Synthesis and Characterization of a Novel Amphiphilic Copolymer Capable as Anti-Biofouling Coating Material

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ABSTRACT: A novel cross-linked copolymer containing hydrophobic perfluoropolyether and hydrophilic oligo(ethylene glycol) units was synthesized and characterized. The anti-biofouling properties of the fluoropolymer were evaluated by laboratory assays using the fouling diatom *Nitzschia* and bacteria *Staphylococcus aureus* and *Escherichia coli.* The results from the preliminary study showed that this fluorinated copolymer has promising anti-biofouling performance. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2071–2078, 2009

Key words: fluoropolymer; synthesis; radical polymerization; amphiphilic; anti-biofouling

INTRODUCTION

Marine biofouling is a worldwide problem costing billions of dollars per year due to the increased fuel consumption in transportation.[1] Marine biofouling is mainly caused by the accumulation of fouling organisms such as marine bacteria, diatoms, and green algae. Biofouling has been controlled traditionally through the use of antifouling paints, but today they have been restricted since these antifouling paints rely on leaching of toxic ingredients such as lead, arsenic, and organotin compounds into the surrounding water.[2] The resulting environmental concerns have led to a search for non-toxic alternatives. One approach is to reduce the use of poisonous paints by using low surface energy coating materials such as siloxane, fluoropolymers, and fluorosiloxanes. For example, poly(dimethyl siloxane) (PDMS) elastomers are widely used in commercial marine foul-release coatings because of their combination of properties such as low surface energies (22 mJ m^{-2}), low microroughness, and low modulus.[3] However, it is well known that marine biofilms dominated by diatoms can not release easily from PDMS-based fouling-release coatings.[4] Fluoropolymer-based fouling-release coatings showed a little better diatoms releasing performance comparing with PDMS, but their anti-biofouling properties need to be further improved to meet the needs of non-toxic antifouling control.

In recent years, to improve anti-biofouling performance of fluoropolymer-based coatings for both green algae and diatoms, a class of novel amphiphilic polymers composed of poly(ethylene glycol)(PEG) and perfluoroalkyl units[5,6] has been introduced because PEG-coated surfaces have protein repellency and fluoropolymer coated surfaces have very low surface energy.[7] Wooley found that amphiphilic surface coated by PEG cross-linked hyperbranched fluoropolymers showed a higher release of green algae compared to PDMS due to the occurrence of phase segregation of the fluoropolymer and PEG domains.[8] Ober and co-workers reported that surfaces coated with comblike block copolymers containing ethoxylated perfluoroalkyl side chains showed a high removal of both green algae and diatoms.[9] The high removal of diatoms from the amphiphilic surface was explained by the fact that the surface could reconstruct to become as hydrophilic as a PEGylated surface when immersed into water and that diatoms adhered weakly to hydrophilic surfaces. The combination of protein repellency of PEG[10–15] and hydrophobicity of perfluoroalkyl chain gives amphiphilic polymers unique anti-biofouling ability. To achieve significant low surface energy and hydrophobic character to the coating surface, a long perfluoroalkyl chain (C_nF_{2n+1},

$n \geq 8$) was used for the preparation of amphiphilic polymers. However, the degradation of polymers containing long perfluoroalkyl chains (C_nF_{2n+1}, $n \geq 8$) gives environmentally persistent perfluorooctanoic acid (PFOA) or perfluorooctanesulfonic acid (PFOS). It is stated by the US EPA that fluorinated compound containing perfluorocarbon chain (C_nF_{2n+1}, $n \geq 8$), especially PFOA and PFOS, can resist degradation, bioaccumulate in human and animal tissue and possess long biological half lives. Therefore, these materials are of concern to the public and some of the materials have accordingly been either banned or voluntarily withdrawn from the market.[16–18] More researchers presently have focused on developing environmentally benign and non-toxic fluorinated alternatives to traditional long perfluoroalkyl chain containing reagents. Recently, perfluoropolyethers (PTFE)-based polymers have attracted increasing attention for functional coatings due to their unique properties such as low surface energies, remarkable chemical resistance, and high thermal stabilities.[19] As the perfluoropolyether-based polymers are biodegradable and do not release perfluorooctanoic acid during the degradation, we think that the perfluoropolyether chain should be an ideal substituent for perfluoroalkyl chain in making hydrophobic coatings. In this article, we described the synthesis and characterization of a novel copolymer containing both PEG units and perfluoropolyether chains. The anti-biofouling properties of the resulting fluorinated copolymer were also investigated by laboratory assays.

EXPERIMENTAL

Materials

Hexafluoropropene oxide trimer, azo-bis-isobutyronitrile (AIBN), 4-vinylbenzyl chloride, sodium hydride, potassium acetate, dimethyl sulfoxide, ethyl acetate, nitrobenzene, sodium hydroxide, ethanol, triethylene glycol, triethylamine, benzene were used as purchased. N,N-Dimethylformamide and dichloromethane were distilled from CaH_2. Distilled water and hexadecane were used for the contact angle measurements.

