Amphiphilic polymer based on fluoroalkyl and PEG side chains for fouling release coating

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Abstract. Under static conditions, fouling release coating could not express good release property to marine organisms. Amphiphilic polymer with mixture of fluorinated monomer and short side group of polyethylene glycol (PEG) was synthesized. And also we studied the ability of amphiphilic polymer to influence the surface properties and how it controlled the adhesion of marine organisms to coated surfaces. By incorporating fluorinated monomer and PEG side chain into the polymer, the effect of incorporating both polar and non-polar groups on fouling-release coating could be studied. The dry surface was characterized by three-dimensional digital microscopy and scanning electron microscopy (SEM), and the morphology of the amphiphilic fouling release coating showed just like flaky petal. The amphiphilic polymer in fouling release coating tended to reconstruct in water, and the ability was examined by static contact angle, which was smaller than the PDMS (polymethylsiloxane) fouling release coating. Also surface energy was calculated by three solvents, and surface energy of amphiphilic fouling release coating was higher than that of the PDMS fouling release coating. To understand more about its fouling release property, seawater exposure method was adopted in gulf of Qingdao port. Fewer diatoms Navicula were found in biofilm after using amphiphilic fouling release coating. In general, coating containing both PEG and fluorinated side chain possessed certain fouling release property.

1. Introduction
During operation, marine biofouling, defined as microbial slimes [1,2], plants [3] and invertebrates [4] onto submerged materials bring huge security risks and economic loss to shipping, aquaculture and ocean engineering. Accumulation of marine organisms accelerate corrosion [5] of ships, also they increase in roughness and frictional drag [6] leading to substantial powering penalties. Marine organisms block culture cages and cooling water pipes, also they could weaken detection performance of sonar and action of naval vessels. So it was estimated that hundreds of billions of dollars was used to conquer marine organisms in the world annually [7], also the invasion by exotic marine species is one of the most irreversible environmental problems facing this habitat. The exotic marine species have produced a great deal of negative impacts on the marine ecosystem [8]. They compete or mate with native species, introduce pathogens and toxic algae that will directly or indirectly damage the marine ecosystem. And to date, the most effective method of marine biofouling control has been the use of biocidal antifouling paints [9], but most of biocides are forbidden by severe environmental protection laws and regulations [10,11]. Thus, in recent years, there is considerable interest in developing environmental-friendly antifouling/fouling release coatings [12]. For instance, polymethyl siloxane (PDMS) fouling release coating (usually referred to as FR coating) is biocides-free, not contaminated
the marine environment and easy cleansed of marine organisms, which has been considered as a potential substitute of biocidal antifouling paints. But this material is easily stained at port or with a low speed of ship; also it could not suffer the adhesion of slime with diatom and bacteria [13], while the evolution process of slime is essential to formation of mature communities. And the performance deficiency limited application of this type of coating.

Much work [14,15] has been done to improve properties (such as resistance to slime) of FR coating on resting or at low speed ship. As we know, fluorinated polymers express outstanding capability in low friction and low surface energy. And in the formation of the layer, fluoroalkyl side chains enrich in the surface of coating, which reduces its surface energy and enhances detachment to marine organisms [16,17]. And also it is reported that coating with PEG (polyethylene glycol) segments offer good inhibition to protein [18,19]. Hydrophilic polymer chains can bond abundant water molecule and form a hydration layer on surface. Protein, biological glue and so on should first overcome energy barrier of hydration layer and then touch to polymer matrix shown in figure 1 (The blue style offers hydrophilicity, while the red style offers hydrophobicity).

![Figure 1. Mechanism of amphiphilic fouling release coating to biofilm.](image)

As we know, some marine organisms prefer to adsorb on hydrophobic surface, but others such as diatom like hydrophilic interface. This paper focuses on amphiphilic polymer, and the amphiphilic polymer combines fluoroalkyl chains as hydrophobic segments and PEG side chains as hydrophilic segments. Fluoroalkyl chains and PEG segments migrate toward to the surface of coating at different speed in seawater, which reconstitute its interface. And this amphiphilic polymer can express blended property to marine organisms. In this paper, amphiphilic polymer with fluoroalkyl and PEG side chains was prepared and its properties were tested by Fourier transform infrared spectroscopy and gel permeation chromatography. FR coating constructed by amphiphilic polymer was obtained and its FR-property was checked at floating raft of Qingdao.

