Ultrafiltration membranes with tunable morphology and performance prepared by blending quaternized cardo poly(arylene ether sulfone)s ionomers with polysulfone

Chunli Liu ^{a, b}, Hongchao Mao ^{a*}, Jianhua Zhu ^{a, b}, Suobo Zhang ^{a, c*}

^aKey Laboratory of Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

^bUniversity of Chinese Academy of Sciences, Beijing 100039, China

^cJiangsu National Synergetic Innovation Center for Advanced Materials (SICAM)

Abstract

The original quaternized cardo poly(arylene ether sulfone)s (QPES-I) ionomers was employed as the virgin polyelectrolyte and its counterions (I⁻) were exchanged with F⁻ and PF₆⁻ to prepare QPES with different anions (QPES-X, X=F, PF₆), then QPES-X/PSF blended ultrafiltration membranes was prepared by the nonsolvent induced phase inversion process. Scanning electron microscopy (SEM) was used to characterize the cross section morphology and surface morphology of blended membranes, and atom force microscopy (AFM) was employed for obtaining the three-dimensional images of QPES-X/PSF blended membranes, respectively. The surface chemical composition of the asymmetric membrane was investigated by X-ray photoelectron spectroscopy (XPS). Under similar preparation conditions, the water contact angle on membrane surface increased in the order of QPES-F < QPES-I < PSF < QPES-PF₆, while the pure water flux of the membranes decreased with that order. The results revealed that the surface and cross section morphology, surface roughness, QPES-X content on membrane surface, as well as the hydrophilicity and performance of blended membranes were closely related to the counterions of QPES-X. Membrane prepared with QPES-F is hydrophilic and possesses outstanding performance among all the investigated materials, demonstrating a water flux of 2163 L m⁻² h⁻¹ and BSA rejection of 93% at an 18wt% polymer concentration and 15% QPES-F content. Antimicrobial activity studies

demonstrate that the **blended membrane** having 15% QPES-F possess a sterilization rate of 73% towards *E. coli*.

Key words: ion exchange; blend; positively charged ultrafiltration membrane; tunable morphology and performance.

1. Introduction

Ultrafiltration membranes have a mean pore radius in the range of 1 nm to 100 nm and a nominal molecular weight cut off (MWCO) between 1 KDa and 500 KDa[1], which is an efficient, energetic separation process for removing proteins[2] and suspended nanoparticulates[3] from pollutant water, and can be used as membrane reactors[4] as well. The heart of membrane separation process is membrane itself, thus, preparation of membrane with specific structure and performance is of vital practical significance. For instance, membrane has sponge like structure has high compression resistance, but low permeation flux, can be used as substrate membrane; while with finger like structure has relatively higher permeation flux, but low compression resistance, being suitable for use as ultrafiltration membrane for low pressure application.

Polysulfone (PSF) is a commercially available material possessing high toughness, thermal and mechanical stability, and is used universally for the fabrication of high-performance ultrafiltration membranes. PSF membranes with sponge like cross-section morphology can be prepared when using DMF as solvent[5]. However, if there are hydrophilic additives, membranes with loose finger like cross-section morphology would be obtained. Rahimpour et al[6] blended sulfonated polyethersulfone (SPES) with polyethersulfone (PES) to prepare asymmetric ultrafiltration membranes, the addition of SPES in the casting solution led to membranes with enhanced membrane hydrophilicity, larger surface pore size and finger like crosslinking morphology with greater sublayer porosity. Vankelecom et al.[7] prepared a series of negatively charged nanofiltration membranes by blending sulfonated poly(ether ether ketone) (SPEEK) with PSF, the results showed that the **blended membrane** had a more open pore structure, and demonstrated higher solvent flux and rejection for negatively charged solutes. Lawler et al.[8] synthesized

quaternized PSF from chloromethylated PSF through an in situ quaternization reaction, and then fabricated the novel positively charged hybrid membranes from blends of PSF and quaternized PSF in combination with graphene oxide (GO) nanosheets. Porous, hydrophilic and positively charged membranes were successfully fabricated. Among all the charged materials illustrated above, they have charged groups located on the backbone. In the NIPS field, the hydrophilic component of casting solution has higher affinity with water and which tend to aggregate and mobile to membrane surface to reduce the surface free energy[9]. Charged groups belonging to side chain type polyelectrolytes could facilitate this mobilization and aggregation trend than those backbone type materials, due to the flexibility of side chains. And if the backbone of charged material is hydrophobic and has similar structure with PSF, the compatibility of blended two components can be improved simultaneously. Therefore, it is promising to look forward on the blending of PSF with a side chain type polyelectrolyte.

