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A new synthetical process of PVDF derivatives via atom transfer radical graft polymerizations and its application in fabrication of antifouling and antibacterial PVDF ultrafiltration membranes

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ABSTRACT

In this study, poly(vinylidene fluoride)-*graft*-poly(2-hydroxyethyl methacrylate) (PVDF-*g*-PHEMA) and poly(vinylidene fluoride)-*graft*-poly(dimethylamino)ethyl methacrylate) (PVDF-*g*-PDMAEMA) covalently binding onto the PVDF polymer synthesized by atom transfer radical polymerization (ATRP), were used as additives in the manufacture of novel PVDF ultrafiltration (UF) membranes. The hydroxyl groups on the PVDF-OH polymer by Fenton reaction were used for the immobilization of alkyl halide ATRP initiator. The effects of chemical composition and surface morphology on blend membrane were investigated by X-ray photoelectron spectroscopy, Fourier transform infrared spectrometer, scanning electron microscopy and thermo-gravimetric analysis. Water contact angles and water intake measurements indicated that the introduction of PHEMA graft chains promoted remarkably the surface hydrophilicity of PVDF membranes. It was also found that PVDF/PVDF-*g*-PHEMA blend membrane provided higher pure water flux of 87.9 l/m^2 h and better anti-protein adsorption ability to PVDF membranes. In filtration studies, blend membranes prepared with PVDF-*g*-PDMAEMA-*g*-PHEMA were found to keep the higher pure water flux than the pristine PVDF UF membrane. The PVDF/PVDF-*g*-PDMAEMA and PVDF/PVDF-*g*-PDMAEMA-*b*-PHEMA blend membranes exhibited excellent antibacterial properties against *Escherichia coliform* reaching more than 80%.

Keywords: Atom transfer radical polymerization (ATRP); Polyvinylidene fluoride (PVDF); Antibacterial; Antifouling

1. Introduction

Ultrafiltration (UF) membrane as a powerful technique has been widely used in food and dairy, paper, textile, chemical, and biochemical industries, wastewater treatment, and reverse osmosis pretreatment. A major challenge to these operations is membrane fouling by proteins, other biomolecules and organic matter. It is generally attributed to the hydrophobic nature of UF membrane materials, which leads to a flux decline that necessitates frequent membrane cleaning and replacement, ultimately increases operating costs [1–3]. Poly(vinylidene

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fluoride) (PVDF) is often employed in the fabrication of UF membranes, as it combines desired thermal, chemical resistance, well-controlled porosity, and good mechanical properties. To further reduce the susceptibility of PVDF membranes to biofouling, various methods to increase their surface hydrophilicity have been described, such as surface-activated ozone-induced graft polymerization of hydrophilic monomers (e.g. polyethylene glycol methacrylate (PEGMA) [4], zwitterionic sulfobetainemethacrylate (SBMA) [5]) and UV irradiation surface coupling of N-vinyl-2-pyrrolidinone(NVP) [6], poly(methyl methacrylate) (PMMA) [7] or coating 3,4-dihydroxyphenylalanine (DOPA) and dopamine and immobilizing heparin [8,9]. However, surface graft polymerization or adsorption methods used for membrane modification tend to reduce the selective layer pore size, often lead to decreased flux [3].

A promising approach to UF membrane modification involves blending an amphiphilic copolymer to the membrane casting solution along with the base material. During precipitation in a water-based coagulation bath, the additive spontaneously segregates to the membrane surface that renders the membrane with fouling resistance [2,3]. For example, poly (methyl methacrylate-*r*-polyoxyethylene methacrylate) P(MMA-*r*-POEM) and amphiphilic hyperbranched-star polymers polyester-*graft*-methoxy poly(ethylene glycol) (HPE-*g*-MPEG) were employed as an additive in PVDF membranes to improve hydrophilicity and protein fouling resistance [10,11]. Recently, cellulose acetate (CA) was used as a hydrophilic additive to blend with PVDF to resist fouling by BSA [12]. Negatively charged PVDF microfiltration membranes were also prepared using direct sulfonation with chlorosulfonic acid to improve the membrane hydrophilicity [13]. Some groups have prepared TiO_2 nanoparticle self-assembly PVDF membrane to improve its antibacterial property [14] and TiO_2-containing poly(styrene-*alt*-maleic anhydride)/poly(vinylidene fluoride) (SMA/PVDF) blend membrane to improve its anti-fouling ability [15].

The atom transfer radical polymerization (ATRP) process can prepare well-controlled polymers of narrow molecular weight distribution without stringent experimental conditions due to its controlled/ "living" nature [16]. ATRP can be linearly controlled by adjusting the concentration of the consumed monomer, the density of introduced initiator, the grafting time and the grafting temperature [17]. The direct preparation of amphiphilic comb copolymer derivatives of PVDF with poly(methacrylic acid) side chains (PVDF-*g*-PMAA) and poly(oxyethylene methacrylate) side chains (PVDF-*g*-POEM) [18] and hydrophilic flat sheet PVDF/PVDF-*g*-PEGMA[19] blend membranes using ATRP has been demonstrated. However, the above fabrication process needs higher reaction temperature and longer reaction time, thereby increases the preparation cost. The grafting yield of PHEMA was determined by molecular number (Mn) which was linearly increased and the polydispersity index of poly(vinylidene fluoride)-*graft*-poly (2-hydroxyethyl methacrylate) (PVDF-*g*-PHEMA) remains narrow Mw/Mn at around 1.02–1.22 with the polymerization time and HEMA content has been investigated in previous report [17]. In this work, we further extend the use of comb copolymer additives PVDF-*g*-PHEMA and PVDF-*g*-PDMAEMA to PVDF membranes to investigate the effect of antifouling and antibacterial PVDF blend UF membranes.

