to ambient temperature. The molar ratio of the HDI, PPC, and 1,4-butanediol was 2:1:1, and the addition of the stannous octoate was 0.3% wt of total weight. The viscosity of reaction mixture increased as the polymerization proceeded. We prepared a series of polymerization products by controlling the reaction times from 0.5 h to 12 h, and the polymerization products were twice precipitated into water, filtered, and dried under vacuum at 50°C for 24 h. The molecular weights of the PPCUs were measured by gel permeation chromatography (GPC). A series of polyurethanes with different molecular weights (PPCU-1, PPCU-2, PPCU-3, PPCU-4, and PPCU-5) were obtained (Table I). ^1H NMR (400 MHz, CDCl_3 , δ): 5.1–4.8 [$\text{CH}_2\text{CH}(\text{CH}_3)\text{OCO}$ of PPC], 4.4–4.0 [$\text{CH}_2\text{CH}(\text{CH}_3)\text{OCO}$ of PPC], 3.6–3.4 [$\text{OCOCH}_2\text{CH}(\text{CH}_3)\text{O}$ of PPC, CH_2O], 3.17 (OCNHCH_2), 1.6 ($\text{CH}_2\text{CH}_2\text{O}$), 1.5 ($\text{OCNHCH}_2\text{CH}_2$), 1.4–1.05 (CH_3 of PPC, $\text{OCNHCH}_2\text{CH}_2\text{CH}_2$).

The synthetic route for PPCU was presented in Scheme 1. PPC diols were reacted with HDI to generate the prepolymer, and then 1,4-butanediol was used for chain extension to yield PPCU. The ^1H NMR spectra of PPC and PPCU were showed in

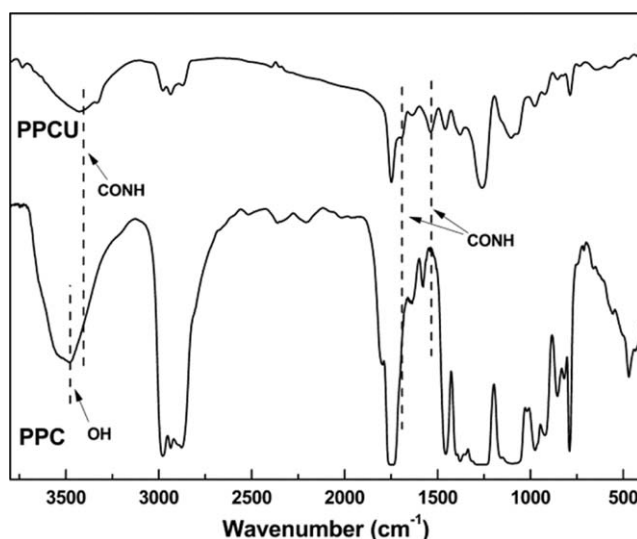


Figure 3. FTIR spectra of PPCU and PPC.

Figure 2 to make comparison. New signals emerged at 3.17 and 1.5 ppm which could be ascribed to the CH_2 protons in the newly formed $\text{OCNHCH}_2\text{CH}_2$ moiety. The signal at 1.6 ppm corresponded to the CH_2 protons in the $\text{CH}_2\text{CH}_2\text{O}$ moiety originally belonging to 1,4-butanediol. FTIR spectra of PPC and PPCU were displayed in Figure 3. It was seen that the band corresponding to the PPC's terminal OH bonds at 3480 cm^{-1} disappeared, and new bands corresponding to the NH and NHCO bonds appeared at 3428 and 1536 cm^{-1} , respectively.^{32–35} GPC results were summarized in Table I. The molecular weight of PPCU increased gradually with step polymerization time. In 12 h, the M_n reached to 12,100 g/mol. These results above indicated that PPCU was successfully prepared.