It has been well established that the properties of polyelectrolytes were closely related to their counterions[10]. Huck et al. [11] found that the coordination of quaternary ammonium groups with different counterions may generate polyelectrolyte brushes with switchable surfaces properties, creating a tunable wettability of the substrate by immobilizing a wide range of counterions. Su et al.[12] also observed the surface properties of the substrate can be changed gradually from superhydrophilicity to superhydrophobicity by exchanging the counterions of the quaternary ammonium groups for the fabrication of a rough surface with switchable wettability, and those processes can be manipulated reversibly. Quaternized material with F anion as the counterion is a hydrophilic material while with PF₆ anion is a hydrophobic material. And the hydrophilicity of those quaternized materials can change gradiently from hydrophilic to hydrophobic in the sequence of counterions: F, I, PF₆. Consequently, it may be assumed that changing the counterion of quaternary ammonium groups of a material could lead to the change of its hydrophilicity, and blending PSF with those polyelectrolytes may produce membranes with viable micro cross section structures and hydrophilicity. This method could be a novel approach to alter membrane

morphology and improve membrane performance when compared with the conventional method, which focused on varying the blending ratio of hydrophilic component. Besides, positively charged membranes having quaternary ammonium groups are expected to have antifouling and antibacterial activities[13, 14]. Surface-initiated ATRPs of poly(ethylene glycol) monomethacrylate(PEGMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) were introduced to modify the surface of polypropylene hollow fiber membrane by Fu et al, then the tertiary amine groups located on the branched chains were quaternized by alkyl bromide producing membranes with good antimicrobial properties[14]. Membranes with antibacterial and hydrophilic surface will restrain the growth of microbe and weaken the membrane fouling by reducing microorganism attachment.

In our previous study, we reported the synthesis of a novel PES containing pendent quaternary ammonium aliphatic side chains (QPES), which avoided the use of toxic chloromethylation reagents and exhibited a distinct phase-separated morphology[15]. In this study, the original quaternized QPES-I ionomers were employed as the virgin modifier and its counterions were exchanged with F^- and PF_6^- to prepare QPES with different counterions(QPES-X, X=F, I, PF_6). Then we employ QPES-X to blend with PSF for the preparation of ultrafiltration membranes. The surface aggregation and enrichment of quaternary ammonium groups were observed and thus altered the surface hydrophilicity of membranes. What's more, the micro structures of obtained membranes could be easily tuned by changing the counterion of QPES additives, and the morphology and performance of blended membranes were closely related to the counterion of QPES-X. The results demonstrated that QPES-F/PSF blended membrane had the best performance and the membrane fabrication conditions, surface properties and antibacterial activities were investigated in detail.

2. Experimental section

2.1 Materials and reagents

Commercial polysulfone (PSF, Udel, P-3500, USA) was purchased from Solvay Company, with Ubbelohde viscosity of 0.42 measured in DMAc. Sodium

hexafluorophosphate (NaPF_6) was obtained from Beijing Ouhe Technology Co.Ltd. Potassium fluoride (KF) and N, N-Dimethylformamide (DMF) were obtained from Aladdin and Beijing Chemical Reagent Corporation, respectively. Polyethylene glycol (PEG) and polyethylene oxide (PEO) were from Alfa Aesar, bovine serum albumin (BSA, $M_w = 68 \text{ KDa}$) was from Roche, Store at 4°C . All the chemicals were of analytical grade and were used without any further purification.

2.2 Preparation and characterization of polymers

Quaternized cardo poly(arylene ether sulfone)s ionomer (QPES-I) were prepared according to literature[16]. QPES-X ($X=\text{F}, \text{PF}_6$) were obtained using the counterion exchange method. The inorganic salts were dissolved in deionized water. QPES-I was added into the salt solution and stored at 40°C for 24h to allow the exchange of iodide to the target anions, which was then filtered and washed. This procedure was repeated three times to ensure the complete exchange of anions.

FI-IR spectra were collected on a Bio-Rad Digilab Division FTS-80 FT-IR spectrometer to reflect the chemical structure of QPES-X. Ion chromatography was conducted on an ICP-1000 spectrometer to determine the fluoride content in QPES- PF_6 .

2.3 Fabrication of asymmetric flat sheet ultrafiltration membranes

The asymmetric flat sheet ultrafiltration membranes were fabricated by employing the classical immersion-precipitation phase inversion method. The membrane preparation process was performed as follows: polymer blends with determined mixing ratio and polymer concentration were dissolved in DMF at 70°C for about 10h, filtered and degassed under vacuum, and aged at 30°C for 12h. The transparent polymer solution was cast onto the polyester nonwoven fabric and was spread by a casting knife with a certain gap of $150 \mu\text{m}$, and then the virgin membrane made of polymer solution was immediately immersed into deionized water ($25\pm 2^\circ\text{C}$) for the phase inversion process. The resulting membranes were washed several times with deionized water and stored in deionized water more than 24h prior to testing.