Synthesis of monomers 3 and 4

Synthesis of 4-vinylbenzyl acetate (1)

4-Vinylbenzyl acetate was prepared by a slight modification of the reported procedures.[20] A mixture of 4-vinylbenzyl chloride (20 mL, 0.142 mol) and potassium acetate (16 g, 0.163 mol) in DMSO (60 mL) was stirred at 40°C for 2 days. The reaction mixture was poured into water (80 mL) and extracted three times with ethyl acetate (100 mL). The collected ethyl acetate layer was dried with anhydrous $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10 : 1) to afford **1** (23.99 g, 96%) as yellow oil. ^{1}H-NMR (400 MHz, CDCl₃, ppm): δ 1.97 (s, 3H), 4.97 (s, 2H), 5.14 (d, $J = 10.9$ Hz, 1H), 5.64 (d, $J = 17.6$ Hz, 1H), 6.59 (dd, $J = 17.6, 10.9$ Hz, 1H), 7.19 (d, $J = 8.2$ Hz, 2H), 7.28 (d, $J = 8.2$ Hz, 2H).

Synthesis of 4-vinylbenzyl alcohol (2)

Sodium hydroxide (10 g, 0.25mol) was added to a solution of 4-vinylbenzyl acetate **1** (23.9 g, 0.136 mol) in ethanol (60 mL) and water (10 mL) at 25°C under a nitrogen atmosphere. After stirring at room temperature for 20 min, the reaction mixture was heated to 80°C and stirred for further 2 h. It was then poured into water (40 mL) and extracted with ethyl acetate (200 mL), dried with anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate = 3 : 1) to afford **2** (17.67 g, 97%) as dark brown oil. ^{1}H-NMR (400 MHz, CDCl₃, ppm): δ 1.85 (s, 1H), 4.58 (s, 2H), 5.17 (d, $J = 10.9$ Hz, 1H), 5.67 (d, $J = 17.6$ Hz, 1H), 6.64 (dd, $J = 17.6, 10.9$ Hz, 1H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H).

Synthesis of fluorinated monomer (3)

To a solution of 4-vinylbenzyl alcohol **2** (1.61 g, 12 mmol) and triethylamine (1.21 g, 12 mmol) in dichloromethane (20 mL) was added 2,3,3,3-tetrafluoro-2-(1,1,2,3,3,3-hexafluoro-2-(perfluoropropoxy)-propoxy)propanoyl fluoride (8.217 g, 16.5 mmol) slowly at −40°C and stirred for further 12 h at −40°C. The mixture was then allowed to warm to room temperature and poured into water (10 mL) and extracted with chloroform (25 mL × 3). The extract was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether) to afford **3** (6.03 g, 82%) as oil. ^{1}H-NMR (400 MHz, CDCl₃, ppm): δ 5.22 (d, $J = 10.9$ Hz, 1H), 5.28 (m, 2H), 5.7 (d, $J = 17.6$ Hz, 1H), 6.64 (dd, $J = 17.6, 10.9$ Hz, 1H), 7.24 (d, $J = 8.2$ Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 2H). ^{19}F-NMR (376 MHz, CDCl₃, ppm): δ −145.21 (m, 1F), −131.52 (m, 1F), −129.67 (s, 2F), −84.7 (m, 1F), −82.2 (d, 3F), −81.74 (m, 2F), −81.46 (m, 3F), −80.15 (m, 3F), −79.41 (m, 1F). IR (neat): ν_{max} 1785, 1638, 1613, 1569, 1511, 1198 cm^{-1}. MS (EI, 70 ev) m/z: 612 (M^+, 17), 117 (100). Anal. Calcd. for $C_{18}H_9F_{17}O_4$: C, 35.31; H, 1.48. Found: C, 35.62; H, 1.58.

Synthesis of PEG-containing monomer (4)[21]

Into a three-necked 100-mL flask equipped with a mechanical stirrer, dropping funnel was placed dry DMF (40 mL) and double distilled triethylene glycol (3.0 g, 20 mmol). NaH (1.84 g; 60 wt % in mineral oil, 46 mmol; hexane washed to remove oil) was added to the rapidly stirring solution, and the reaction mixture was stirred at room temperature for 1 h. The flask was immersed in a cold water bath (10°C), and 4-vinylbenzyl chloride (6.70 g, 43.9 mmol) was added dropwise at a rate to keep the temperature below 25°C. Nitrobenzene (1 mg) was added to inhibit polymerization, and the mixture was stirred in the dark at room temperature for 36 h. It was then concentrated *in vacuo* at 55°C to about 10 mL of solution. Water (50 mL) was added, and the solution was extracted three times with diethyl ether (70 mL). The combined ether extracts were concentrated *in vacuo* to give a pale yellow oil that was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate = 10 : 1) to afford **4** (4.73 g, 62%) as colorless oil. ^{1}H-NMR (400 MHz, CDCl$_3$, ppm): δ 3.62–3.68 (m, 12H), 4.54 (s, 4H), 5.2 (d, *J* = 10.9 Hz, 2H), 5.73(d, *J* = 17.6 Hz, 2H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 4H), 7.37 (d, *J* = 8.2 Hz, 4H).