QCM-D Analysis

In the ocean, microorganisms can degrade the polymer chain with their enzymes.^{22,36} Herein, lipase PS was employed to degrade the PPCUs and QCM-D measurement was utilized to monitor the process. Figure 4 presented the time dependence of

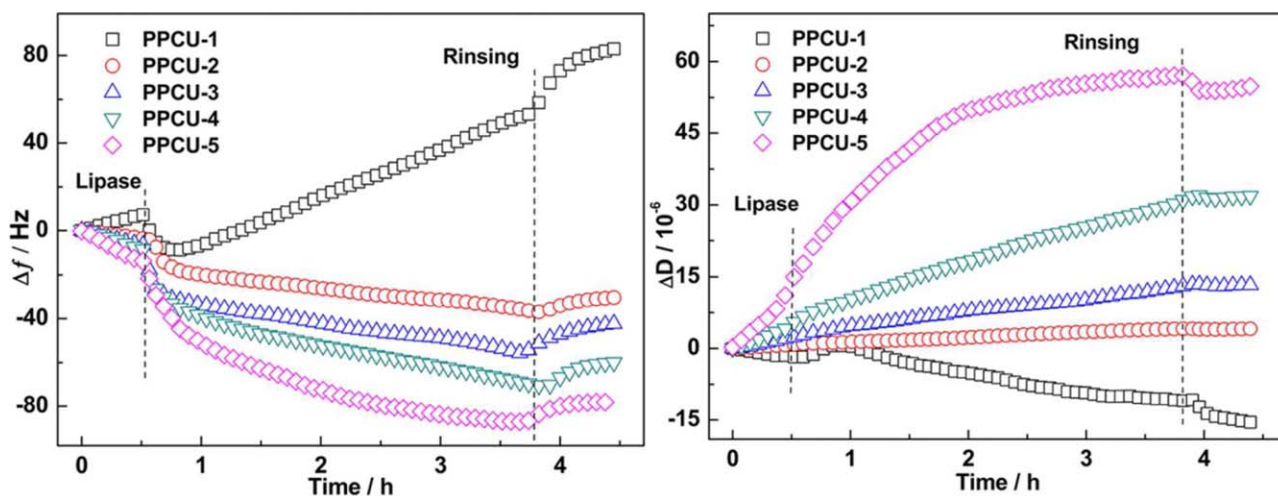


Figure 4. Time dependence of the frequency shift (Δf) and the energy dissipation shift (ΔD) for the enzymatic degradation of PPCUs in artificial seawater at 25°C . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

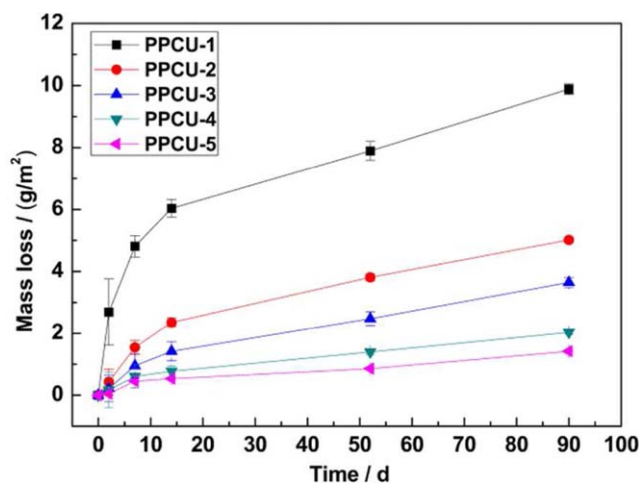


Figure 5. Time dependence of mass loss of PPCU coatings in ASW at 25 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Δf and ΔD for enzymatic degradation of PPCUs with different molecular weights. It has been known that Δf decreases and ΔD increases with the increase of mass on the sensor surface.^{25,28,37} Hence, if the polyurethane film well degrades into small molecules and disperses into the solution, an increase of Δf will be observed.

In the initial 30 min, before the lipase PS was added, for PPCU-1, a small increase of Δf was seen, which may be caused by the dispersion of some polymer chains with lower molecular weight into water or the slight hydrolytic degradation. After the addition of the lipase PS, Δf first decreased probably due to the absorption of the lipase PS on the film surface, and then, Δf started to increase, implying that the degradation occurred. In contrast, in the initial 30 min, for the samples, PPCU-2 to PPCU-5, Δf decreased. It was speculated that the water absorption rate of the polyurethane is initially faster than the degradation rate. After the addition of the lipase PS, for the samples, PPCU-2 to PPCU-5,