2. Experimental method and materials

2.1. Raw materials

Xylene and n-butyl alcohol were technical grade and were purchased from Qingdao Yongan Chemical Reagent Co., Ltd. (China). Azobisisobutyronitrile (AIBN) was laboratory grade and was obtained from Tianjin Damao Chemical Reagent Co., Ltd. (China). [3-(Methacryloyloxy)propyl]trimethoxysilane (A174) was technical grade and was bought from Momentive. Poly (ethylene glycol) acrylate (PEA6, CH₂CHCO (OCH₂CH₂)xOH, average Mn=336, x≈6) was technical grade and was got from Shanghai Polydex Industry Co., Ltd. (China). 1H, 1H,7H-Dodecafluoropropyl methacrylate (G04) was technical grade and was purchased from XEOGIA (China). Silanol-terminated polydimethylsiloxane was technical grade and was purchased from Dow Corning. Defoamer was technical grade and was obtained from BYK. Thixotropic agent R972 was technical grade and was
obtained from Evonik Degussa GmbH. Iron red was technical grade and was bought from yipin pigment in shanghai. Dibutyltin dilaurate was laboratory grade and was obtained from BASF. PDMS fouling release coating was obtained from State Key Laboratory of Marine Coatings.

2.2. Synthesis of amphiphilic polymer

Xylene and n-butyl alcohol (w/w 1:1) were poured into a four-neck round bottom flask with a thermometer, a Teflon stirrer and a water condenser pipe. The flask was expelled air by bubbling nitrogen and heated to 85°C. Then required quantities of A174, G04, PEA6, AIBN, xylene and n-butyl alcohol were mixed and dropped into the flask in 1 h, and the temperature was kept for 2 h after the addition. Then, some AIBN, xylene and n-butyl alcohol were introduced into the flask and the system temperature was maintained for 2 h. After that, reddish brown mixture was obtained. And the reaction scheme for the preparation of amphiphilic polymer was shown in figure 2.

![Figure 2. Synthetic route of amphiphilic polymer.](image)

The red style: hydrophilic segment, the blue style: hydrophobic segment

2.3. Preparation of amphiphilic fouling release coating

To obtain amphiphilic fouling release coating, three-component products were used. Part A required silanol-terminated polydimethylsiloxane, defoamer, thixotropic agent R972, xylene, iron red; all the substances were mixed and grind to 40 µm or below. Part B used amphiphilic polymer as the crosslinking agent also with some xylene, which made the fouling release coating amphipathic, while part C applied dibutyltin dilaurate and some xylene as a catalyst system. Amphiphilic fouling release coating was a mixture of the three-component products (w/w/w 10:2:1) and dried naturally for 24 h.

2.4. Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC) of Amphiphilic polymer

Reddish brown mixture was removed of solvents through rotary evaporator as much as possible, and then it was on the vacuum drying condition to be purified to get amphiphilic polymer concentrate. After that, amphiphilic polymer concentrate was painted over the KBr tablet evenly and carried out on AVATAR-380 Spectrophotometer (Thermo Nicolet Company) in the wavelength region 500-4000 cm⁻¹ at room temperature.

The number and average molecular weights of amphiphilic polymer, Mn and Mw, respectively, were determined by size exclusion chromatography on Waters 1515 gel permeation chromatograph (Waters Company, USA). Amphiphilic polymer was extracted by rotary evaporator, tetrahydrofuran was served as solvent. The differential refractive index detector was used at 40°C; the flow was slowly increased to 1 mL/min at a rate of 0.01 mL/min.

2.5. Contact angle and surface energy tests

Amphiphilic fouling release coating was pasted on pretreated tin plates with dimensions of 50 mmx120 mmx0.3 mm, and dried naturally. Water contact angle measurements [20] were conducted by the sessile drop method on an OCA 20 contact angle system (Dataphysics Instruments GmbH, Germany) at ambient temperature. After placing the panel with amphiphilic fouling release coating on
the horizontal workbench, a 3-μL droplet of distilled water was put on the surface using a syringe. Digital images of the droplet silhouette were captured with a charge-coupled device (CCD) camera and the contact angles were evaluated using the measuring angle method. Every database was obtained within 30 s after the droplet contacting with the film surface. For each sample, the average of three measurements was calculated. Surface energy [21] of amphiphilic fouling release coating was calculated through distilled water, ethylene glycol and cyclohexane.

2.6. Surface morphology of amphiphilic fouling release coating
Scanning electron microscope (SEM) images [22] were recorded with an electronic microscope HITACHI TM-1000 operating at 15 kv, solid state backscattered electron detector (BSE) was adopted for its detector. Amphiphilic fouling release coating (one layer, 70-100 μm) was pasted by air spraying and dried naturally on tin plates. Also surface morphology and advanced 3D digital observation were obtained on HIROX KH-7700 digital microscope by the way of progressive scan.