2.4 Ultrafiltration experiments

Flat sheet ultrafiltration membranes were tested using a cross-flow filtration cell apparatus at 25 °C, the effective area of the membranes was 23.7 cm². Initially, the membrane was compacted at 0.2 MPa for 40 min. Next, the pressure was lowered to 0.1 MPa and the ultrafiltration experiments were carried out at this pressure. A protein solution of 1000 ppm BSA was used as the standard solution for the rejection studies. The pure water flux (F) could be calculated from:

$$F = \frac{V}{A \times t} \quad (1)$$

where V is the permeate volume (L), A is the effective membrane area (cm²), and t is the filtration time (h). Protein rejection (R) is calculated as follow:

$$R = \left[1 - \frac{C_p}{C_f} \right] \times 100\% \quad (2)$$

where C_p and C_f are the concentrations of BSA in the permeate and feed solution, respectively. The BSA concentration of the permeation and feed solution were determined using a UV-vis spectrophotometer measuring absorbance at 278 nm.

2.5 Characterization of ultrafiltration membranes

The membrane morphology was characterized by a scanning electron microscope (SEM, XL 30 ESEM FEG, FEI Company). The membranes were peeled off from the supporting polyester fabric, frozen in liquid nitrogen, and then fractured carefully to obtain a clean break surface for cross-section observation. The specimens for surface observation were fixed on a metal support, freeze-dried and gold sputtered before testing.

Microscopic investigation of the surface roughness of the obtained membranes was conducted by an atomic force microscopy (AFM, Dimension Icon SPM, Bruker). All samples were freeze dried under vacuum for about 5 hours before testing in order to maintain the archetypal surface morphology of the membranes. Small pieces of the prepared membranes (approximately 1 cm²) were attached on a silicon wafer and imaged in tapping mode in air.

The chemical compositions of the membrane surfaces were recorded by X-ray photoelectron spectroscopy (XPS, ESCALAB 280 system), employing Al/Kα ($h\nu$

=1486.6 eV) as the radiation source. Nitrogen spectra were collected ten times over a range of 392.2–412.2 eV, (step size: 0.1) in order to give a quantitative analysis of nitrogen on the membrane surface. The survey data was collected one time over a range of 0–1200 eV, (step size: 1). When compared with PSF, nitrogen is the unique element of QPES-X series ionomers, therefore nitrogen content of the surface was employed as an indicator to illustrate the segregation phenomenon of QPES-X on membrane surface. The nitrogen content on membrane surface was employed to evaluate the near-surface coverage ratio $\varphi_s(\%)$ of QPES-X on the asymmetric membrane surface [17] using the following equation.

$$\varphi_s(\%) = \frac{W(N)/28}{W(N)/28 + (1 - \frac{W(N)}{28} * M_{QPES})/M_{PSF}} \quad (3)$$

where $W(N)$ is the nitrogen content on membrane detected by XPS, M_{QPES} is the molecular weight of each repeat unit in QPES-X, and M_{PSF} is the molecular weight of each repeat unit in PSF.

The porosity of the wet membranes was determined by gravimetric method[18]. The membranes were peeled from the supporting fabrics, the excess water was removed using filter paper, and the wet weight was measured. The wet membranes were then dried at 80°C for 6 h prior to measuring the dry membrane weight. The equation is defined as following:

$$\varepsilon(\%) = \frac{W_w - W_d}{\rho_w A \delta_0} \quad (4)$$

where W_w (g) and W_d (g) are the weight of wet and dry membrane, respectively. ρ_w (g/cm³) is the density of pure water, A (cm²) is the effective membrane area, and δ_0 (cm) is the thickness of the wet membrane(without the non-woven fabrics).

The streaming potential measurement was carried out using Ag/AgCl electrodes in a 0.01M KCl background electrolyte solution. The pH of the solution was accommodated using the 0.1M HCl and 0.1M NaOH acid-base adjust-pair. The surface zeta potential ξ was calculated by the Helmholtz-Smoluchowski equation(5):

$$\xi = \frac{\Delta E}{\Delta P} \frac{\eta \kappa}{\varepsilon \varepsilon_0} \quad (5)$$

where ΔE is the streaming potential of the membrane, ΔP is the applied pressured, ε is the dielectric constant of the streaming solution, ε_0 is the vacuum permittivity, η is the

solution viscosity and κ is conductivity of bulk solution.