Polymerizations

Monomer **3** (3.0 g, 4.9 mmol) and monomer **4** (1.8 g, 4.7 mmol) were added to a dry three-necked 50-mL flask containing a magnetic stir bar. This was followed by addition of anhydrous benzene (20 mL) and AIBN (0.18 g, 1 wt % relative to monomer). The copolymerization was then carried out at 70°C for 24 h under a nitrogen atmosphere. After the solvent was removed by rotary evaporation, the crude product was purified by repeated precipitations from 1,1,2-trichlorotrifluoroethane (F113) solution into methanol to obtain a viscous compound **5** which was finally dried *in vacuo* for 2 days at room temperature (57% yield). IR (neat): ν$_{max}$ 3058, 3029, 2917, 2851, 1785, 1611, 1515, 1457, 1237, 1134, 811 cm^{-1}.

Characterization

^{1}H-NMR spectra were recorded on a Bruker AV 400 (400 MHz) spectrometer, using CDCl$_3$ as solvent and TMS as internal standard.[19] F-NMR spectra were obtained on a Bruker AV400 (376 MHz) spectrometer with CFCl$_3$ as an external standard, the downfield shifts being designated as positive. Mass spectra were recorded on Finnigan MAT-8430 instrument with electron-impact ionization at 70 eV. IR spectra were recorded on a FT-IR Avatar 380 spectrometer. The water and oil contact angles were measured using an automatic video contact-angle testing apparatus (Model OCA 40, Dataphysics). A volume (3 μL) of the test liquid (distilled water or n-hexadecane) was applied to the treated metal, and the contact angle was determined from the video camera images of the drop in the course of its formation. The contact angle measurements were performed 20 s after a drop of the test liquid was placed on the treated metal. Dynamic thermo-gravimetric analysis (TGA) was performed on a Netzsch (German) TGA 209 F1 system on powder samples at a heating rate of 10°C min^{-1} from 25 to 600°C under nitrogen atmosphere. The structural and surface morphology of metal plates treated with the synthesized polymer was recorded by scanning electron microscope (SEM) (JSM-5600 LV, JEOL). The chemical composition of the treated surface was characterized by X-ray photoelectron spectroscopy (XPS, XSAM800, Kratos, UK).

Preparation of adsorbed thin films on surfaces of metal plates

Aluminum plates, copper plates, iron plates (10 × 10 × 2 mm) were thoroughly cleaned by ultrasonic washing in acetone, then dried in a 60°C drying oven. The corresponding cleaned and dried substrates were immediately immersed in the solution of polymer **5** (1 wt %) in 1,1,2-trichlorotrifluoroethane (F113) and kept at 40°C for 2 h. The substrates were dried at room temperature for several minutes, and then heated at 120°C for 2 h to enhance the adsorption of polymer molecules onto the surfaces.

Contact angle measurements

For contact angles experiments, measurements of droplets on polymer films were recorded at 25°C using doubly distilled water (surface tension = 73.4 mN m^{-1}) and n-hexadecane (26.0 mN m^{-1}) by an optical contact angle meter (Model OCA 40, Dataphysics). To achieve an equilibrium state, the measurement of contact angles was begun at the fifth minute of contact. Five drops of each liquid were placed at different locations on a horizontal surface, and five readings of contact angle were recorded, and the average value of the five readings was taken as the contact angle of the sample surface.

XPS analysis

To confirm the exist of fluorinated polymer films on treated substrates, the chemical composition and structure of the treated Iron was analyzed using an Axis Ultra multi-technique electron spectrometer (Kratos, UK) with an AlKa X-ray source and a pass

energy of 40 ev. The Al anode voltage was 15 kev and the filament current was 20 mA. The pressure in the spectrometer during analysis was typically in the 10^{-9} torr range. XPS spectra were recorded automatically. Using a least-square curve fitting program installed in the spectrometer, the C_{1S} for the fluorous polymer films surface was split into several sub-peaks of functional groups.

Bacterial attachment experiments

Escherichia coli and *Staphylococcus aureus* were used for cell adhesion test according to the literature.[22] Iron coated with the fluorinated polymer was exposed to the bacterial culture under consideration in an appropriate broth; bacterial attachment was assessed by scanning electron microscopy (SEM) (JSM-5600 LV, JEOL).

