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14. ABSTRACT This grant from ONR to Zwitter Technology, LLC is to develop, scale up and formulate a low-fouling and high-fouling-release marine coating by integrating nonfouling zwitterionic materials and fouling-release silicone materials together. This work facilitates the efforts to develop next-generation marine coatings exceeding the performance of existing commercial coatings. It serves to meet the long-term goal of the ONR coatings program for the development of environmentally benign, effective and long-lasting marine coatings.					
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Program Objective

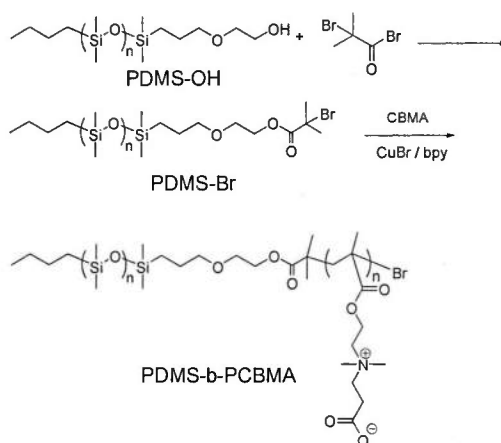
This grant from ONR to Zwitter Technology, LLC is to develop, scale up and formulate a low-fouling and high-fouling-release marine coating by integrating nonfouling zwitterionic materials and fouling-release silicone materials together. This work facilitates the efforts to develop next-generation marine coatings exceeding the performance of existing commercial coatings. It serves to meet the long-term goal of the ONR coatings program for the development of environmentally benign, effective and long-lasting marine coatings.

Work progress and significant events by task

1. Synthesis of zwitterions modified PDMS.

Controlled/Living radical polymerization is well established method to make block copolymers. Among several Controlled/Living radical polymerization techniques, Atom Transfer Radical Polymerization (ATRP) is most commonly used method. With the support of previous SBIR project, an ATRP protocol for the synthesis of the PDMS-PCBMA block copolymer (see Scheme 1) has been well established.

In this work, a similar procedure has been used, but large scale synthesis was preformed. Below are synthesis details.



Scheme 1: The syntheses of the PDMS-PCB block copolymer via ATRP.

Synthesis of PDMS-based macro ATRP initiator

In order to produce PDMS-b-PCBMA diblock copolymers using ATRP method, the PDMS-OH precursor need to be converted to an ATRP macroinitiator. In this step, PDMS-OH ($M_n = 5,000$, 200 g, 4 mmol) and 55.6 mL of TEA was dissolved in 1000 mL of anhydrous CHCl_3 in 2L round bottom flask. The flask was put in ice bath for 30 min. Then, 49.6 mL of α -Bromoisobutyryl bromide (BIBB) was drop added into the solution using addition funnel. The reaction was allowed to be conducted at 0 °C for 4 hours and subsequently at room temperature for overnight. The resulting PDMS-Br macro-ATRP initiator was purified by washing 5 times using excess ethanol, followed by vacuum dry at 60 °C for 6 hours.

Synthesis of diblock copolymer PDMS-b-PCBMA via ATRP

The ATRP polymerization of CBMA was conducted in the presence of PDMS-Br macro-initiator in the presence of CuBr and 2,2'-bipyridine (Bpy) in CHCl_3 /Methanol Mixture.

CBMA (114.5 g, 0.5 mol) and PDMS-Br (265.0 g, 50.0 mmol) were added along with CHCl₃/Methanol (250 mL/250 mL) mixture to an ampule. The ampule contents were sparged with nitrogen for 30 min. Then 50.0 mmol CuBr (7.15 g) and 100.0 mmol Bpy (15.6 g) in 200 mL degassed methanol was added into the ampule. Then the ampule was placed in a preheated oil bath at 60 °C. The reaction was terminated after 8 h by cooling the reaction tube in an ice bath followed by exposure to air. The resulting PDMS-PCBMA diblock copolymer was obtained by dialysis against DI water to remove copper, and then isolated by lyophilization.

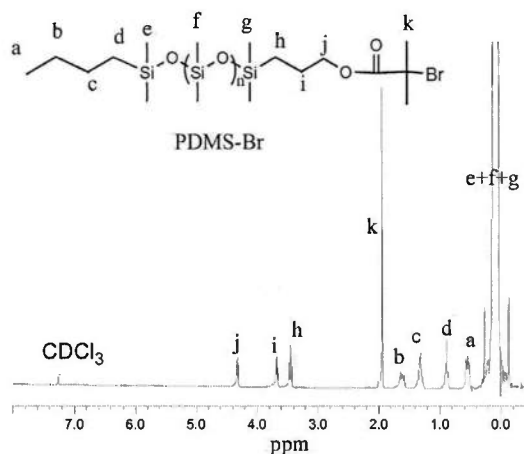


Figure 1: The ¹H NMR spectrum of the PDMS ATRP macroinitiator.