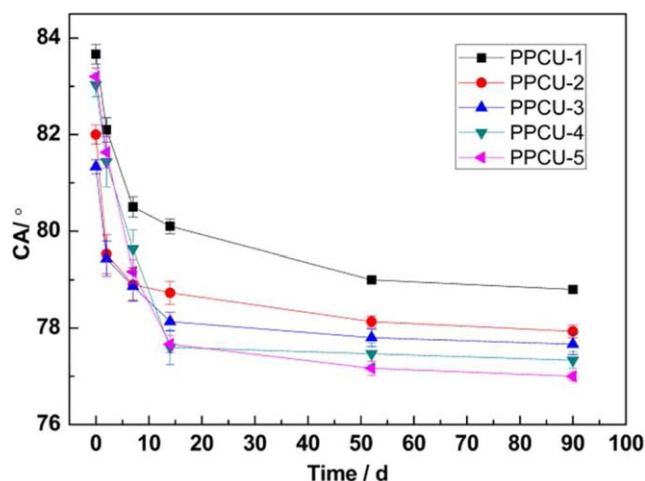


Figure 6. Time dependence of the CA of PPCU coatings in ASW at 25 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

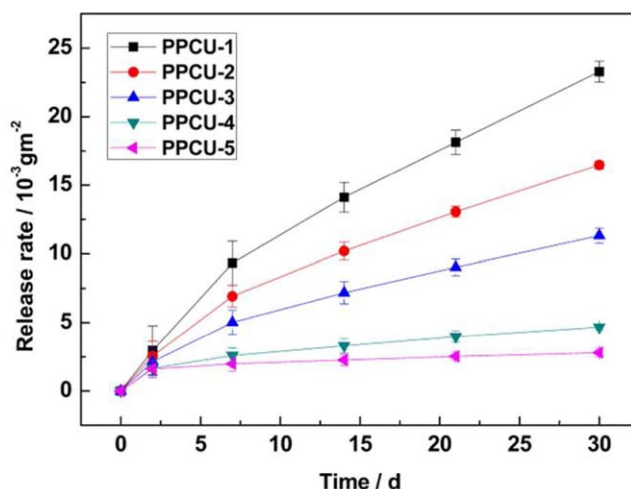


Figure 7. Time dependence of the release of DCOIT in PPCU coatings in ASW at 25 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Δf first decreased a little rapidly and then decreased slowly. It was explained that the mass increase rate of water and lipase absorption was higher than the mass loss rate of hydrolytic and enzymatic degradation. It can be found that the slope of the frequency of each sample is increased with time for a different speed. The sample PPCU-1 shows the slightest increase of slope, while the sample PPCU-5 shows the highest. It means that, for the polyurethane, the attack of enzyme helped improving the enzymatic degradation and a higher molecular weight leads to a higher improvement. In a recent study, polyurethane with poly(ϵ -caprolactone)(PCL) segments in the main chain showed a better enzymatic degradation rate with the help of lipase PS.³⁸

Generally, ΔD increases with the thickness but decreases with the rigidity of a layer. A dense and rigid structure results in a small dissipation of energy, while an incompact and supple structure leads to a large dissipation. For PPCU-1, the degradation dominated and the film thickness reduced resulting in a decrease in ΔD . For PPCU-2 to PPCU-5, water absorption led to a supple film and thus an increase in ΔD .

Hydrolytic Degradation Analysis

Hydrolytic degradation experiments were carried out in ASW at 25 °C. Figure 5 showed the degradation behavior for PPCU-1, PPCU-2, PPCU-3, PPCU-4, and PPCU-5. In the initial 14 days, all the coating samples lost weight fast probably due to the dispersion of lower molecular weight polymers into water. As immersion time went by, the degradation rate became steady. The mass loss dates of the 14th day (M_1) and 90th day (M_2) of the samples were calculated according to the formula $v = (M_2 - M_1)/(90 - 14)$ and the values of the constant hydrolysis rates were measured in the range 0.012–0.051 g/(m²d). Samples of lower molecular weight exhibited higher mass loss rate, implying that mass loss rate could be controlled by varying the molecular weight. This is significant for design of marine antibiofouling coating. As it is reported, the surface hydrophilicity can be improved due to the carboxyl or alcohol end groups generated by the hydrolysis of the polymer.³⁹ Figure 6 revealed that after