2.7. Seawater exposure methods
Low carbon steel panels were applied to substrates with the dimension of 350 mm×250 mm×3 mm. After surface treatment, the anti-corrosive primer, sealer coating, tie-coat and amphiphilic fouling release coating were coated on tested substrates in sequence. When the amphiphilic fouling release coating was hard-dry, test panels were immersed in shallow submergence [23,24] at a depth of one meter in Qingdao Port. Also the PDMS fouling release coating was employed as the blank. The gulf of Qingdao port has mature biomass and vigorous marine life, with the seawater flow less than 2 m/s. Observation by photographing was carried out to investigate fouling-resistance property of amphiphilic fouling release coating after two weeks.

3. Presentation and discussion of test results

3.1. Synthesis of Amphiphilic polymers
Amphiphilic polymers consisted of a block of PEG side chain and a block of fluoroalkyl side chain. In the structure of amphiphilic polymers [25,26], PEA6 acted as hydrophilic part while G04 gave hydrophobicity. This dual hydrophilic-hydrophobic nature provided an amphiphilic character to the material, and the amphiphilic fouling release coating derived therefrom were anticipated to respond to contact with water or seawater.
The amphiphilic polymers were synthesized by a free radical solution polymerization method [27], whereby AIBN was used as initiator. In order to get homogeneous system, xylene and n-butanol were used as the mixed solvents. The FTIR spectra of amphiphilic polymers showed peaks corresponding to the functional groups in the polymeric chains in figure 3: the observed strong peaks at 2870 cm\(^{-1}\) and 1109 cm\(^{-1}\), corresponding to Si-OMe stretching; 1724 cm\(^{-1}\), corresponding to the C=O of A174; 1636 cm\(^{-1}\) corresponding to the C=O of PEA6 and G04; 1296 cm\(^{-1}\) corresponding to the C-F stretching of G04; 1194 cm\(^{-1}\) corresponding to aliphatic ether C-O stretching of PEA6. Obvious C=C stretching was not found, which showed three monomers all contributed to the structure of amphiphilic polymer.

Accordingly, the number average molecular weight (Mn) and weight-average molecular weight (Mw) of amphiphilic polymer were 788 g/mol and 1597 g/mol, respectively. The polymer was monomodal and characterized by a polydispersity Mw/Mn≈1.97.

3.2. Static contact angles and surface energy

Surface energy [28] is closely related to bacterial attachment behavior. Low surface energy could reduce attachment of bacterial and microbial and enhance fouling release properties. The static contact angles of water (\(\theta_w\)), ethylene glycol (\(\theta_e\)) and cyclohexane (\(\theta_c\)) on amphiphilic fouling release coating were measured by the sessile drop technique. The measured values of \(\theta\) were then used to obtain the surface energy of the polymer films referring to the so-called Owens-Wendt-Kaelble approach [29]. This regards the surface energy as being composed of two or more additive components, the dispersion (\(\gamma^d\)) and the hydrogen bonding and dipole-dipole(\(\gamma^p\)) components (equation (1)), and the greater difference in solvent polarity, the more accurate the results obtained. A geometric mean relationship is postulated both of the solid-liquid and liquid-liquid interfacial tensions (equation (2)).

\[
\gamma = \gamma^d + \gamma^p \\
\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{0.5}
\]
Combination with the well-known Young’s equation leads to equation (3).

\[ \gamma_L(1+\cos \theta)=2\left[(\gamma_S^d \gamma_L^d)^{0.5}+(\gamma_S^p \gamma_L^p)^{0.5}\right] \]  

(3)

Where \( \gamma_S \) is the surface tension of the solid surface and \( \gamma_L \) is that of the wetting liquid. As there are two unknowns (\( \gamma_S^d \) and \( \gamma_S^p \)) of the solid surface, static contact angle of three different liquids with known \( \gamma_L^d \) and \( \gamma_L^p \) on the solid surface. After that, the surface energy of the amphiphilic fouling release coating was got through the three simultaneous equations.

Static contact angles of amphiphilic fouling release coating with three different solvents were tested; the average of three measurements for each solvent was showed in table 1, and also its surface energy. Blank referred to PDMS fouling release coating without graft modification using amphiphilic segment. By comparing the contact angle values of amphiphilic fouling release coating and the blank, all of them were smaller for amphiphilic fouling release coating than for the blank [30], and the difference was more pronounced for \( \theta_w \) than for the other two angles.