2. Experimental

2.1. Materials

The PVDF polymer was purchased from Shanghai 3F New Materials Co., Ltd. and dried at 70℃ for 12 h before use. 1-methyl-2-pyrrolidinone (NMP) was obtained from BASF Chemical Co., Ltd., (Tianjin, China). Poly(ethylene glycol) (PEG) with a molecular weight of 20,000 as additives was purchased from Sinopharm Chemical Reagent Co., Ltd. 2-bromoisobutyryl bromide (BIBB, Alorich, 98%) were used as received. 2-hydroxyethyl Methacrylate (HEMA) (Mn = 130.14, 98%), N,N-dimethyl aminoethyl methacrylate (DMAEMA) (Mn = 157.21, 98%), N,N,N′,N′,N′′-pentamethyldiethlyenetriamine (PMDETA,99%), 1-bromodecane (98%), copper(I) bromine (CuBr, 99%), and copper(II) bromine ($CuBr_2$, 97%) were also obtained from Aldrich Chemical Co. HEMA and DMAEMA were passed through an inhibitor-remover column to remove the inhibitors and then stored in refrigerator. CuBr was dissolved in acetic acid, filtered, washed with anhydrous ethanol and ether,finally dried in vacuum oven at room temperature, restored under an argon atmosphere. Methylene dichloride (CH_2Cl_2), triethylamine (TEA), ferrous sulfate ($FeSO_4.7H_2O$), hydrogen peroxide (H_2O_2), anhydrous ethanol and methanol were all supplied by Guangdong Guanghua Chemical Factory Co., Ltd. Both CH_2Cl_2 and TEA were dehydrated via 0.4 nm molecular sieve before use. Sulfuric acid (H_2SO_4) was obtained from Laiyang Fine Chemical Plant in Economic and Technological Development Zone. Bovine albumin (BSA) was purchased from Shanghai Guoyao Chemical Co., Ltd. *Escherichia coliform* (*E. coli*) was self-stored in lab. Other chemicals were all of commercially analytical

grade. Deionized water (dW) was prepared by EDI system in laboratory.

2.2. Preparation of additives

The hydroxyl groups-containing PVDF (PVDF-OH) polymer was produced by Fenton reaction. About 1 g of PVDF, 0.139 g of $FeSO_4{\cdot}7H_2O$, 0.606 g of H_2O_2, 5 ml of ethanol and 5 ml of deionized water were put into a flask. The Fenton reaction was carried out in a water bath of 50˚C for 1 h. The resultant product was filtered and washed thoroughly with excess H_2SO_4 and water to remove the Fe^{3+} salt adsorbed on the polymer. The polymer was then dried in a vacuum oven overnight.

The immobilization of BIBB was carried out by the reaction of hydroxyl groups on PVDF-OH with BIBB to produce the 2-bromoisobutyryl bromide -immobilized polymer (PVDF-Br) for the subsequent ATRP. A 100-ml flask was cooled quickly in an ice box at 0˚C, then 1 g of PVDF-OH polymer, 20 mL of dried CH_2Cl_2 and 1.65 ml of TEA were introduced into the reactor flask. The reaction mixture was gently stirred and 1.5 ml of BIBB was added into the mixture dropwise. With continuous stirring, the reaction was performed over a period of 1 h. Then, the reaction proceeded at ambient temperature for 24 h. The resultant polymer with -Br groups were obtained by washing thoroughly with ethanol and water alternatively to remove the $(C_2H_5)_3N{\cdot}HBr$ salt adsorbed on the polymer.

Poly(vinylidene fluoride)-*graft*-poly(hydroxyethyl methacrylate) (PVDF-*g*-PHEMA) and poly(vinylidene fluoride)-*graft*-poly(dimethyl aminoethyl methacrylate) (PVDF-*g*-PDMAEMA) were synthesized by ATRP. 1 g of PVDF-OH, 3.2 ml of HEMA (25 mmol) or 4.05 ml of DMAEMA (25 mmol), 3.725 mg of CuBr (0.25 mmol), 11.6 mg $CuBr_2$ (0.05 mmol) ([HEMA/DMAEMA]:[CuBr]:[$CuBr_2$]:[PMDETA] molar feed ratio of 100:1:0.2:1.5), 50 ml of solution (methanol and deionized water in 1:1 volume ratio) were put into a three-mouth flask, respectively. The solution with magnetic stirring was degassed by passing a continuous stream of dry argon for 20 min. Then, 80 μl of PMDETA (0.375 mmol) was added to the HEMA or DMAEMA reaction solution with a syringe. The graft polymerization was allowed to proceed for 20 min in a water bath of 40˚C. PVDF-*g*-PDMAEMA blocking PHEMA was performed in the same way of PVDF-*g*-PHEMA. The recovered product was filtered and washed thoroughly with excess anhydrous ethanol and water to remove the remaining solvent and monomer. The polymer was then dried in a vacuum oven overnight.

About 1 g PVDF-*g*-PDMAEMA or PVDF-*g*-PDMAEMA-PHEMA polymer was exposed to 20 ml of 1-bromodecane for the quaternization reaction. After stirring in the alkyl halides at 50˚C for 48 h, the polymer was filtered with water and anhydrous ethanol, and dried in vacuum oven for 24 h (see Fig. 1).

2.3. Fabrication of UF membrane with synthetic additives

Casting solutions of PVDF/PVDF-*g*-PHEMA, PVDF/PVDF-*g*-PDMAEMA and PVDF/PVDF-*g*-PDMAEMA-*b*-PHEMA membranes were prepared by adding blend polymer (17 wt.%, PVDF and copolymer in 9:1 weight ratio) and PEG20000 (3 wt.%) to NMP and heating to approximately 50˚C. The casting solutions were vigorously stirred for homogeneous mixing, and left for 4 h to allow complete release of bubbles. The solutions were cast on glass plates with a steel knife, and the glass plate was subsequently immersed in a coagulation bath of deionized water. The formed membranes were peeled off and washed thoroughly with deionized water to remove residual solvent and pore-forming agent, and immersed in deionized water before use.

2.4. Evaluation of fabricated UF membrane

2.4.1. Water contact angles and water intake measurements

Water contact angles were measured with an angle-meter (Automatic Contact Angle Meter, Model DSA100, KRUSS, Germany) at 25˚C. Pure water intake was measured by the liquid adsorption method. The sample membranes were dried in a vacuum oven for 24 h, and then, the dry membranes were measured. The percent water content was calculated by Eq. (1):

$$A = \frac{W_w - W_d}{W_w} \times 100\% \quad (1)$$

where A is the water content (%), W_w and W_d (mg) are the wet and dry weight of the measured membranes, respectively.