Table II. Compositions of Antifouling Coating Samples, S1–S10

	S1	S2	S3	S4	S5	S6	S7	S8	S9 ^a	S10
Polymer	PPCU-1	PPCU-2	PPCU-3	PPCU-4	PPCU-5	PPCU-5	PPCU-5	PPCU-5	PPCU-5	PPCU-5
DCOIT/wt %	10	10	10	10	10	0	1	5	10	20
Adhesion strength/MPa	4.05	4.54	4.68	4.70	4.66	4.87	4.62	4.70	4.66	4.58

^aThe S9 was the same with the S5, we marked "S9" here instead of "S5" for the sake of convenience in writing.

immersion in ASW, the CA for each sample gradually decreased and finally leveled off after 14 days. Moreover, the final CA decreases as the molecular weight increased from PPCU-1 to PPCU-5 which may be influenced by the degradation rate of the samples.

Release Test Analysis

Figure 7 showed the results of the release rate of DCOIT in PPCU coatings in ASW at 25 °C. In the first 7 days, a higher release rate of DCOIT could be found for each sample probably due to the dispersion of lower molecular weight polymers together with the DCOIT into water. Then, the release rate of each sample came to a constant numerical value as the immersion time went by. Appa-

rently, the release rate of the coating was increased as the molecular weight decreased from PPCU-5 to PPCU-1.

Biofouling Test Analysis

The PPCU was dissolved into DMF and mixed with the antifoulant, DCOIT. Coatings 1–5 were composed of PPCU-1, PPCU-2, PPCU-3, PPCU-4, and PPCU-5, respectively, and 10 wt % of DCOIT. Coatings 6–10 were composed of PPCU-5, and 0%, 1%, 5%, 10%, and 20% of DCOIT, respectively. All samples were immersed in the sea after drying. Three measurements were carried out for each sample. The samples were signed as S1–S10 together with the adhesion strength results showed in Table II. The results revealed that the peel strength between the PPCU