Settlement and adhesion assays with diatom nitzschia

Slides with experimental coating were incubated at about 20°C for 2 days in a 30 L tank of recirculating deionized water. Slides were transferred to natural seawater for 2 h before the start of the bioassay. *Nitzschia* was obtained from the college of marine life science of Ocean University of China. The diatom *Nitzschia* was cultivated in a climate chamber at 20–22°C with a light intensity of 49.5–66 µmol photons $m^{-2}s^{-1}$. Cell suspension (10 mL; 1×10^4 cells mL^{-1}) was added to polystyrene culture dishes each containing a glass microscope slide. After 8 days, the slides were very gently washed in seawater to remove cells that had not properly attached. The density of cells attached to the surfaces was counted on each slide using an image analysis system attached to a fluorescence microscope.

RESULTS AND DISCUSSION

Monomer syntheses and radical copolymerization

In this work, we focused on developing environmentally benign and effective diatom releasing material as marine anti-fouling coatings. The strategy was to combine the advantages of both PEG and perfluoropolyether, accordingly, monomers **3** and **4** were chosen (Fig. 1) for making an amphiphilic polymer. The monomer **3** was a perfluoropolyether modified styrene that acts as a non-PFOA alternative and will endue the resulting copolymer with low surface energy. The monomer **4** containing PEG units will enhance the protein repellency of the resulting copolymer. Treatment of 4-vinylbenzyl alcohol with 2,3,3,3-tetrafluoro-2-(1,1,2,3,3,3-hexafluoro-2-(perfluoropropoxy)propoxy)propanoyl fluoride in the presence of triethylamine gave monomer **3** in 82% yield.
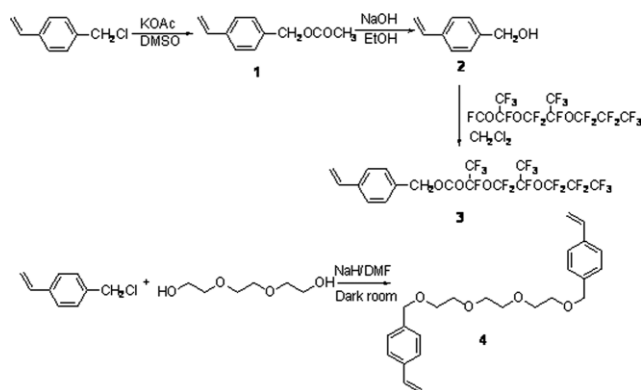

Figure 1 Preparation of monomers **3** and **4**.

PEG monomer **4** was prepared by alkylation of triethylene glycol with 4-vinylbenzyl chloride in the presence of sodium hydride. The radical copolymerization of PEG monomer **4** and fluorinated monomer **3** was accomplished in the presence of radical initiator azo-bis-isobutyronitrile (AIBN) under oxygen-free conditions (Fig. 2). During the polymerization, it was necessary to keep the concentration of monomers lower than 0.5 mol L^{-1} to prevent sudden polymerization. Additionally, the molar ratio of monomers **3** and **4** is the key to influence the solubility of the final copolymer **5** during the polymerization. The use of excess PEG monomer **4** could lead to a highly cross-linked product which has very poor solubility even in 1,1,2-trichlorotrifluoroethane. On the other hand, the less use of **4** could lead to a low cross-linked product which was not suitable for making films. Experimental results indicated the appropriate dosage of **3** is about 1.0–1.6 equivalent to **4**. The final fluorinated copolymer **5** was obtained by using 1.05 molar ratio of **3**/**4** and exhibited very poor solubility in common organic solvent. A fluorinated solvent 1,1,2-trichlorotrifluoroethane was proved to be a good solvent for the purification and application of copolymer **5**. The molecular weight of **5** was not determined by GPC analysis as the material could be retained by the pre-column during the analysis.