2.4.2. Chemical composition

The chemical composition of modified PVDF membranes was characterized using Fourier transform infrared spectrometer (FT-IR) spectrophotometer (Bruker optics). Each spectrum was captured by averaged 32 scans at a resolution of 4 cm^{-1}. X-ray photoelectron spectroscopy (XPS) spectra for the top surfaces of these membranes were recorded on a PHI 5000C ESCA System (PHI Co., America) employing Al Ka excitation radiation (1486.6 eV). The cross-section morphologies of modified membranes were observed by scanning electron microscopy (SEM) using a

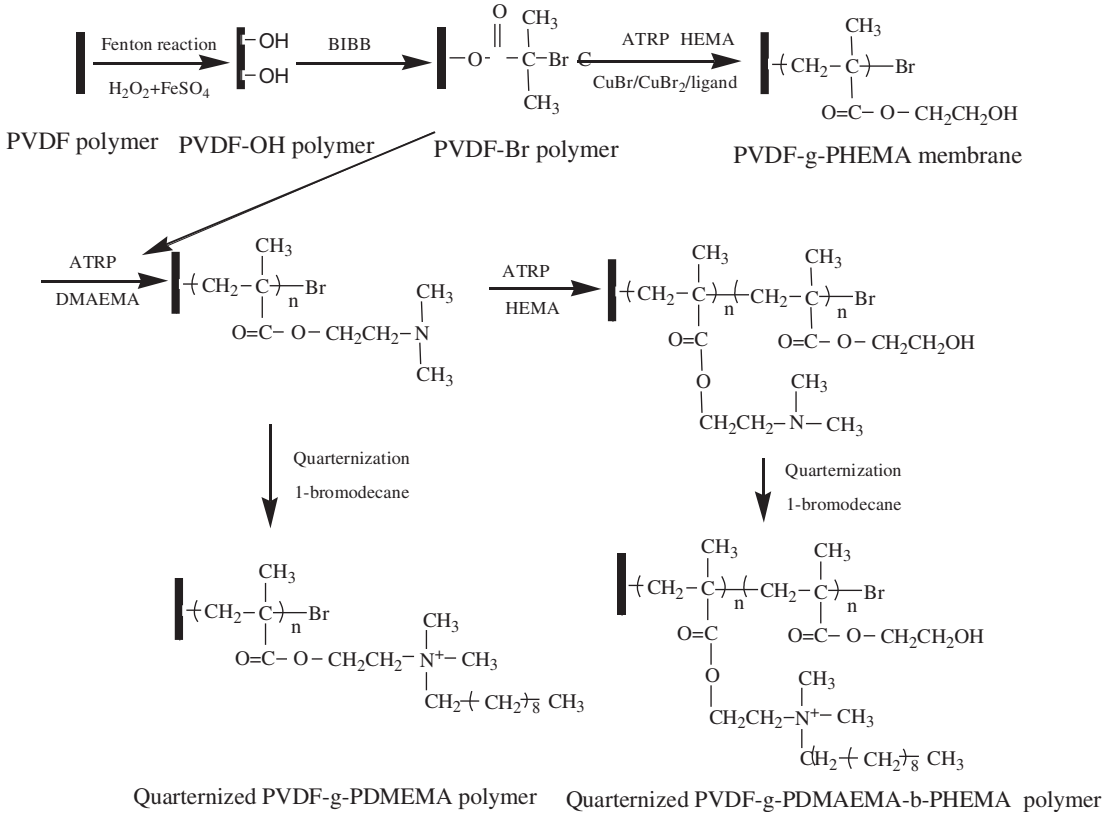

Fig. 1. Schematic diagram illustrating the process of ATRP from PVDF polymer and quaternization of PVDF-*g*-PDMAEMA polymer and PVDF-*g*-PDMAEMA-b-PHEMA polymer.

HITACHI S-4,800 scanning microscope. The membranes frozen in liquid nitrogen were broken and sputtered with gold before SEM analysis.

2.4.3. BSA adsorption experiments

To evaluate the fouling resistance of the pristine membrane and modified membranes, BSA adsorption experiments were performed. A membrane with an area of 25 cm^2 was immersed into a 1.0 g/L BSA solution prepared with phosphate buffer solution (PBS, pH = 7.4). The membrane samples were saturated thoroughly in anhydrous ethanol and PBS for 30 min, respectively, and the tubes with 10 ml of solution and membranes were placed in a water bath of 37℃ to incubate for 24 h. The concentration of BSA solution was determined using a UV spectrophotometer (UV-2450 Shimadzu) at 280 nm wavelength. The apparent amount of protein adsorbed by the membrane was calculated from the concentration difference of BSA solution before and after adsorption. The average of at least five measurements was reported.

2.4.4. Cross-flow membrane filtration and fouling reversibility experiments

A cross-flow membrane filtration (CMF) unit was constructed. A gear pump (Kflow, 1 l) was used to circulate the feed solution through the CMF unit. Deionized water was first passed through the membrane until the flux remained stable over at least a half an hour. Then, the pressure was reduced to 100 kPa of the operating pressure, The permeate flux was collected in a 10 ml of tube so that DI water flux (Jw_0) was calculated by determining the filtrate volume at fixed operation time. The cell was then emptied and refilled with the model protein solutions comprised 1 g/L BSA in PBS with a pH of 7.4, the fouling experiments were carried out. After performing for 30 min, the samples of 10 ml permeate was collected in order to calculate BSA retention. After BSA UF, The fouled unit and membrane were cross-flow cleaned with deionized water for 10 min, and then refilled with DI water as a feed to determine the reversibility of fouling. All circles were performed three times.

2.4.5. Determination of antibacterial activity

Antibacterial efficiency tests were conducted using aqueous suspensions of *E. coli* which were cultivated in 50 ml of a yeast-dextrose broth (pH of 7.2) at 37˚C. The *E. coli* concentration was estimated from the optical density at 540 nm, whereby the *E. coli* number was calculated based on the standard calibration that an optical density was equivalent to $\sim 10^9$ cells per ml [20]. All glassware and plastics were sterilized with the electric sterilizer before experiments. Polymer samples were sterilized with UV irradiation. About 0.05 ml of the bacteria suspension was pipetted out into 50 ml of yeast-dextrose broth and resuspended bacterial solution was at a concentration of 10^6 cells/ml. About 50 mg of the quaternized PVDF-*g*-PDMAEMA and PVDF-*g*-PHEMA-*b*-PDMAEMA polymer or blend membrane were introduced into 50 ml bacterial suspension in different flasks, respectively. The flask was shaken at 3.33 Hz (200 rpm) at 37˚C. A control experiment was carried out using 50 mg of pristine PVDF membrane under the same conditions. After the membrane was in contact with the bacteria suspension for 1 h, 0.1 ml of the bacteria suspension was pipetted out from the flask and 0.9 ml of the PBS (containing 5.4 g of sodium dihydrogen phosphate monohydrate and 8.66 g of anhydrous disodium hydrogen phosphate in 1 l of dionized water, adjusted to pH 7.0) was added to this suspension. The suspension was diluted several times, and 0.1 ml of the diluted suspension was spread onto a triplicate solid agar plate. The plates were then sealed and incubated at 37˚C for 48 h and the numbers of the viable cells were counted. Each antibacterial efficacy in repeated applications was investigated for three times.