2.6 Membrane rejections for PEG and PEO

Solute separation experiment conducted in aqueous feed solutions containing 100 ppm of neutral solutes (PEG or PEO) with different molecular weights were employed to determine the mean effective pore size and molecular weight cutoff (MWCO) of ultrafiltration membranes. The rejection of solutes was determined according to the concentration of solutes in the feed and permeates, which were analyzed by a total organic carbon (TOC) analyzer (TOC-VCPH SHI-MADZU). The Stokes radius (d_s) of a neutral solute at 50% rejection rate could be used to express the mean effective pore size (μ_p), and the molecular weight of that at 90% rejection rate were used to present the MWCO of the blended membranes. The μ_p and d_s of blended membranes were calculated using Equation (6) [19].

$$d_s = 10.44 \times 10^{-12} \times M_{\text{PEO}}^{0.587} \quad (6)$$

2.7 Antimicrobial activity of the blended membranes

The antimicrobial activity of QPES-F/PSF blended membranes was tested against the gram negative bacteria *Escherichia coli*. (ATCC 1655) and evaluated using the plate counting method. The bacteria strains were cultivated in liquid media by placing in a shaking incubator at 37°C for 12h. Then the colonies were centrifuged and resuspended in normal saline solution for about 10^9 colony forming units per milliliter (CFU mL⁻¹) and diluted to 10^6 CFU mL⁻¹. Subsequently, 5μm diluted bacterial suspension was added to a 1cm×1cm dimension membrane surface and it was covered with another membrane in the same size, the sandwiched bacteria and membranes were placed in separated culture dish to sterilize for 30min. Finally, the membranes were washed with saline solution and then 100μm of the solution were coated on BHI agar and placed in an incubator at 37°C for 24h. The used membranes were sterilized by ultraviolet radiation for 30min previously. As a control, the antimicrobial tests were also performed for PSF ultrafiltration membrane.

3. Results and discussion

3.1 Preparation and characterization of polymers

QPES-F and QPES-PF₆ were obtained by counterion exchange between QPES-I and KF, QPES-I and NaPF₆, respectively. No visible changes of polymers were observed after the counterion exchange experiment.

The FT-IR spectra of QPES-X are shown in Fig.1. All polymers exhibited characteristic adsorption at 1244 cm⁻¹(Ar-O-Ar), 1150 cm⁻¹ (S=O=S), and 1689 cm⁻¹ (N-phthalimide carbonyl). Strong bands are observed at 557 cm⁻¹ and 830 cm⁻¹ are assigned to the stretching and bending vibration of the P-F bond, respectively.

Fig.1 FT-IR spectra of polymeric materials

In order to give a quantitative analysis of the anion exchange process, ion chromatography was employed to detect the fluoride mass fraction in the QPES-PF₆. The ion exchange ratios for QPES-PF₆ were above 97%, which implied that the anion exchange experiment was successful.

3.2 Preparation and characterization of ultrafiltration membrane

3.2.1 Preparation of blended QPES-X/PSF membrane

Ultrafiltration membranes were prepared by blending QPES-X (X=F, I, PF₆) with PSF in DMF at polymer concentration of 18w% and predetermined blending ratio. Membrane casting condition is at 40% relative humidity and in room temperature (25±2°C), with exposure time of 5s and coagulation bath temperature of 25°C.

3.2.2 Hydrophilicity of blended QPES-X/PSF membrane

The water contact angles of asymmetric membranes were measured and the

results are illustrated in Fig.2. The water contact angle of membrane illustrates its hydrophilicity; the lower the water contact angle, the higher the hydrophilicity of membrane. As shown in Fig.2, blending PSF with QPES-X bearing different counterions generated membranes with different hydrophilicity, which is in the order of QPES-PF₆ < QPES-I < QPES-F.

Fig.2 Contact angle of asymmetric membrane

3.2.3 The morphology of blended QPES-X/PSF membrane

The cross section morphology and surface morphology of the QPES-X/PSF series blended flat sheet ultrafiltration membranes are showed in Fig.3(a-h). The QPES-PF₆/PSF membrane (Fig.3a) shows a relatively tight and uniform sponge-like structure, which is similar to the PSF ultrafiltration membrane (Fig.3b). QPES-I/PSF blended membrane (Fig.3c) shows an obviously asymmetric structure with a thick sponge-like top layer, consisting of the polymer matrix and a sublayer containing dispersed tear-like macrovoids. The QPES-F/PSF blended membrane (Fig.3d) presented the typical finger-like cross-section morphology with a dense top layer and a porous sublayer. A similar structure has been found by incorporating hydrophilic poly(sodium 4-sryrene sulfonate) grafted SiO₂ (PSS-SiO₂) in polyethersulfone to fabricate negatively charged loose nanofiltration membranes[20]. The diversity in membrane morphology of QPES-X/PSF may be explained by the hydrophilicity of the counterions and the kinetics of the immersion precipitation phase inversion