The chemical structure of the copolymer **5** was confirmed by Fourier transform infrared (FT-IR) analyses. The IR spectra of monomer **3**, monomer **4,** and the copolymer **5** were presented in Figure 3. In addition to the characteristic absorption bands of C—F bonds in the region of 1100–1400 cm^{-1}, there were also characteristic absorption bands of C=O (1783 cm^{-1}), C—H stretch (2854–2927 cm^{-1}), C=C stretch (1636 cm^{-1}), and aromatic bands (1450–1615 cm^{-1}) for the monomer **3**. In the infrared spectrum of monomer **4**, characteristic absorption peaks at 1632 (C=C) and 1511–1615 cm^{-1} (aromatic absorption) could also be found. The disappearance of the characteristic absorption of C=C (1631–1636 cm^{-1})
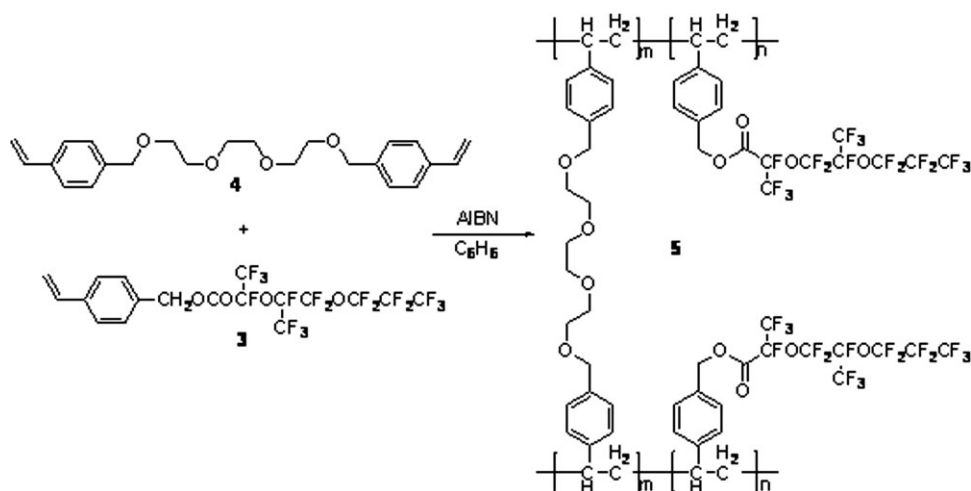
Figure 2 Preparation of cross-linked fluorinated copolymer **5**.

in the spectrum of the polymer **5** indicates that two monomers were transferred into the polymer. Further structural characterization of the polymer by NMR was not carried out because the solubility of the polymer was poor in common organic solvents, so we adopt XPS analytic technique (see XPS analysis) to further confirm the successful synthesization of the copolymer **5.**

Thermogravimetric analysis

The TG/DTG curves of the polymer **5** were shown in Figure 4. The polymer exhibited temperatures corresponding to 5% weight loss at 258°C under nitrogen, and the onset decomposition temperature (T_d)

was determined at about 298.1°C. After that, the weight loss rate greatly increased with the temperature increasing, and the most dramatic weight loss rate occurred at about 353.2°C. The results of thermal analysis demonstrate that the resulting polymer holds good thermal stability.

Contact angle measurements and surface energy calculations

The static contact angles of the polymer coatings on different substrates were listed in Table I. It was found that the substrates modified with polymer **5** did not show high hydrophobicity and oleophobicity. The contact angles of water and hexadecane for
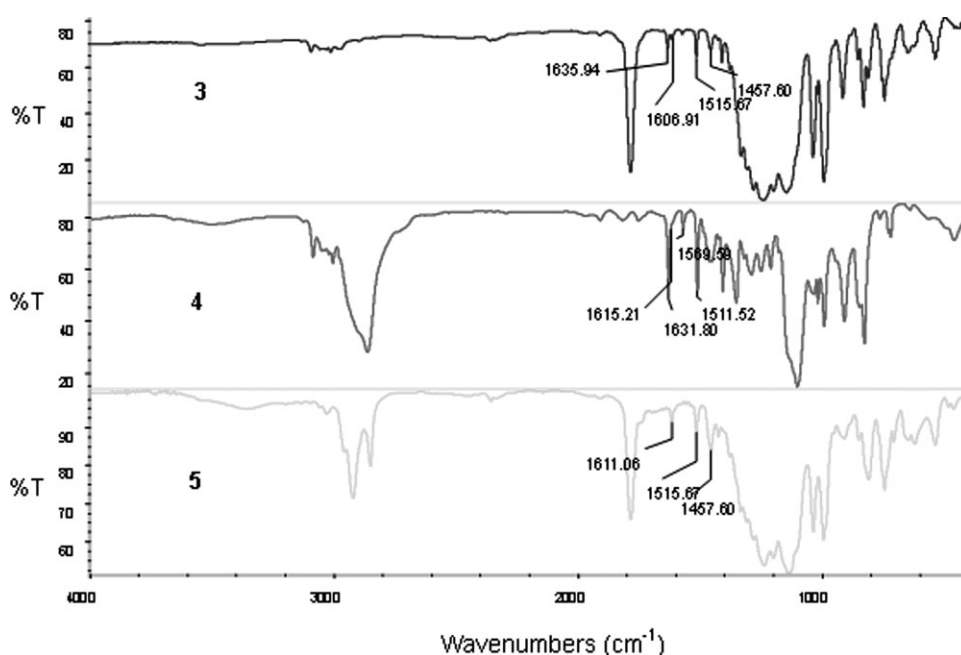