Table 1. Contact angles and surface energy for amphiphilic fouling release coating.

| Film type                             | \( \theta_w/^\circ \) | \( \theta_e/^\circ \) | \( \theta_c/^\circ \) | Surface energy/mJ·m\(^{-2} \) |
|---------------------------------------|------------------------|------------------------|------------------------|-----------------------------|
| amphiphilic fouling release coating   | 103.9                  | 85.9                   | 29.6                   | 21.39                       |
| blank                                 | 111.0                  | 88.9                   | 31.5                   | 21.24                       |

This suggested that the inclusion of fluoroalkyl and PEG chains in amphiphilic fouling release coating caused the top layer turned to be both hydrophobic and hydrophilic at the same time, especially in the hydrophilic character. This was a further confirmation of the preferential and selective segregation of the fluoroalkyl and PEG segment at the top layer–air interface. And the chemical incompatibility of fluoroalkyl and PEG segment lowered hydrophobic property. And hydrophilic segment dominated in the interaction of polar material to the coating.

Measurements of liquid-solid static contact angles are commonly used to evaluate solid surface energy. The Owens-Wendt-Kaelble approach was used to extract the surface energy for amphiphilic fouling release coating and the blank from experimental \( \theta \) values, and the results are shown in table 1. The surface energy of the blank (PDMS fouling release coating) was slightly lower than amphiphilic fouling release coating, which was due to the contribution of the PEG side chain permitted polar interaction with three solvents. And it also gave the occurrence of microphase separation of the incompatible blocks in the surface.

3.3. **Surface morphology of amphiphilic fouling release coating**

The use of the phase separation behavior of fluorinated polymer is well-suited to generate ordered, self-assembled, low surface energy materials. We used HIROX KH-7700 digital microscope to investigate the morphological features of amphiphilic fouling release coating in figure 4.

![Figure 4. Morphology of coatings with different magnification.](image)

The uniform and dense distributed pores are observed on the surface of amphiphilic fouling release coating.
coating (figure 4(a)), for the PEG side chain and fluoroalkyl segment could not merge in the silicone release coating system, tending to migrate out of the system. At figure 4(b), we could see the pore in the surface was regular circular at the magnification of 3500 times. Also we could get the actual size of the pore from figure 5.

![Figure 5. Size of pores for amphiphilic fouling release coating.](image)

Figure 5. Size of pores for amphiphilic fouling release coating.

The diameter of the circular hole was measured; most of them were within a few microns. The measured values obtained in figure 5(a) were from 1.9 μm to 4.8 μm. The depth of the pores was got from figure 5(b), the values of them were within a few microns, too.

SEM images on amphiphilic fouling release coating were showed in figure 6. Many micro- and nanosized pores appeared on the surface in figure 6(a). And by magnification of ten thousand times in figure 6(b), several flower-like shapes present in front. Fluoroalkyl and PEG side chain like slender petals were grafted in the fouling release coating, while some of them were straight and others were bending, which gave the microstructure construction on amphiphilic fouling release coating.

Seawater exposure methods were carried out lasting two weeks during a period of mature biofilms. After that, test board with amphiphilic fouling release coating was taken out of the seawater. And photos were taken about marine biofilm on testing board as shown in figure 7. The biofilm was transparent just like jell. And then, the biofilm was sampled from the test board. Biological microscope KH7700 (HIROX) was used to observe marine organisms in the biofilm.

![Figure 6. SEM images of amphiphilic fouling release coatings.](image)
Figure 7. Biofilms on test boards.

*Naviculaceae* in elliptical solid line on figure 8(a) belongs to *Bacillariophyceae*, and the shape of *Naviculaceae* is just like a boat. Comparing two pictures of figure 8, it could be said that fewer diatoms *Navicula* were seen in biofilm of amphiphilic fouling release coating than in biofilm on blank sample (PDMS fouling release coating). The same tendency was observed for species of *Chlorella*. It is obvious that amphiphilic fouling release coating had certain inhibition during initial stage of biofilm formation.

![Figure 8](image_url)

*Figure 8.* Biological community in biofilm of (a) amphiphilic fouling release coating and (b) PDMS fouling release coating.

### 4. Conclusions

Amphiphilic surface-active copolymers with fluroalkyl and PEG side chains were synthesized through the polymer modification reaction of a free radical solution polymerization method. The resultant polymer was characterized using FTIR spectra and gel permeation chromatography confirming the attachment of the hydrophobic fluoroalkyl segments and hydrophilic PEG side chains. The amphiphilic nature of the fouling release coating was characterized with static contact angle measurements and surface energy which suggested that the surface was highly populated with the functional side chains, that the PEG side chains migrated to the surface, and the fluoroalkyl chains became slightly buried. The seawater exposure method with immersed coating showed lower diatoms *Navicula* adsorption and confirmed that the hydrophilic PEG side chains and hydrophobic fluoroalkyl side chains migrated to the surface and substrate, respectively. The FR profile of amphiphilic fouling release coating was different from those of PDMS, which contained only PDMS side chains. The combination of fluoroalkyl and PEG chains at the coating surface offered potential advantages over conventional silicone-based FR coatings, which tend to perform poorly with respect to diatom fouling.

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