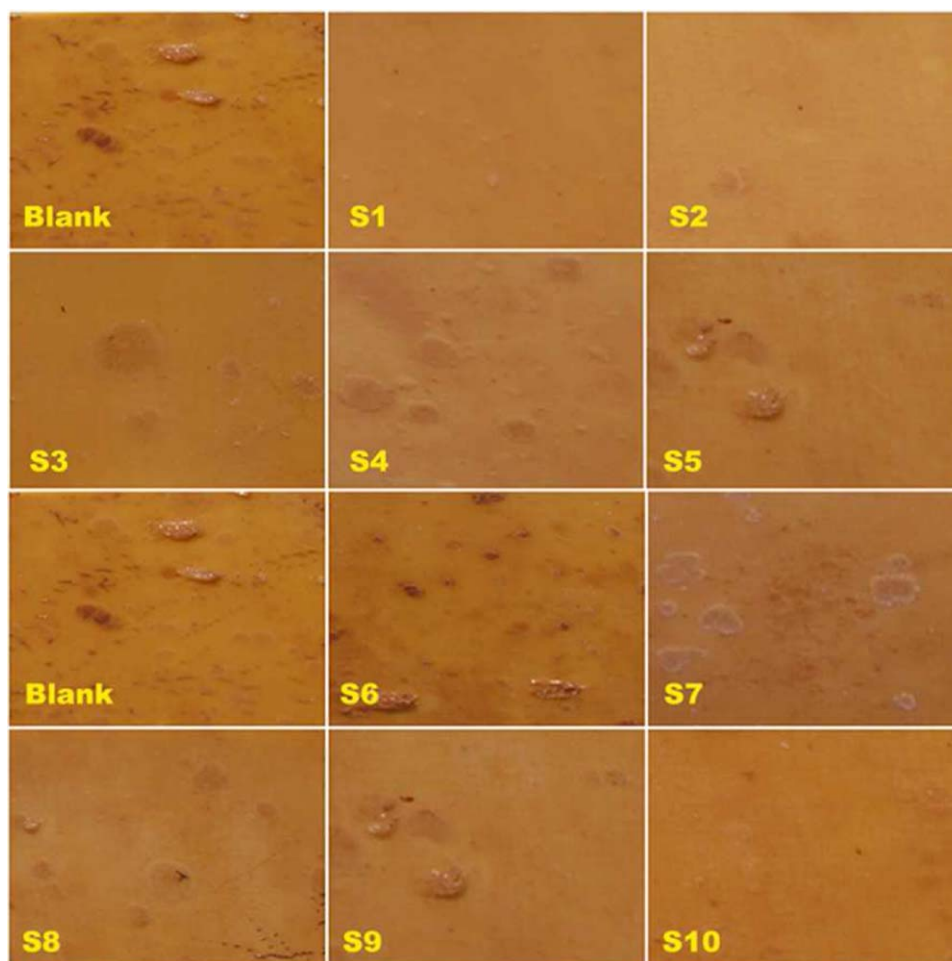


Figure 8. Pictures of field-tested coatings with PPCUs of different molecular weight and DCOIT of different contents (132 days, Zhoushan, China). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

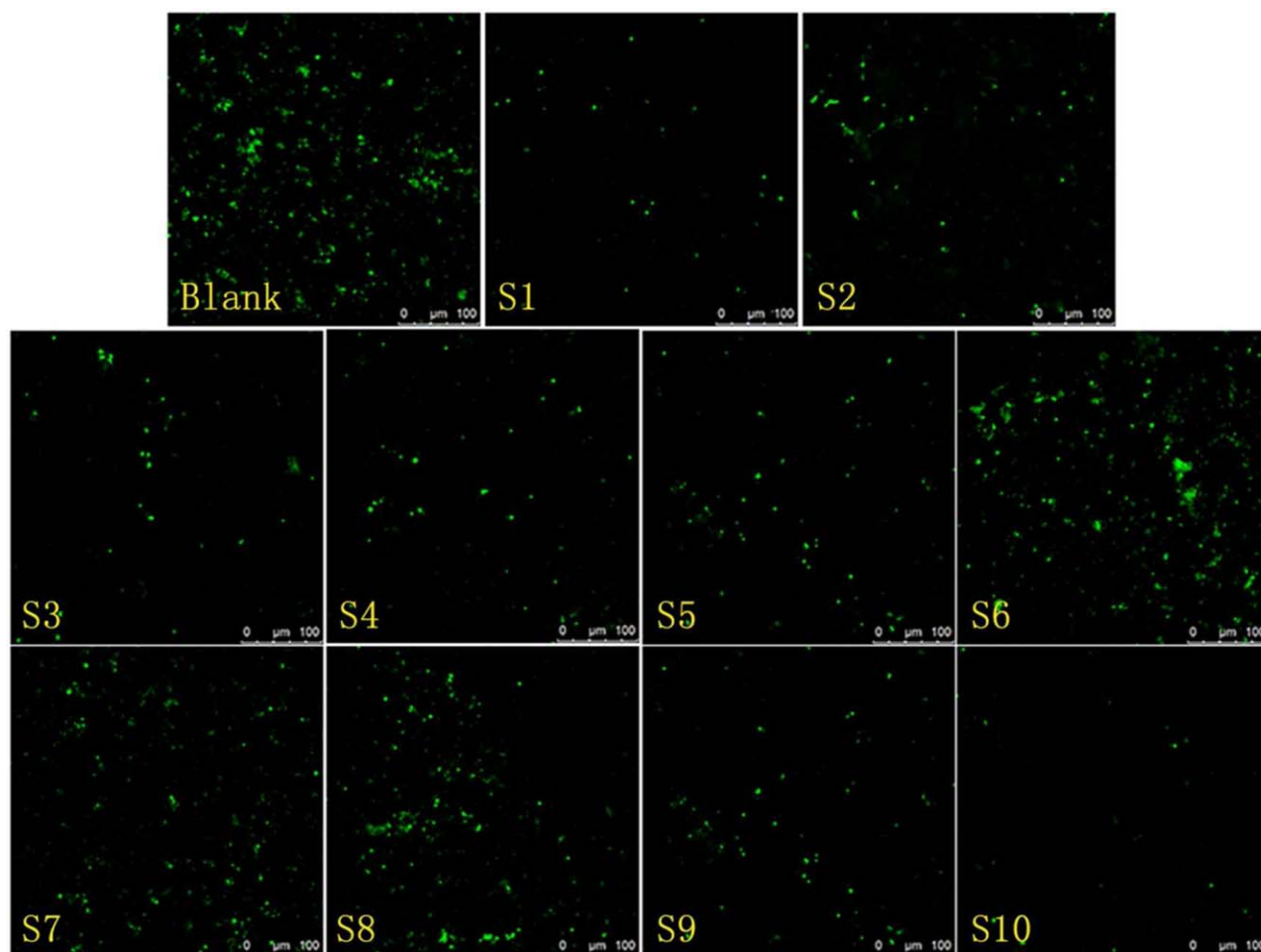


Figure 9. Fluorescent images of Chlorella settled on the PPCU coatings for 7 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

coatings and epoxy resin panels were all above 4 MPa and fracture occurred at the epoxy resin panels.