Figure 3 FT-IR spectra of monomers **3, 4**, and copolymer **5**.
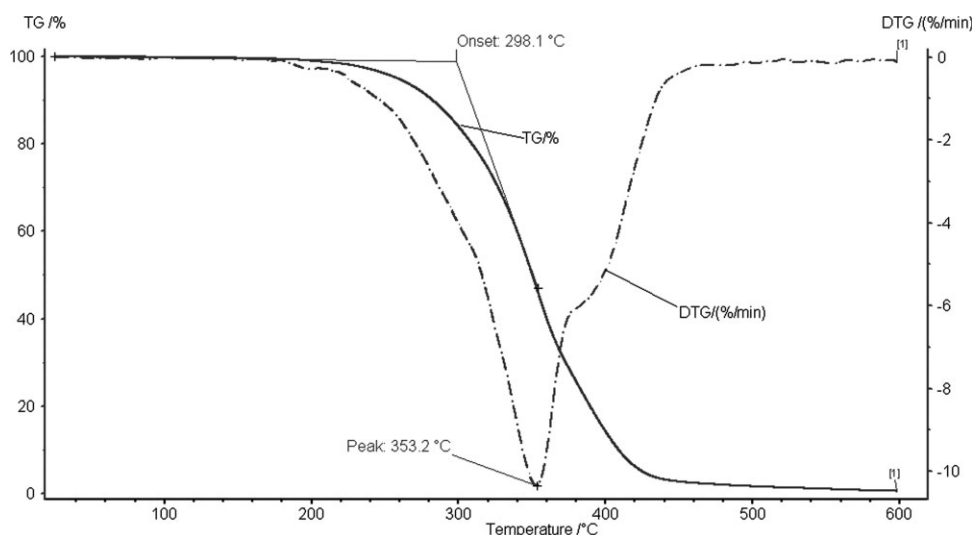
Figure 4 TG and DTG curves of copolymer **5**.

all treated substrates were around 118° and 70°, respectively. This can be explained by the extensive existence of hydrophilic oligoalkyl ether units in the polymer.

Surface free energy is an important factor for adhesive performance of solid surfaces. Low surface free energy may lower the microorganism and cells adhesion to surfaces. By using two different probe liquids (water and hexadecane) with known surface tensions[23] as shown in Table II, the surface free energy can be estimated according to the Owens-Wendt method [eqs. (1) and (2)].[24,25]

$$\gamma_{LV}(1 + \cos\theta) = 2(\gamma_{SV}^d\gamma_{LV}^d)^{1/2} + 2(\gamma_{SV}^P\gamma_{LV}^P)^{1/2} \quad (1)$$

$$\gamma_{SV} = (\gamma_{SV}^P + \gamma_{SV}^d) \quad (2)$$

where d and p are the dispersion and polar components of each surface free energy, the contact angle (θ_c), and γ_{LV} and γ_{SV} are the interfacial tensions at liquid–vapor and solid–vapor interfaces, respectively. Subscripts: S = solid, L = liquid, V = vapor.

The calculated critical surface tensions for the synthesized polymer film treated substrates were summarized in Table III. The very close value of surface free energy (from 11.5 to 12.72 mN m^{-1}) for

these three treated surfaces indicated that polymer **5** has formed a thin film on the surface of metal substrates. Moreover, the surface free energy of coating material **5** (<13 mN m^{-1}) is lower than that of PDMS (22 mN m^{-1}), which implies a better antifouling performance of **5** than that of PDMS.

XPS analysis

To confirm the existence of the fluorinated polymer thin films on treated substrates, the chemical composition and structure of the treated Iron plate was analyzed by using X-ray photoelectron spectrometer (XPS) as shown in Figure 5. As it can be seen, the peak of F$_{1s}$ was at 687.6 ev [Fig. 5(a)] and the peaks of C$_{1s}$ in the spectra could be assigned to groups as CF$_3$ at 293.64 eV, CF$_2$ at 291.68 eV, C=O at 290.2 ev, C=C and C—C at 284.8 ev [Fig. 5(b)]. The C$_{1s}$ and F$_{1s}$ XPS spectra further confirmed the formation of the polymer film on the surface of substrates.

Biofouling assays

As we know, bacterial adhesion on surfaces underwater is a prerequisite for further biofouling caused by marine organisms.[26] Therefore, it is necessary to prevent or reduce its formation. The comparison of the numbers of bacterial cell colonies attached to

TABLE I
Contact Angles of Water and Hexadecane on Different Substrates Coated with Polymer 5

	Contact angle θ_c (°)	
Substrates	H$_2$O	Hexadecane
Aluminum oxide plate	117	72
Iron plate	118	70
Copper plate	118	67

TABLE II
Test Liquids and Their Surface Tension Components[23]

Surface tension data (mN m^{-1})	γ_{LV} (mN m^{-1})	γ_{LV}^P (mN m^{-1})	γ_{LV}^d (mN m^{-1})
Water	72.4	50.8	21.6
Hexadecane	26.0	0.0	26.0