3. Results and discussions

In order to further investigate the grafting yield of branched HEMA and DMAEMA chains [20,21] incorporated to PVDF polymer using ATRP, the thermo-gravimetric analysis (TGA) curves for PVDF, PVDF-OH, PVDF-*g*-PHEMA and PVDF-*g*-PDMAEMA-*b*-PHEMA polymer are presented in Fig. 2. The weight loss temperature (10% loss) of PVDF and (5% loss) of PVDF-OH occurred at the temperature range of 450–500˚C, exhibiting an outstanding thermal stability. Two degradation steps are observed in the curves of PVDF-*g*-PHEMA. The first step, from 300 to 450˚C, is attributed to the decomposition of PHEMA chains. The second decomposition step, beginning at about 450˚C, is corresponding to the damage of PVDF-OH backbones. From the weight loss ratio at the first decomposition step, the content of PHEMA chains in the product can be evaluated approximately [22]. In the present work, according to the TGA curves, the PHEMA content in PVDF-*g*-PHEMA is about 5 wt.%. The obtained PVDF-*g*-PHEMA was used as hydrophilic additive in the preparation of PVDF membranes. About 20 wt.% of PDMAEMA (from 150 to 300˚C) and 20 wt.% of PHEMA (from 300 to 450˚C) are contained in the blocking copolymer PVDF-*g*-PDMAEMA-*b*-PHEMA. Therefore, the bulk of PVDF blend membranes (PVDF and copolymer in 9:1 weight ratio) would maintain a good thermal resistance, despite the deteriorated thermal stability for PVDF after the grafting of PHEMA and PDMAEMA chains.

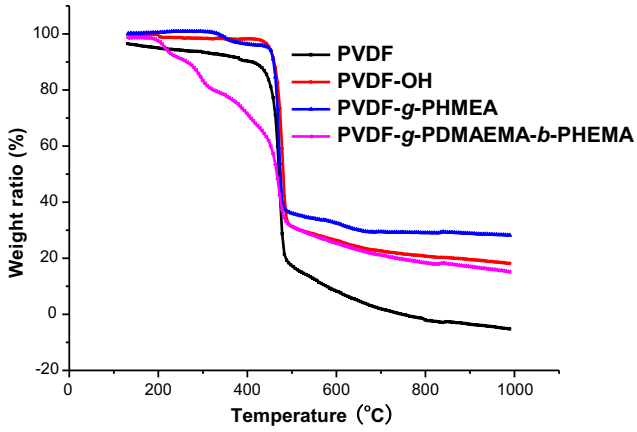

Fig. 2. TGA curves for the pristine PVDF polymer, PVDF-OH polymer, PVDF-*g*-PHEMA polymer with an ATRP time of 20 min and PVDF-*g*-PDMAEMA-b-PHEMA polymer obtained from a polymerization time of 20 min of DMAEMA and subsequently 20 min of HEMA.

3.1. Chemical compositions and morphology of blend membranes

The surface compositions of PVDF pristine membrane, PVDF-OH membrane and PVDF/PVDF-*g*-PHEMA membrane, PVDF/PVDF-*g*-PDMAEMA membrane and PVDF/PVDF-*g*-PDMAEMA-*b*-PHEMA membrane were analyzed by XPS. Only peaks at 290 and 285 eV are observed in Fig. 3(a1), which attributable to CF_2 and C–H/C–C groups of the non-treated PVDF membrane. The C1s spectrum of PVDF-OH membrane is curve-fitted with four peak components for CF_2, C–OH, C–H/C–C, and C=C species, at the binding energies of about 290, 286.5, 285, and 284 eV, respectively (Fig. 3(b1)). The presence of C=C and C–OH peaks is attributed to the Fenton reaction on the PVDF polymer and the O1s spectrum of C–OH (532.8 eV) can be seen in 3(b_2). Furthermore, the peak at 289 eV is the contribution of O–C=O species from PHEMA, which also appears in Fig. 3(c2) at O1s core