Figure 8 displayed the antifouling performances of drug-loaded coatings. For panels with no coating, juvenile barnacles and other organisms already existed on the surface. For panels

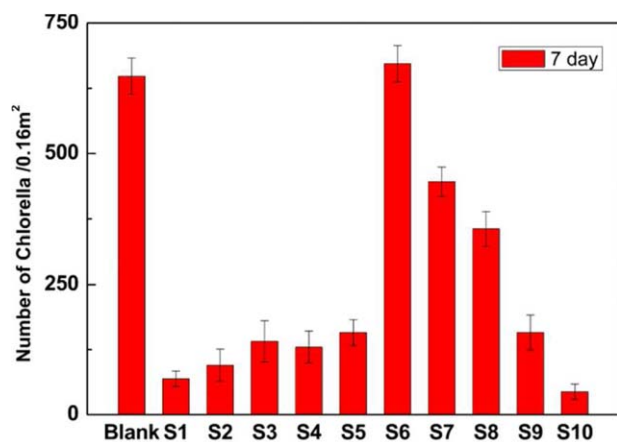


Figure 10. Chlorella adhesion data on different samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with 10 wt % of DCOIT, less barnacles and organisms colonized. As reported before, degradable polymer can form self-renewal surface, which polishes out the attached marine organisms if the polishing is faster than the attachment and growth of marine organisms.²¹ For the panels coated with PPCU/DCOIT, as the molecular weight decreases from S5 to S1, the surface became less fouled. This is due to the degradation rate increases as the molecular weight decreased which was in accordance with the hydrolytic degradation experiment discussed above. Coatings made with PPCU-5 and DCOIT of different contents from 0 to 20 wt %, S6 to S10, were also prepared. S10 showed the best anti-biofouling property that there is almost no marine organism on it. In comparison, the polyurethane with a biodegradable PCL main chain and hydrolyzable PTIPSA side chains also showed a similar anti-fouling performance.⁴⁰

Algae Settlement Assay Analysis

Figure 9 and 10 revealed the adhesion amount of attached Chlorella on different samples after 7 days. It could be found that, after Chlorella settlement for 7 days, except the amount of algae adhered on the S6 was a little higher than that of the blank sample all other samples had positive influence on the

anti-Chlorella ability. This is due to the fact that the degradation of the PPCU coating affects the Chlorella's attachment to the coating surface. Apparently, a similar trend could be observed in the experiment. At first, the amount of algae decreased from S5 to S1 gradually indicating that lower molecular weight polyurethane performed better anti-Chlorella ability. Moreover, the antifoulant, DCOIT, played a very important role in the anti-Chlorella ability and the S10 showed the best antifouling property.

CONCLUSIONS

Degradable PPCU polymers were obtained by reaction of isocyanate-terminated PPC prepolymers with 1,4-butanediol as chain extender. The chemical structure and molecular weight were determined by means of ^1H NMR spectroscopy, and GPC, respectively. Both enzymatic degradation and hydrolytic degradation proved that PPCU with smaller molecular weight degraded faster. The biofouling field test indicated that the degradable PPCU could act as self-polishing resins to get rid of attached organisms, and the addition of DCOIT could significantly enhance the coatings' antifouling performance. The best antifouling performance was achieved by the PPCU of $M_n = 4500$ g/mol, probably because it possessed the highest degradation rate and release rate. According to the above data, it is speculated that the lifetime of the coating with the best performance is about 6 months or longer. In conclusion, the degradation rate of the PPCU which is vital for antifouling performance is closely related to its molecular weight, a lower molecular weight leads to a higher degradation and antifoulant release rate and a better antifouling performance.

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