method. The introduction of a hydrophilic component by a second polymer in the blending method has a positive effect on the hydrophilicity of the membrane casting solution. The motivation of adding QPES-F into PSF is to improve the hydrophilicity of the casting solution. The hydrophilic component has great affinity with water and will accelerate the inflow rate of nonsolvent into the cast membrane. This acceleration will boost the exchange rate of solvent and nonsolvent at the interface between the casting solution and coagulation bath, and then trigger the instantaneous liquid-liquid demixing, and polymer-rich phase and polymer-lean phase to develop[21-23]. The polymer-rich phase then formed the porous pore walls and the polymer-lean phase gave rise to the finger-like pores or larger macrovoids, membrane with a relatively porous structure was prepared. Blending the hydrophobic QPES-PF₆ with PSF did not affect the hydrophilicity of the casting solution. The QPES-PF₆/PSF casting solution has low affinity with water and the delayed solvent-nonsolvent exchange would occur during the phase inversion process, leading to the formation of a tight sponge-like structure [24, 25].

Fig.3 The cross section morphology, surface morphology and three-dimensional images of ultrafiltration membranes. a), b), c) and d) are the cross section morphology, e), f), g) and h) are the surface morphology, i), j), k) and l) are the three-dimensional

images. a), e) and i) for QPES-PF₆/PSF, b), f) and j) for PSF, c), g) and k) for QPES-I/PSF, d), h) and l) for QPES-F/PSF.

In conclusion, the cross section morphology of blended membranes changed gradually from a tight sponge-like structure observed for QPES-PF₆/PSF membrane, to a thick sponge-like top layer and tear-like macrovoids in sublayer for QPES-I/PSF membrane, to a dense and thinner skin layer and looser finger-like structure for QPES-F/PSF membrane. The variation of membrane morphology is in accordance with the hydrophilicity of QPES-X, from QPES-PF₆, QPES-I to QPES-F. Membranes prepared by blending PSF with hydrophobic QPES-PF₆ have thick and dense structure while with hydrophilic QPES-F have loose and opening structure.

The surface morphology of the asymmetric membranes are shown in Fig.3(e-h). The QPES-X/PSF (X=I, PF₆) and PSF membrane have a smooth surface structure (Fig.3e-g), whereas QPES-F/PSF membrane has a nodular surface structure (Fig.3h). In contrast to I⁻ and PF₆⁻ anions, F⁻ anions are small, electron-ample in density, therefore the quaternary ammonium groups (QA⁺) and F⁻ ions are held tightly together by the strong Coulombic forces, known as an ionic bond, in QPES-F. The cation-anion pair between QA⁺ and F⁻ is an intimate ion-pair. Barrett et al. [26] observed F⁻ has the biggest average ionic binding energy with the target alkali cations among all the halogen ions, and the displacement of the smallest F⁻ counterion was in a relative rate of 53% of that of the larger I⁻. These phenomena suggest that F⁻ were tightly bound to the QA⁺ group, so the exchange of I⁻ to F⁻ can be done in high efficiency and conversion rate. Additionally, F⁻ ion can form a hydrogen bond with water, which is the strongest among all the hydrogen bonds. Considering these two considerations, F⁻ may attach to QA⁺ through an ionic bond and to water by hydrogen bond. In the phase inversion process, the QA⁺-F⁻ ion-pair is predicted to mobilize toward the membrane surfaces or pore walls more readily than other counterion pairs (QA⁺-I⁻ pair and QA⁺-PF₆⁻ pair), because of F⁻ has the greatest affinity for water. The flexible side chains containing QA⁺-F⁻ ion-pairs may then precipitate prior to PSF and aggregate to form minor nuclei because of its affinity for water. The nuclei grow but cannot be dissolved into the coagulation water bath when the main phase inversion

process takes place. The nuclei remain on the membrane surface and coexisted with PSF because of chain entanglement in the polymer solution. As a result, a nodule surface structure was achieved on the QPES-F/PSF membrane. The same spherical structure on microfiltration membrane surfaces has been observed through a salt-induced phase inversion process by the Jin group [27]. In Jin's study, sodium chloride was added into the coagulation bath to function as nucleating agents at the interface of two liquids during the solvent diffusion to induce the assembly of PAA-g-PVDF micelles. Then the micelles assembled at the interface leading to spherical nodules on the membrane surface, providing the membrane with superhydrophilic and under-water superhydrophobic properties.

AFM is an effective way for study membrane surface morphology. The three-dimensional images are shown in Fig.3(i-l). QPES-F/PSF blended membranes showed the highest root mean square roughness (RMS) of 38.1 nm, far more than that of PSF membrane, QPES-I/PSF and QPES-PF₆/PSF blended membranes, suggesting a nodular structure on membrane surface.

3.2.4 The performance of blended QPES-X/PSF membrane

Fig.4 Performance of asymmetric membrane

The pure water flux and BSA rejection of the membranes are plotted in Fig.4. The water flux of the blended membrane ranked in the order of QPES-PF₆ < QPES-I < QPES-F, whereas the rejection ranked in a reverse order of that of membrane flux.