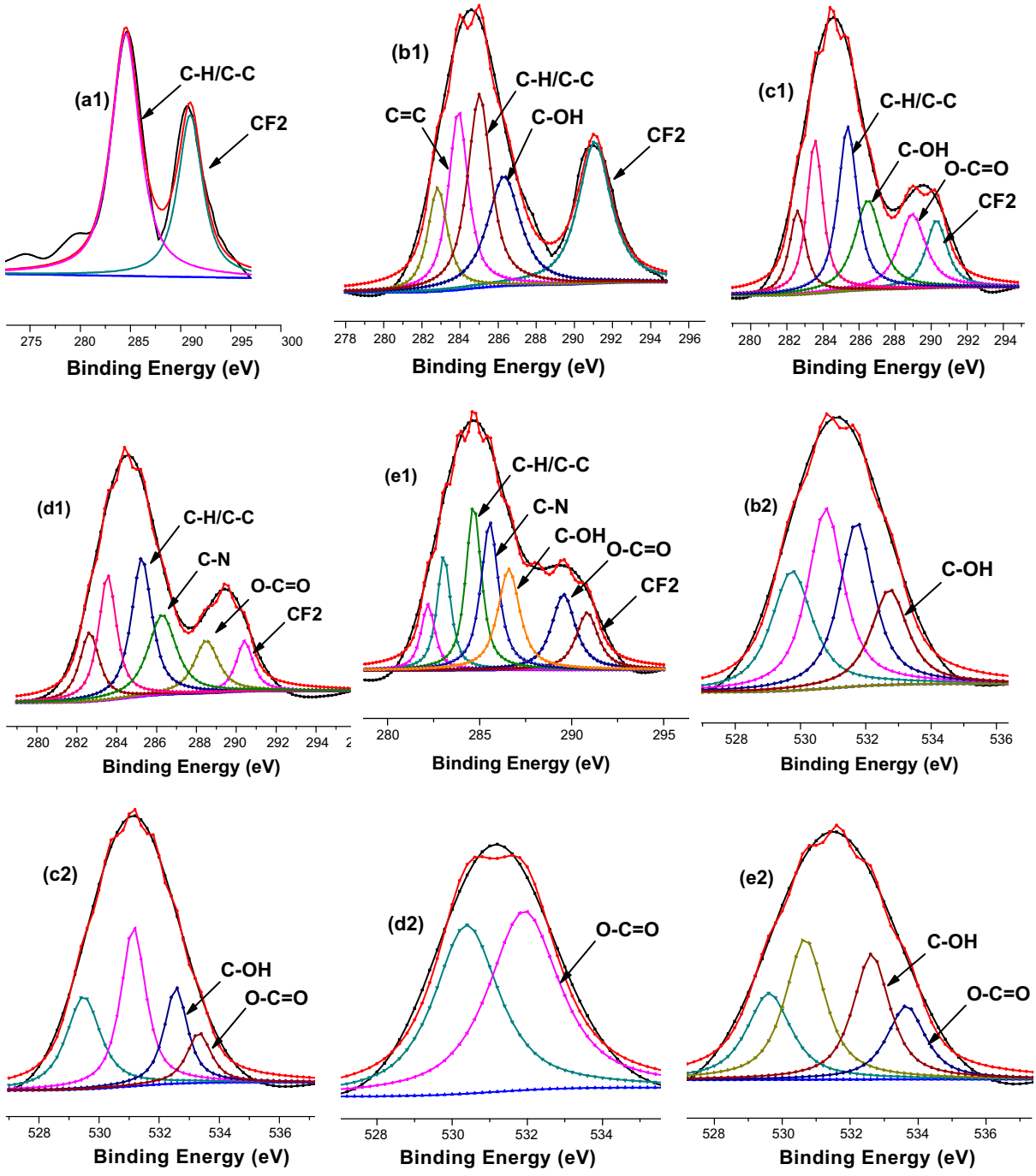

Fig. 3. XPS curve-fitted spectra of C1s and O1s of sample membranes: (a) pristine PVDF membrane (b) PVDF-OH membrane (c) PVDF/PVDF-*g*-PHEMA membrane (PVDF-*g*-PHEMA with an ATRP time of 20 min) (d) PVDF/PVDF-*g*-PDMAEMA membrane (quarternized PVDF-*g*-PDMAEMA with an ATRP time of 20 min) (e) PVDF/PVDF-*g*-PDMAEMA-b-PHEMA membrane (quarternized PVDF-*g*-PDMAEMA-b-PHEMA obtained from a polymerization time of 20 min of DMAEMA and subsequently 20 min of HEMA).

levels of about 533.7 eV. The C–OH peak signal can also be easily observed on PVDF/PVDF-*g*-PHEMA membranes. The XPS analysis for PVDF/PVDF-*g*-PDMAEMA membranes has similar results except that the peak for C–OH at a binding energy of 286.5 eV shifted to C–N peak at 286 eV (Fig. 3(d1)). The results of core-level C1s spectra for PVDF/PVDF-*g*-PDMAEMA-*b*-PHEMA membranes prove the existence of

C–OH and C–N at the BE of 286.5 eV and 286 eV apparently, which is ascribed to PHEMA and PDMAEMA chains presenting on PVDF blend membrane surface. Based on O1s spectra in Fig. 3((c2) and (e2)), it can be easily noticed that the spectra around 532.8 and 533.7 eV are the corresponding C–OH and O–C=O peaks. It indicates the introduction of HEMA and diblock copolymer on the PVDF blend membrane. The C–OH peak at 532.8 eV disappear in the XPS O1s spectrum of PVDF/PVDF-*g*-PDMAEMA membrane.

Table 1 lists the atomic percentage on the membrane surface measured by XPS. According to the data, the oxygen compositions presents the hydroxyl groups on PVDF-OH polymer via Fenton reaction and the content of fluorine (F1s) is remarkably decreased. After the ATRP reactions of HEMA, the contents of carbon (C1s) and oxygen (O1s) on PVDF/PVDF-*g*-PHEMA (9:1, wt.%: wt.) are apparently the same as PVDF-OH membrane and fluorine (F1s) is slightly decreased, indicating the presentation of PHEMA chain on membrane surface. The nitrogen content on the PVDF/PVDF-*g*-PDMAEMA and PVDF/PVDF-*g*-PDMAEMA-*b*-PHEMA membrane surface is 2.12 and 1.10%, indicating the presentation of PDMAEMA chain on membrane surface. The XPS survey and the atomic percentage data on the membrane surface provide definitive evidence for surface segregation of the comb additive.

The FT-IR measurement was used to characterize the chemical composition of the unmodified and the modified PVDF membranes and the spectra are presented in Fig. 4. For the PVDF-OH membrane, compared with the pristine PVDF membrane, the new absorption peak at 3,440 cm^{-1} is ascribed to the hydroxyl group aroused from Fenton reaction. After polymerization, the intensity of the peak at 3,440 cm^{-1} is enhanced due to the overlapping of the skeletal vibration of C–OH originated from PHEMA chains. In the spectra of PVDF/PVDF-*g*-PDMAEMA and PVDF/PVDF-*g*-PDMAEMA-*b*-PHEMA membranes, stretching vibration peak at about 3,440 cm^{-1} is attributed to a stretching combination mode of the C–N in PDMAEMA and the C–OH in PHEMA. In the spectra of

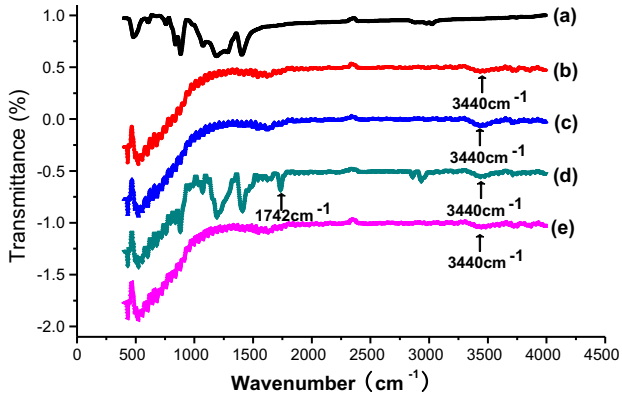

Fig. 4. FT-IR spectra of (a) the pristine PVDF membrane, (b) PVDF-OH membrane, (c) PVDF/PVDF-*g*-PHEMA membrane (PVDF-*g*-PHEMA with an ATRP time of 20 min), (d) PVDF/PVDF-*g*-PDMAMA membrane (quarternized PVDF-*g*-PDMAEMA with an ATRP time of 20 min), (e) P VDF/PVDF-*g*-PDMAEMA-b-PHEMA membrane (quarternized PVDF-*g*-PDMAEMA-b-PHEMA obtained from a polymerization time of 20 min of DMAEMA and subsequently 20 min of HEMA).

