



# Mimetic marine antifouling films based on fluorine-containing polymethacrylates



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## ABSTRACT

Novel methacrylate copolymers containing catechol and trifluoromethyl pendant side groups were synthesized by free radical polymerization of *N*-(3,4-dihydroxyphenyl)ethyl methacrylamide (DMA) and 2,2,2-trifluoroethyl methacrylate (TFME) with  $\alpha,\alpha'$ -azobisisobutyronitrile (AIBN) as initiator. A series of copolymers with different content of TFME ranging from 3% to 95% were obtained by changing the molar ratio of DMA to TFME from 25:1 to 1:25. Fourier transform infrared (FT-IR) spectroscopy, gel permeation chromatography (GPC), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) were used to characterize the copolymers, which displayed a certain degree of hardness and outstanding thermostability reflected from their high glass transition temperatures. The copolymers could adhere to surfaces of glass, plastics and metals due to introduction of catechol groups as multivalent hydrogen bonding anchors. Water contact angle on the polymer films was up to 117.4°. Chemicals resistance test manifested that the polymer films possessed excellent resistance to water, salt, acid and alkali. Moreover, the polymer films displayed fair antifouling property and might be used as promising environmentally friendly marine antifouling coatings.

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## 1. Introduction

Mankind has been fighting against biofouling for more than 2000 years. Biofouling arises from the undesirable attachment and colonization of marine organisms, plants, algae [1], or animals on surfaces submerged in seawater. Serious adverse impact from biofouling has been recognized including impairment of the operation efficiency of ships and other oceanographic equipments or instruments, increased fuel consumption, corrosion, emission of gases such as CO<sub>x</sub>, SO<sub>x</sub> and NO<sub>x</sub> into the atmosphere, and incursion of invasive species into marine habitats. Various approaches for the suppression of biofouling have been envisaged, including enzymatic degradation, sonication and chemical modification of the substrates. Although the self-polishing coatings based on tributyltin (TBT) or copper pyrithione are effective on removing or reducing biofouling over the last few decades because of slow release of tin, copper or other toxins in time, their use has been restricted through legislation due to environmental concerns. Subsequently, development of non-toxic and environmentally benign

antifouling coatings has become an attractive and challenging field and a main trend in marine industry. Enormous antifouling materials were developed to alter the physical and/or chemical properties of the surface in order to prevent the accumulation of the organisms on the substrates. To date zwitterionic polymers [2–5], biodegradable hydrophilic or amphiphilic polymers [6–8], bioinspired engineered topographies [9,10], (nano-structured) organic-inorganic hybrid systems [11–13], low surface energy elastomers specifically silicone or fluoropolymers [14,15], agricultural and natural products [16,17], and self-assembly of a low molecular weight peptide [18] have been used for preparation of antifouling coatings. Shark skin effect has also been highly valued for fabrication of biomimetic anti-biofouling coatings [19].

Poly(tetrafluoroethylene) (PTFE) is the benchmark low surface energy material but is far from efficient as antifouling material due to its low oil repellency and to its microcrystalline surface structure [20]. Therefore considerable research efforts have been directed toward the development of alternative low surface energy polymeric materials with good film-forming property. In this respect catechol 3,4-dihydroxyphenylalanine (DOPA), as one of the most important functionalities of adhesive proteins in mussels, has exerted a very important role because it can strongly adhere a wide variety of organic and inorganic solid surfaces including PTFE

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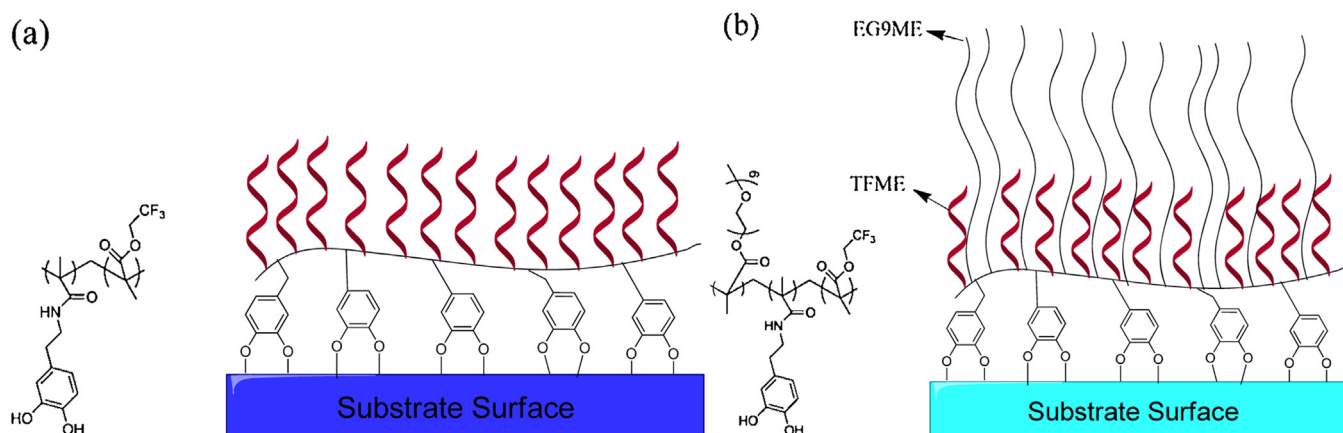


Fig. 1. Molecular structural model of copolymer (a) and ternary polymer (b).

surfaces and the adhesion properties are present even in water [21,22]. Owing to this high adhesion property in water, DOPA-functionalized poly(ethylene oxide) has been applied to antifouling surfaces in the biotechnology [4]. Messersmith and colleagues designed and synthesized DOPA-containing peptide-PEG conjugates for antifouling purposes, reasoning that DOPA-containing peptides would provide robust and versatile anchors for the immobilization of antifouling polymers onto metal, metal oxide, and polymer surfaces [23,24]. Recently DOPA was used for deposition of antifouling coatings on stainless steel via catechol-amine reaction [25].