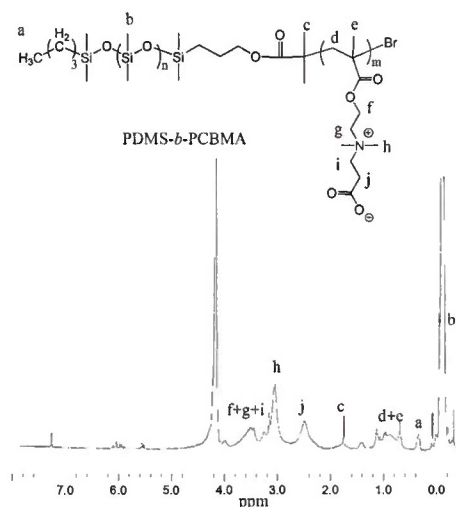


Figure 2: The ¹H NMR spectrum of the synthesized PDMS-PCBMA block copolymer.

In summary, under the support of this ONR grant, the synthesis of diblock copolymer was able to be scaled up, from previous 30 g scale to current 300 g scale. This ensured that enough panels can be prepared for field test.

2. Coating formulation.

Previous effort has been taken to incorporate the zwitterionic copolymer into the PDMS base coating system, and formulate the whole system into applicable marine coating. With the support of this grant, we are able to test even more coating parameters, including zwitterionic compound amount, pigment, crosslinker type and catalyst amount. The details are shown below,

1. PDMS coating with zwitterionic copolymer incorporated.

PDMS-PCBMA diblock copolymer (1 g, 3 g and 5 g, respectively) was dissolved into 45 grams toluene, 28 grams of PDMS base coating was then added together with 80 uL catalysts. Toluene was then removed by vacuum evaporation. The obtained viscous liquid was then mixed with 3 g PDMS crosslinker, and applied onto aluminum panels. The coating can be cured within 3.5 hours.

2. PDMS coating with pigment incorporated.

Various amount of the pigment cadmium sulfoselenide (1 g, 2 g, 3 g and 4 g, respectively) was added into 28 grams of PDMS base coating together with 80 uL catalysts. The mixture was stirred vigorously until all the solid were dispersed uniformly. The obtained viscous liquid was then mixed with 3 g PDMS crosslinker, and applied onto aluminum panels. The coating can be cured within 3 hours.

3. PDMS coating with different amount of catalyst incorporated.

5 grams of PDMS-PCBMA diblock copolymer and 28 grams of PDMS base coating was added into 45 grams toluene. The obtained viscous liquid was then mixed with 3 g PDMS crosslinker. Then various amount of catalyst, dioctyldilauryltin, (20 uL, 40 uL, 80 uL and 160 uL, respectively) was added. The mixture was stirred vigorously until all the solid were dispersed uniformly. The obtained viscous liquid was then coated on aluminum testing panels. The coating with 80 uL of catalyst can be cured within 2.5 hours.

Based on the above coating condition test, we have applied the various formulations onto epoxy (Intershield 300) coated alumina panels (4 × 8 inches), see below for detailed information.

Coating Formulations.

Formulation Code	Coating formulation
ZX151	Epoxy + Tie Coat + (PDMS + pigment + Block Copolymer1)
ZX152	Epoxy + Tie Coat + (PDMS + pigment + Block Copolymer 2)
ZX153	Epoxy + Tie Coat + (PDMS + pigment + Block Copolymer 3)
ZX154	Epoxy + Tie Coat + (PDMS + Block Copolymer 1)

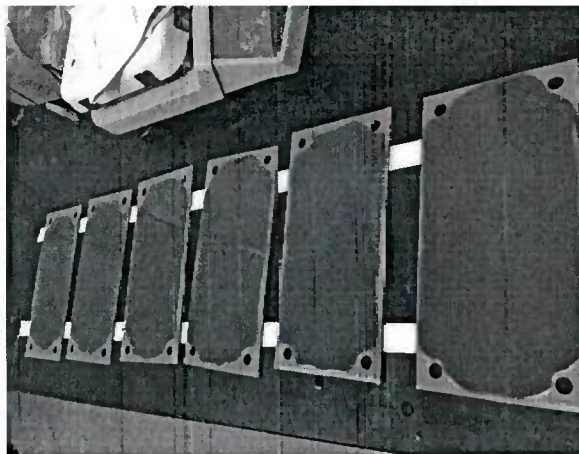


Figure 3. Aluminum panels coated by nonfouling and fouling-release zwitter/PDMS coatings.

3. Field Test.

Under the support of this grant, in Oct, 2015, 24 4"×8" panels (4 formulations; 3 panels per formulation) were provided to ZT's collaborated field test sites in Florida and Singapore. These panels are currently immersed in seawater for performance evaluation. The outcome will be utilized to identify optimal formulations through field test results.

Conclusions:

In conclusion, extensive work has been carried out to scale up the synthesis of PDMS-PCBMA diblock copolymer. The synthesis of large scale of copolymers was proved to be applicable which is important for making large quality coatings. These copolymers were mixed into PDMS base to formulate nonfouling and fouling-release marine coatings. By carefully adjusting various parameters (pigment, solvent, catalyst etc.), four formulations were developed to optimize the coating condition. These four formulations with various compositions are applied onto aluminum panels for field evaluation. Thus, this grant allows us to scale up the synthesis of PDMS-PCBMA diblock copolymer, to investigate several key parameters, to prepare panels for field tests and to move our coatings one step forward for practical applications.

Identification of any technical and/or programmatic issues

No issues; the project is going on well as planned.

Transition progress or updates to plan

No update to the plan.