The QPES-F/PSF membrane has the highest flux of $2163 \text{ L m}^{-2} \text{ h}^{-1}$ and BSA rejection of 93%, while QPES-PF₆/PSF membrane had the lowest flux of $67 \text{ L m}^{-2} \text{ h}^{-1}$ and BSA rejection of 100%, and QPES-I/PSF membrane had a flux of $995 \text{ L m}^{-2} \text{ h}^{-1}$ and BSA rejection of 94%, which is in the middle of the performance of QPES-F/PSF and QPES-PF₆/PSF membrane. The water flux of the membranes is correlated to its hydrophilicity and morphology. Membranes with high hydrophilicity and loose structure have higher water flux, whereas membranes with low hydrophilicity and tight structure have lower water flux. With the highest hydrophilicity and loosest structure, the QPES-F/PSF membrane possesses the highest flux; QPES-I/PSF membrane comes after it with the mediate flux and the QPES-PF₆/PSF membrane with tight structure and being hydrophobic, has the lowest flux. The flux of QPES-PF₆/PSF membrane is lower than that of PSF membrane, attributed to the hydrophobic nature of QPES-PF₆, which inhibits the penetration of water into the nano-sized pores[28]. The rejection of membrane is mainly determined by the skin layer of membrane. The as-prepared three kinds of blended membranes all have integrally skinned surface structure, which determines the protein rejection to a higher extent, therefore they have similar rejection for proteins, from 93% to 99%.

3.2.5 Zeta potential of blended QPES-X/PSF membrane

Fig.5 Zeta potential of QPES-F/PSF and QPES-I/PSF membrane at the 15% QPES-X content at pH 4.0-10.0.

In order to better understand the charged properties of the membrane surfaces, the zeta potential of blended membrane was measured in a KCl aqueous solution with varied pH and is plotted in Fig.5. The blended membrane had positive charge at the pH =7. The QPES-F/PSF membrane at a 15% blending ratio had a zeta potential of 25 mV, higher than 15 mV measured for the QPES-I/PSF blended membrane. This data suggests QPES-F has great affinity with water, and the affinity between QPES-F and water facilitates the aggregation of QPES-F toward the membrane surface during the phase inversion process and much charged side chains of the QPES-F was assembled on the membrane surface. At higher pH values (pH=10), the zeta potential was negative, which could be ascribed to the dissociation of phenolic hydroxyl group at the end of QPES-X chains.

3.2.6 Chemical analysis of blended QPES-X/PSF membrane

Fig.6 Chemical analysis of the QPES-X/PSF blended membranes. a) Chemical structure of QPES-X. b) XPS spectra and c) the N1s high-resolution spectra of asymmetric membrane surface.

XPS is a sensitive technique to measure elemental composition and chemical binding information of materials. The XPS spectra and nitrogen content of the membrane surface are shown in Fig.6 and Table1. From Fig.6c, the high-resolution XPS scan for nitrogen 1s indicated the presence of ternary amines (398.4eV) and

quaternary ammonium groups (402.2eV), and the nitrogen content, near-surface chain coverage information of membranes are shown in Table1. The surface nitrogen content was higher than the average nitrogen content, and the near-surface coverage ratio of QPES-F chains were higher than that of QPES-I and QPES-PF₆, indicating the aggregation of charged flexible side chains of QPES-X on the membrane surface during the phase inversion process, in consistent with the results of zeta potential. The aggregation trend of charged flexible side chains is a result of the minimum of the interface free energy between hydrophilic polymer and nonsolvent in the phase inversion process. The greater the affinity between QPES and water is, the greater the surface nitrogen content is.

Table1 Surface nitrogen composition (mass fraction) and near-surface chain coverage of polyelectrolyte (ϕ_s) of the asymmetric membrane.

Sample	Nitrogen content (%)		ϕ (%)		ϕ_s (%)
	^a Surface content	^b Average content	ϕ_{QPES}	ϕ_{PSF}	
QPES-F/PSF	2.01	0.646	7.18	12.04	37.35
QPES-I/PSF	1.89	0.554	6.75	11.03	37.97
QPES-PF ₆ /PSF	1.74	0.540	6.21	13.73	31.16

^aSurface content of nitrogen was determined by XPS results. ^bAverage content of nitrogen was calculated on account of stoichiometry and blending ratio of ultrafiltration membranes, based on the hypothesis that all polymers were uniformly distributed in membrane matrix.

3.3 QPES-F content on the membrane morphology and performance

Fig.7 Cross section morphology of ultrafiltration membranes with a) 5%, b) 10% and c) 15% QPES-F.