TABLE III
Surface Tensions of Different Substrates Coated with Polymer 5

Substrates	γ_{SV}^d (mN m^{-1})	γ_{SV}^P (mN m^{-1})	γ_{SV} (mN m^{-1})
Aluminum oxide plate	11.14	0.36	11.5
Iron plate	11.7	0.22	11.92
Copper plate	12.57	0.15	12.72

polymer **5** coated irons ($\gamma = 11.7$ mN m^{-1}) and bare iron substrates ($\gamma = 39.62$ mN m^{-1}) were shown in Figures 4 and 5. Bacterial attachment experiments demonstrated that the films from copolymer **5** containing amphiphilic groups possess good resistance to colonization of *S. aureus* and *E. coli.* The bacterial colonies and biofoulings could be identified on bare substrates obviously by scanning electron microscope (SEM) as shown in Figures 6(a) and 7(a). On the contrary, only slight bacterial colonies were
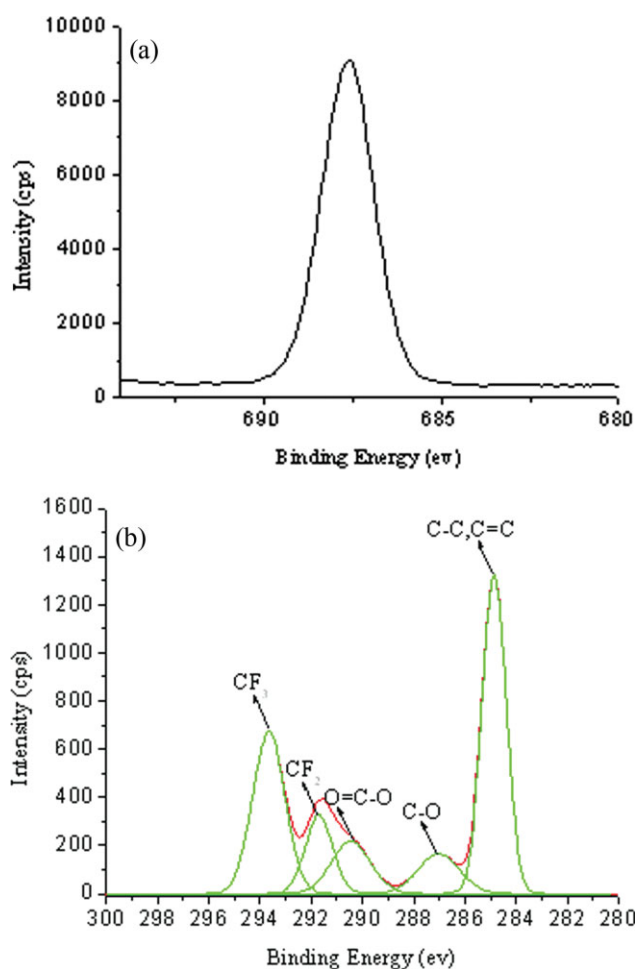
found on the coated iron plate after exposed to culture of *S. aureus* for 48 h [Fig. 6(b)]. In addition, the coated iron plate was found to be consistently resistant to bacterial attachment when exposed to culture of *E. coli* up to 48 h [Fig. 7(b)]. It is believed that the numbers of bacterial cell colonies attached to surfaces decreased with lowering surface energy. The antibacterial performance of the lowering surface energy material has been reported by Thorpe et al.[22] Besides, the good anti-biofouling property may also have been caused by the existence of hydrophilic oligoalkyl ether groups which could resist cell adhesion to the surface. This proposal can be supported by the similar result reported by Whitesides and coworkers.[27,28]

Furthermore, the test results of the fouling diatom *Nitzschia* attachment on PDMS and amphiphilic polymer **5** were shown in Figure 8. From which, it can be seen that number of diatom on commercial available PDMS was 380×10^3 per square centimeter. As expected, only about 270×10^3 number of *Nitzschia* cells per square centimeter was found on the surface of the amphiphilic polymer **5**. This can be explained by the secretion of specific protein of
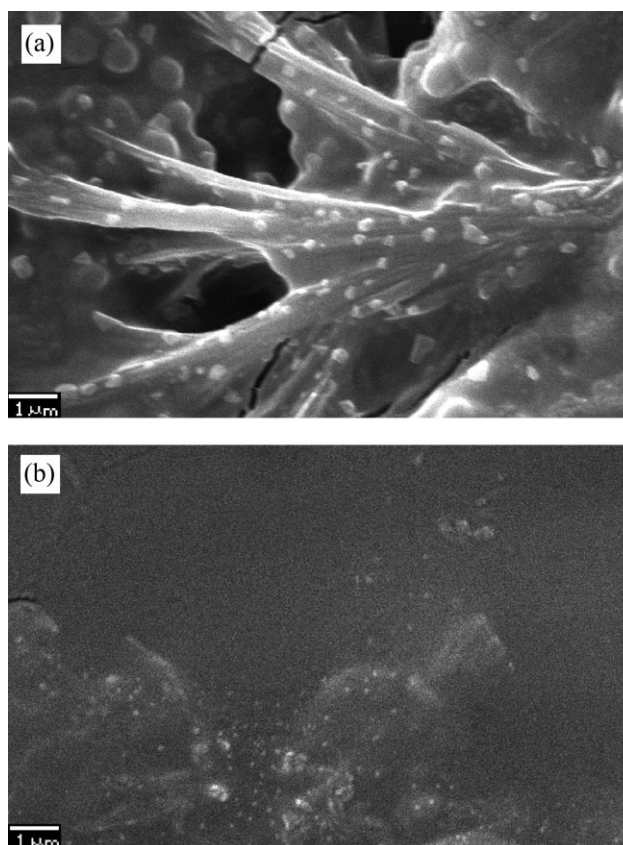