PVDF/PVDF-*g*-PDMAEM membrane, a new peak appears at about 1,742 cm^{-1} which can be assigned to O–C=O groups, while the peak in the other grafted membrane is not obvious compared with the whole spectrum. These results indicate that PHEMA and PDMAEMA chains are introduced onto the PVDF membrane surface.

For the PVDF-modified membranes investigated here, addition of grafting polymer is also found to affect selective layer morphology. Fig. 5 shows representative SEM micrographs of the selective layer and cross-section of PVDF pristine membrane, PVDF-OH membrane and those blend membranes cast under similar conditions. All the membranes exhibit typical asymmetrical structures consisting of a compact top layer and a porous sub-layer and fully developed macropores at the bottom. The surface morphology of PVDF membrane after blend PVDF-*g*-PDMAEMA polymer is much rougher than other membranes (as shown in Fig. 5(d1). From the cross-sectional amplified images in Fig. 5((d3) and (e3)) it can be seen that the holes on the pore walls of PDMAEMA-containing

Table 1
Elements composition (at.%) on the membranes surface determined by XPS

Membrane	C1s	N1s	O1s	F1s
PVDF pristine membrane	51.05			48.96
PVDF-OH membrane	54.48		8.94	36.59
PVDF/PVDF-*g*-PHEMA membrane	55.79		8.59	30.81
PVDF/PVDF-*g*-PDMAEMA membrane after quaternization	56.68	2.12	7.84	33.35
PVDF/PVDF-*g*-PDMAEMA-b-PHEMA membrane after quaternization	57.55	1.10	6.82	34.53

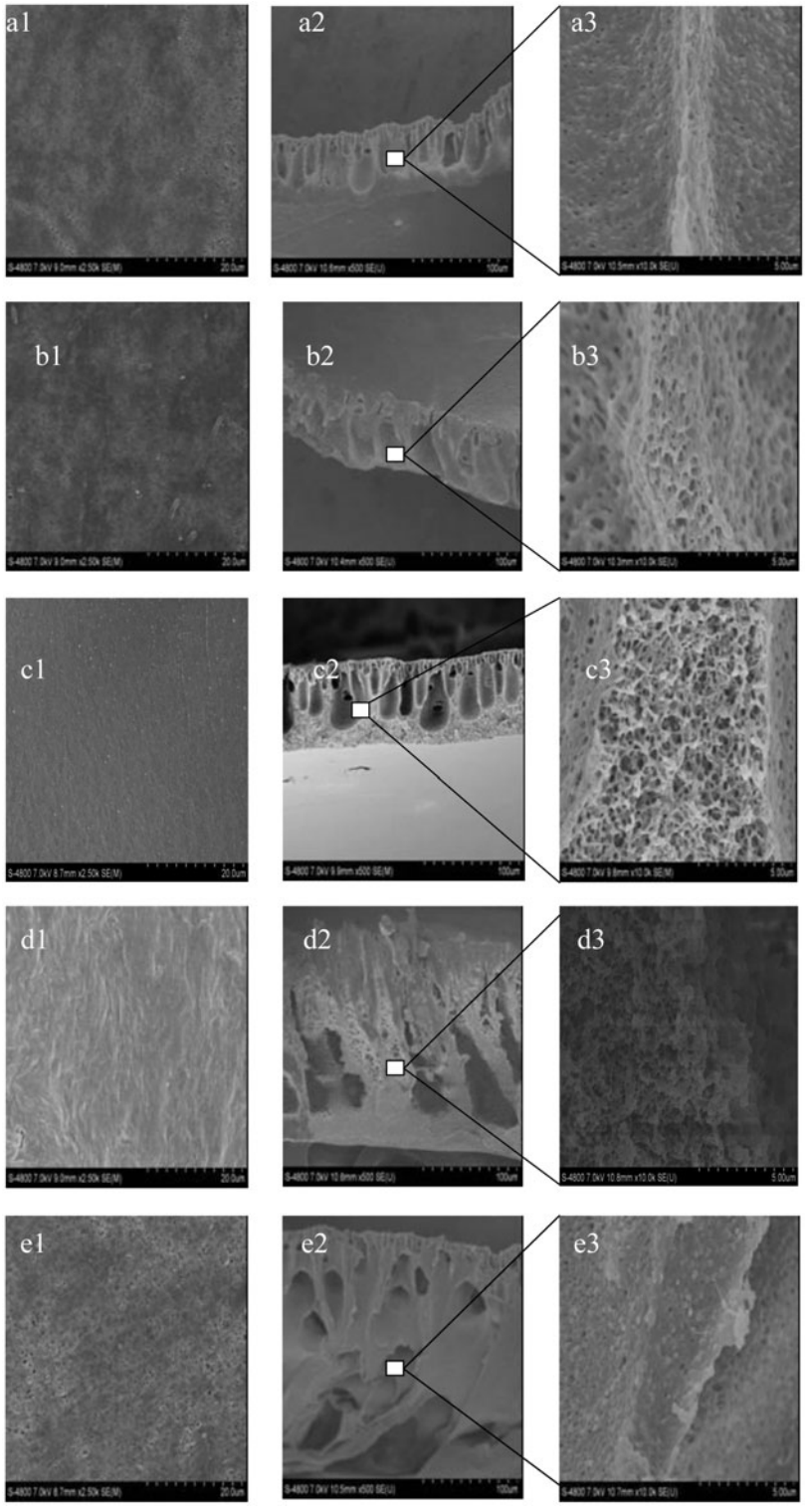

Fig. 5. SEM images of surface morphology, cross-sectional and amplified morphology of (a) PVDF pristine membrane (b) PVDF-OH membrane (c) PVDF/PVDF-*g*-PHEMA membrane (PVDF-*g*-PHEMA with an ATRP time of 20 min) (d) PVDF/PVDF-*g*-PDMAMA membrane (quarternized PVDF-*g*-PDMAEMA with an ATRP time of 20 min) (e) PVDF/PVDF-*g*- PDMAEMA-b-PHEMA membrane (quarternized PVDF-*g*-PDMAEMA-b-PHEMA obtained from a polymerization time of 20 min of DMAEMA and subsequently 20 min of HEMA).

blend membrane are densely smaller than that without PDMAEMA.