The influence of QPES-F content on the membrane morphology and

performance are shown in Fig.7 and Fig.8, respectively. As shown in Fig.8, the cross section morphology is correlated to QPES-F content in polymer solution. The **blended membrane** presents distinct finger-like cross section morphology with a dense top layer and a porous sublayer. As the QPES-F fraction increased, the membrane skin layer becomes thinner, the sublayer becomes more porous, and the supporting layer shows thinner pore walls. The QPES-F/PSF blended polymer solutions are thermodynamically unstable, resulting from the large variation between the polarity of the quaternary ammonium groups and PSF backbone; increasing the QPES-F fraction results in a more unstable polymer solution. During the phase inversion process, instantaneous phase separation may occur, leading to porous finger-like structures in the membrane matrix. On the other hand, the kinetic aspects of the phase inversion process are also related QPES-F content. As the hydrophilicity of polymer solution increases with increasing QPES-F concentration, the water diffusion rate increases during the separation process and the solvent-nonsolvent diffusion rate is accelerated. This results in a more polymer-lean phase, then developing to a porous structure with thinner skin layer, and finger-like pore structure.

Fig.8 Performance of membranes at different QPES-F content

The ultrafiltration performance of **blended membranes** was shown in Fig.8. The water flux of the **blended membranes** increased from 440 L m⁻² h⁻¹ to 2163 L m⁻² h⁻¹ as the composition of QPES-F increased from 5% to 15% in polymer casting solution,

whereas the protein rejection for BSA decreased from 96 % to 93%. The addition of QPES-F in the casting solution greatly improved the membrane performance, because QPES-F accelerated the phase inversion process, membrane with a loose and porous structure was formed. Membranes with higher water flux exhibited a lower rejection, supporting the trade-off relationship [29] between flux and rejection. Membranes prepared at the blending ratio of 15% had the best performance, and this result is used for the orthogonal experimental design for finding of optimum membrane preparation conditions.

3.4 Membrane porosity and molecular weight cutoff (MWCO)

Fig.9 (a)The porosity, (b)PEG and PEO rejection of blended membranes.

The porosity of blended membranes was investigated by the gravimetric method via measuring the dry-wet weight of membrane; the results are depicted in Fig.9a. When compared with PSF membrane, the porosity of QPES-F/PSF blended membranes is much higher, but it did not vary greatly with the amount of QPES-F in the casting solution. This phenomenon suggested that QPES-F played as a pore forming agent during the phase inversion process and triggered pore formation in membrane matrix. Since QPES-F was a hydrophilic polyelectrolyte, and water-insoluble material, the pore forming mechanism of this material was distinct from that of other water-soluble materials. Z. Jiang [30] developed a novel mechanism to describe the pore forming process for water-insoluble materials. Firstly, during the formation of a dense skin layer, the hydrophilic side chains of QPES-F accelerate the diffusion of nonsolvent into the sublayer and nascent voids form in the

sublayer. Meanwhile, the water-insoluble material may migrate from polymer-rich to polymer-lean environment, due to its great affinity with water, then delay the solidification of polymer-rich phase to form fully developed macrovoids. Therefore the number of pores in membrane sublayer increased along with the increasing of QPES-F content in the casting solution. The porosity of the blended membrane did not vary greatly with the amount of QPES-F in the casting solution. This could be attributed to the entrapment of water molecules in the membrane matrix through intermolecular hydrogen bonding interactions with quaternary ammonium groups and fluoride ions in QPES-F [8]. The content of bound water in the membrane matrix increased with increasing QPES-F content, and bound water could not be removed from membrane in the drying process.

Table 2 The mean effective pore size (μ_p) and MWCO of membranes (determined by PEG/PEO separation experiment).

QPES-F content	5%	10%	15%
μ_p (nm, R=50%)	5.493	6.990	10.651
d_s (nm, R=90%)	8.964	16.242	18.187
MWCO (KDa)	99.53	273.98	332.20

The mean effective pore size and molecular weight cutoff (MWCO) of blended membranes were determined by the filtration experiment of PEG and PEO. Fig.9b shows the PEG and PEO rejections of blended membranes as a function of their molecular weight, and the μ_p and d_s of blended membranes were summarized in Table 2. The MWCO of QPES-F/PSF blended membranes was a function of QPES-F content, which increased from 99.53KDa for membrane having 5% QPES-F content, 273.98 KDa for 10% QPES-F content to 332.20 KDa for 15% QPES-F content. Membrane has higher QPES-F content offering a higher MWCO, suggesting that the incorporation of QPES-F could lead to an increment of the mean pore radius of blended membranes.

3.5 Antimicrobial activity of the blended membranes

Fig.10 Antimicrobial activities of QPES-F/PSF series membranes against *E.coli*. with various QPES-F content: a) pure PSF, b) 5%, c) 10% and d) 15%.