Figure 5 The XPS spectra of the polymer coating surface (a) F$_{1s}$ and (b) C$_{1s}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6 SEM images of *S. aureus* colonies after 48 h exposure, (a) the bare iron plate and (b) the polymer modified iron plate.
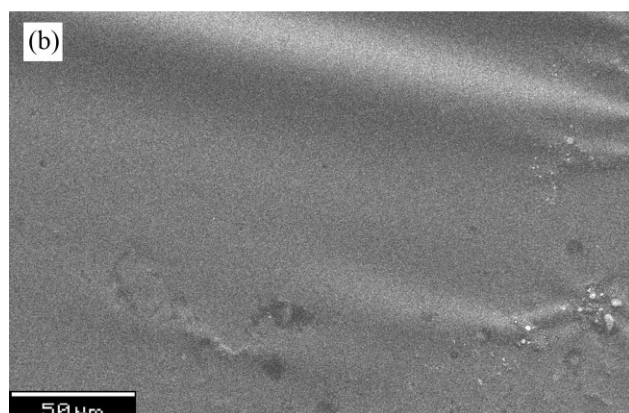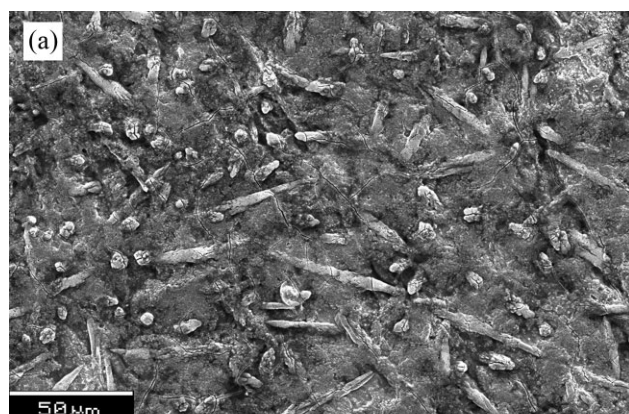
Figure 7 SEM images of *E. coli* colonies after 48 h exposure, (a) the bare iron plate and (b) the polymer modified iron plate.

the diatom which was composed of hydrophobic cores and hydrophilic coronas.[29] This preliminary study suggests that the novel amphiphilic copolymer **5** composed of environmental benign hydrophobic perfluoropolyether rather than perfluorocarbon chain has promising anti-biofouling performance.
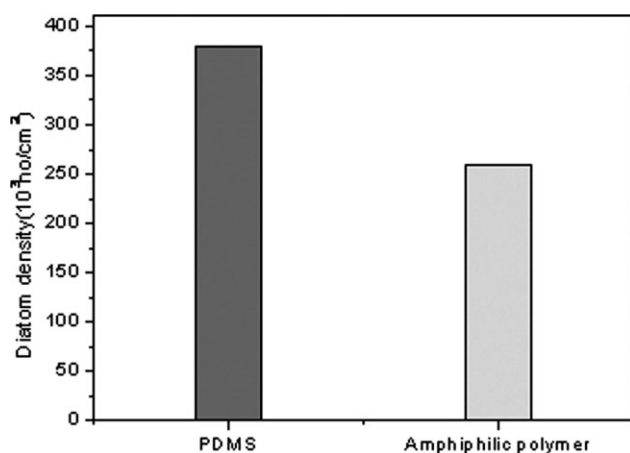

Figure 8 Settlement of diatom *Nitzschia* on surfaces of PDMS and amphiphilic polymer **5**.

CONCLUSIONS

A novel cross-linked fluorinated copolymer **5** with amphiphilic groups was readily synthesized by radical copolymerization. Polymer **5** possessed a good thermal stability ($T_d = 298.1°C$) and very low critical surface energy (<13 mN m^{-1}). The preliminary studies showed that the novel copolymer **5** held very good bacterial resisting abilities for *S. aureus* and *E. coli*, and further investigation indicated that the anti-biofouling performance of **5** is comparable to that of the commercial available PDMS elastomer.

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