3.2. Membrane hydrophilicity and BSA adsorption resistance

The membrane sample was further investigated by degree of water intake and water contact angle (Table 2). The water adsorption on the pristine PVDF membrane and PVDF-OH membrane is 19.6 and 25.05%, respectively. It is ascribed to the trapping water molecules in the porous structure of the pristine PVDF membrane and binding water molecules around the hydroxyl groups on the PVDF-OH membrane. The water intake of PVDF/PVDF-*g*-PDMAEMA-*b*-PHEMA membrane (with polymerization time of 20 min of DMAEMA, following grafting HEMA blocks for 20 min) is 24.27%, whereas the water intake of the PVDF/PVDF-*g*-PHEMA membrane with polymerization time of 20 min close to 34.71%. It indicates the introduction of DMAEMA species due to the addition of hydrophobic methyl chains after quarternization reduce the hydrophilic effect of modified membrane.

The water contact angle of non-treated hydrophobic PVDF membrane is 89.1˚. A lower water contact angle of 82.16˚ is observed with the PVDF-OH membrane surface. After 20 min ATRP reactions, the water contact angle of PVDF/PVDF-*g*-PHEMA membranes reaches a low value of 85.8˚. The result shows that the grafting of hydrophilic PHEMA brushes brings higher hydrophilicity to the PVDF membrane. The water affinity of PVDF/PVDF-*g*-PHEMA membrane mainly attributes to the hydration effect between its hydroxyl groups and water. Obviously, the water contact angle of the PVDF/PVDF-*g*-PDMEMA membranes (quaternized PVDF-*g*-PDMEMA with 20 min polymerization) is a higher value of 91.8˚. The higher water contact angle indicates that the PDMEMA-containing blend membrane is more hydrophobic. The water contact angle of the PVDF/PVDF-*g*-PDMAEMA-*b*-PHEMA membrane is lower than that of PVDF/PVDF-*g*-PDMAEMA membrane due to the introduction of hydrophilic HEMA monomer.

Antifouling properties of modified PVDF membrane displays nonspecific protein adsorption. Nonspecific protein adsorption is a dominant factor for membrane fouling, and the reduction of protein adsorption enhances the antifouling properties of membranes. In this study, BSA was used as model protein to probe the fouling resistance ability of the modified and unmodified membranes. The amount of adsorbed BSA from 1 g/L BSA solution is 60 μg/cm^2 for the original PVDF membrane. The amounts of

Table 2
Membrane hydrophilicity and Permeation properties

Membrane	Water intake (%)	Water contact angle (˚)	BSA adsorption (μg/cm^2)	Water permeation properties (l/m^2 h)	BSA permeation properties (l/m^2 h)	BSA rejection (%)
PVDF pristine membrane	19.6 ± 1.69	89.1 ± 2	60 ± 1.91	40.02 ± 0.8	14.13 ± 0.8	87.31 ± 5.93
PVDF-OH membrane	25.05 ± 0.69	82.16 ± 0.66	55.34 ± 1.25	46.15 ± 1.26	22.24 ± 2.45	94.6 ± 1.19
PVDF/PVDF-*g*-PHEMA membrane	34.71 ± 0.69	85.8 ± 0.44	46.7 ± 1.54	87.9 ± 3.37	65.15 ± 3.28	87.51 ± 5.39
PVDF/PVDF-*g*-PDMAEMA membrane after quaternization	20.3 ± 0.37	91.8 ± 0.52	209.55 ± 13.13	35.02 ± 1.6	6.17 ± 1.5	98.32 ± 3.17
PVDF/PVDF-*g*-PDMAEMA-b-PHEMA membrane after quaternization	24.27 ± 1.01	88.55 ± 0.68	136.71 ± 15.31	55.23 ± 2.85	10.74 ± 1.84	95.29 ± 4.08

adsorbed BSA are decreased for both PVDF-OH and PVDF/PVDF-*g*-PHEMA membranes in comparison with the pristine hydrophobic PVDF, PHEMA-based copolymers took up large quantities of free water; which built up the stable defense layer to resist protein invasion [23]. However, the relative protein adsorption on PVDF/PVDF-*g*-PDMAEMA and PVDF/PVDF-*g*-PDMAEMA-*b*-PHEMA membranes are increased to 3.5 times and 2 times that on pristine PVDF, respectively, indicating positively charged quarternized amine groups displays strong nature of BSA adsorption, even though the presence of PHEMA blocking chains. It also indicates that PDMAEMA-containing polymer can segregate to the surface of blend membrane due to the residence of hydrophilic ester groups.

3.3. Permeation properties and flux recovery ratio

The separation performance and the biofouling characteristics of the modified PVDF membrane were evaluated by cyclic filtration tests. It is found that the Jw_0 of the PVDF-OH membrane is higher than that of the pristine PVDF membrane. The permeation flux of BSA solution decreases rapidly compared with the flux of pure water (Jw_0) because of protein fouling and concentration polarization. The effects of concentration polarization on the permeation flux can be effectively reduced using high speed cross-flow flushing during the UF experiments. With ATRP time of 20 min, the water flux and BSA flux of the PVDF/PVDF-*g*-PHEMA blend membranes is increased, the permeability is observed to increase to over two times that of the PVDF-only membrane. The increase in BSA permeability suggests membrane fouling for the membranes with a graft brush of HEMA is lowered due to the "size-exclusion effect" of hydrated PHEMA brushes [24]. The BSA rejection ratios of the pristine PVDF, PVDF-OH and PVDF/PVDF-*g*-PHEMA blend membrane in the first cycle is about 87.31, 94.60 and 87.51%, respectively. However, the permeability for PVDF/PVDF-*g*-PDMAEMA blend membrane is a substantial reduction due to the membrane hydrophobicity and BSA adsorption to positively charged PDMAEMA chains. For PVDF/PVDF-*g*-PDMAEMA-*g*-PHEMA blend membrane, the pure water permeabilities of blend membranes are observed higher than pristine PVDF membrane. The BSA rejection ratios of the PDMAEMA-containing blend membranes in the first cycle are higher than other membranes because of the adsorption and pore blocking of BSA protein.