Herein, we report synthesis, characterization and property study on biodegradable copolymers containing both catechol groups able to anchor onto the substrates to form coatings and fluorinated alkyl chains to impart the surfaces of the copolymers with low surface free energy. Thus DMA was combined with TFME to produce a new type of antifouling copolymers poly(DMA-co-TFME) as showed in Fig. 1(a) and a ternary polymer poly(DMA-co-TFME-co-EG9ME) (DFE) by introduction of the third monomer poly(ethylene glycol) methyl ether methacrylate (EG9ME) as showed in Fig. 1(b). Different copolymers could be obtained by varying the feed ratio of DMA to TFME. Specifically, the antifouling polymers described here not only can be designed to promote adhesion between two dissimilar surfaces, they can also be designed to prevent adhesion of undesirable particles, i.e. cells, proteins, and bacteria. For example, a high DMA content may be required for a coating that promotes adhesion, as enough DMA is needed to coat the support substrates as well as to promote adhesion to a second substrate. On the other hand, a lower DMA content may be needed for an antifouling coating since excessive DMA could promote unwanted adhesion. In this work the starting materials are inexpensive and the polymers containing short fluorinated alkyl chains are easy to degrade.

## 2. Experimental

### 2.1. Materials

Methacryloyl chloride (AR), 2,2,2-trifluoroethanol (AR) and poly(ethylene glycol) methyl ether methacrylate (EG9ME,  $M_n \sim 475$ ) were purchased from Shanghai Energy Chemicals Co., Ltd. and were used as received. Dopamine hydrochloride was obtained from Beijing HWRK Chemical Co., Ltd. Triethylamine (AR), methacrylic acid (AR), 4-dimethylaminopyridine (DMAP, AR), thionyl chloride (AR), phenothiazine (AR) and other reagents were supplied by China National Pharmaceutical Group Chemical Reagent co., Ltd. AIBN (AR) was purchased from Aldrich and was

used after purification by recrystallization in ethanol. Methanol and *N,N*-dimethylformamide (DMF) were dried over CaH<sub>2</sub> and distilled just prior to use. Other reagents and solvents obtained from commercial suppliers were used without further purification.

### 2.2. Instrumentation and characterization

FT-IR spectra were collected on an Avatar 380 spectrophotometer with a computer running PE-Spectrum v5.3 software. Liquid samples were presented on KBr disks and solid samples were mixed with KBr pellets to give a tablet. Then 32 scans were recorded over the range 4000–400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> at intervals of 1 cm<sup>-1</sup>.

Nuclear magnetic resonance (NMR) spectra were measured on a Bruker Avance-400 spectrometer with tetramethylsilane (TMS) as an internal reference (*s*=singlet, *d*=doublet, *t*=triplet, *m*=multiplet, *br*=broad). The chemical shifts are reported on the ppm scale for <sup>1</sup>H NMR with a resonance frequency of 400 MHz.

GPC results were obtained on a Waters BI-MWA instrument with tetrahydrofuran (THF) or DMF as eluent at a flow rate of 1 mL min<sup>-1</sup> using polystyrene as a standard. Samples of polymer DF25-1 were dissolved in THF while those of other polymers (DF1-1, DF1-2.5 and DF3-1) were dissolved in DMF.

TGA was carried out by NETZSCH TG209F1. Samples (no more than 5.0 mg) in ceramic crucible were heated from room temperature to 900 °C with a heating rate of 10 K min<sup>-1</sup> under a nitrogen atmosphere (flow rate: 40 mL min<sup>-1</sup>). All analyses were repeated to ensure consistency.

DSC was performed on NETZSCH DSC204F1 under a nitrogen atmosphere (flow rate: 20 mL min<sup>-1</sup>). Samples (no more than 5.0 mg) in hermetically-sealed aluminium pans were heated at 10 K min<sup>-1</sup> from room temperature to 200 °C just below the degradation temperature of the sample (previously determined by TGA).

SEM images were obtained on a TM-1000 with Hitachi desktop scanning electron microscope at 15 kV.

Contact angle measurements were carried out on DSA30 contact angle goniometer (polymers drop-casted from ethyl acetate (EtOAc) solution onto a glass surface, triplicates for each sample with standard variation below 5%, static contact angle of deionized water against the surfaces). Deionized water was chosen as testing liquid because advancing water contact angle analysis is a rapid and convenient means of determining if a coating was successfully applied. Contact angle values of the polymer films were determined at 25 °C by using a goniometer interfaced to image capture software via injecting a 3 μL drop of the test liquid onto the surface. The contact angle values were then quantified using image analysis software Image. The average contact angle value for each

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