To monitor the irreversible membrane fouling, the pure water flux (Jwi) was measured after membrane cleaning. The water flux recoveries for pristine PVDF and PVDF-OH membranes are 44.75 and 71.87% in the successive three UF cycles, respectively, whereas it increases to 100% for the PVDF/PVDF-*g*-PHEMA blend membrane. The PHEMA-containing blend membrane recovers its flux completely after the same treatment, indicating that the fouling observed was still fully reversible by treatment with water alone, obviating the need for aggressive chemical cleaning procedures. Such membranes might be expected to exhibit substantially longer operational lifetimes, reducing membrane process costs. The analysis of BSA filtration indicates that the presence of PDMAEMA chains on the membrane surface and the pore surface, which greatly increases the irreversible membrane fouling. The protein molecules deposited on the membrane surface can not be flushed clean by water. Considering the antibacterial property of PDMAEMA-containing membranes which will be introduced below and better water permeability of PVDF/PVDF-*g*-PDMAEMA-*g*-PHEMA blend membrane, the blend membrane with diblock copolymer maybe remain popular in the application of the pure water available filtration treatment.

3.4. Antibacterial activity of the quaternized PDMAEMA-containing polymer and membrane

The antibacterial activities of PDMAEMA-containing membrane are another concern in this study. It is well-known that the quaternized PDMAEMA exhibits excellent antibacterial effect [20]. The cations on PDMAEMA chains can adsorb the negatively charged bacteria by electrostatic, hydrogen bonding and hydrophobic binding with the protein molecules, gathering in the cell wall and resulting in chamber resistance effect, ultimately leading to bacterial growth inhibition and death. Meanwhile, the hydrophobic alkyl groups on PDMAEMA chains can react with hydrophilic groups on the bacteria, changing the film permeability, and subsequent causing cell lysis, ultimately destroying the cell structure and causing cell death. The antimicrobial assays were conducted with suspensions of bacteria (*E. coli*), containing 1×10^6 cells/ml. Fig. 6 shows that the pristine PVDF membrane exhibits minimal antibacterial effect. The quaternized PVDF-*g*-PDMAEMA polymer (with an ATRP time of 20 min) and PVDF-*g*-PDMAEMA-*b*-PHEMA (from 20 min of ATRP of DMAEMA and subsequently 20 min of ATRP of HEMA) have antibacterial rate of 99 and 100% after being contacted with *E. coli* for about 1 h, respectively. With the increase in the ATRP time of DMAEMA from 20 min to 3 h, the bactericidal

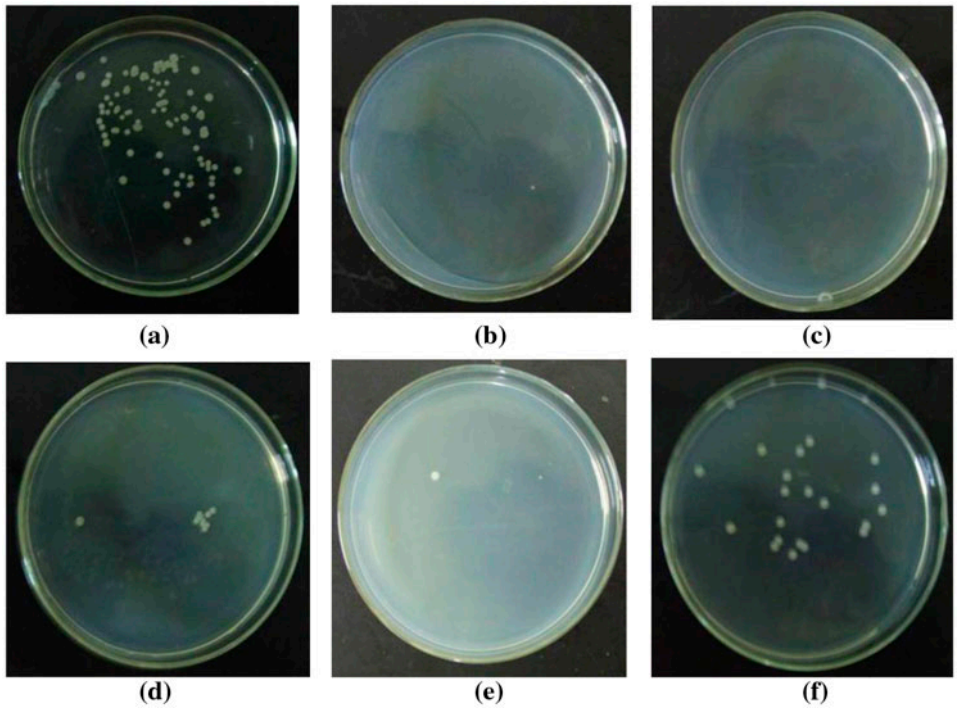

Fig. 6. Photo images of pristine PVDF membrane (a) quaternized PVDF-*g*-PDMAEMA polymer grafted for 20 min (b) quaternized PVDF-*g*-PDMAEMA-b-PHEMA polymer (from 20 min of ATRP of DMAEMA and subsequently 20 min of ATRP of HEMA) (c) PVDF/PVDF-*g*-PDMAEMA membrane (quaternized PVDF/PVDF-*g*-PDMAEMA polymer with an ATRP time of 20 min (d) and 3 h (e) PVDF/PVDF-*g*-PDMAEMA-b-PHEMA membrane (quaternized PVDF/PVDF-*g*-PDMAEMA-b-PHEMA polymer from 20 min of ATRP of DMAEMA and subsequently 20 min of ATRP of HEMA) (f) after antibacterial assay.

efficiency achievable of blend membranes increases from 90.0 to 99.0%. And the anti-bacterial efficiency of the PVDF/PVDF-*g*-PDMAEMA-*b*-PHEMA blend membrane can reach 80.0% as well.

4. Conclusion

Comb-like PHEMA and PDMAEMA brushes were successfully bound from PVDF polymer by atom transfer radical graft polymerizations. The antifouling and antibacterial property of PVDF blend membrane was improved by PHEMA and PDMAEMA-containing brushes, respectively. The water intake measurement and the water contact angles indicated the improvement of the surface hydrophilicity by the addition of PVDF-*g*-PHEMA. The BSA adsorption resistance and the cyclic filtration test of the blend membrane showed perfect anti-fouling characteristics. The antibacterial effects against *E. coli* of quaternized PVDF/PVDF-*g*-PDMAEMA blend membrane and PVDF/PVDF-*g*-PDMAEMA-*b*-PHEMA blend membrane were examined and the antibacterial efficiency reaches more than 80% when PDMAEMA brushes was grafted for 20 min. The modified PVDF blend membranes would have a potential application to reduce protein and bacterial fouling in pure water available treatment process.

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