The antimicrobial activity of water treatment membrane is a significant ingredient for improving the performance and extending the lifetime of membranes [31, 32]. The antimicrobial activity of PSF **blended membranes** containing different amount of QPES-F were evaluated against *E.coli*. And the results are shown in **Fig.10**. **Fig.10(a)** is pure PSF membrane used as a control; **Fig.10(b-d)** are the antimicrobial activity results of **blended membranes** at QPES-F concentration of 5-15%. The PSF membrane and **blended membrane** having 5% QPES-F showed no expressive antibacterial activity against *E.coli*; the membrane containing 10% and 15% QPES-F demonstrate a moderate antibacterial activity against *E. coli*. QPES-F/PSF 15% **blended membrane** has a sterilizing rate of 73% after 30min contact with bacteria when compared with the PSF control, suggesting that the positively charged membrane was active towards the gram negative bacteria *E. coli*.

4. Conclusions

The hydrophilicity of QPES-X is counterion-dependent and can be tuned by exchanging the counterions of quaternary ammonium groups. The original iodine ion (I⁻) in QPES was replaced by hexafluorophosphate ion (PF₆⁻) and fluoride ion (F⁻) **via** the counterion exchange method. The obtained QPES-PF₆ and QPES-F were

hydrophobic and hydrophilic, respectively. Then three kinds of QPES-X polymers were employed to blend with PSF for the fabrication of asymmetric ultrafiltration membranes via the classical nonsolvent induced phase inversion method (NIPS), and the prepared membranes showed variation in morphology and performance. At a polymer concentration of 18wt% and QPES-F content of 15%, QPES-F/PSF blended membrane presented finger-like cross-section morphology with a dense top layer, having the highest water flux of $2163 \text{ L m}^{-2} \text{ h}^{-1}$ and a moderate BSA rejection of 93%. The QPES-I/PSF blended membrane had an obviously asymmetric structure with thick sponge-like top layer and dispersed tear-like macrovoids in the sublayer, having a flux of $955 \text{ L m}^{-2} \text{ h}^{-1}$ and rejection of 94%. The QPES-PF₆/PSF membrane showed a relatively tight and uniform sponge-like structure, having the lowest flux of $67 \text{ L m}^{-2} \text{ h}^{-1}$ and highest rejection of 100%. The results suggest that QPES-F/PSF blended membrane had the best performance, and membrane preparation conditions on membrane performance and morphology were investigated. The optimal preparation conditions were achieved at a polymer concentration of 18wt% and QPES-F content of 15%. Then the antimicrobial activity studies of the blended membranes revealed that membranes with 15% QPES-F content has a sterilization rate of 73% towards *E. coli*. compared with pure PSF ultrafiltration membrane, the hydrophilic membrane with antimicrobial properties was very attractive in waste water treatment by restrict microbe growth and attachment on membrane surface.

Acknowledgements

The authors gratefully acknowledge the National Basic Research Program of China (no. 2015CB655302), the National Science Foundation of China (no. 51473163, 51503199 and 21374116) and the Development of Scientific and Technological Project of the Jilin Province (Nos. 20160101316JC) for financial support.

Nomenclature

F	Pure water flux
R	Protein rejection
C_p	Concentrations of solute in the permeate

C_f	Concentrations of solute in the feed solution
V	The permeate volume
t	Filtration time
ε	Porosity of membrane (Equation(3))
W_w	Weight of wet membrane
W_d	Weight of dry membrane
ρ_w	Density of pure water
A	The effective membrane area
δ_0	The thickness of the membrane
ζ	Zeta potential
ΔE	Streaming potential of membrane
η	Solution viscosity
κ	Conductivity of bulk solution
ε	Dielectric constant of streaming solution(Equation(5))
ε_0	Vacuum permittivity
μ_p	mean effective pore size
d_s	Stokes radius
BSA	Bovine serum albumin
BHb	Bovine Hemoglobin
SEM	Scanning electron microscope
XPS	X-ray photoelectron spectroscopy
FRR	Flux recovery ratio
TOC	total organic carbon
MWCO	molecular weight cutoff
PSF	Polysulfone
PBS	phosphate buffer solutions
QPES	Quaternized Cardo poly(arylene ether sulfone)s
DMF	N,N-Dimethylformamide
NIPS	nonsolvent-induced phase inversion

References

- [1] R. Han, S. Zhang, X. Jian, Effect of additives on the performance and morphology of copoly (phthalazinone ether sulfone) UF membrane, *Desalination*, 290 (2012) 67-73.
- [2] Q. Li, Q.-y. Bi, H.-H. Lin, L.-X. Bian, X.-L. Wang, A novel ultrafiltration (UF) membrane with controllable selectivity for protein separation, *Journal of Membrane Science*, 427 (2013) 155-167.
- [3] J.-n. Shen, D.-d. Li, F.-y. Jiang, J.-h. Qiu, C.-j. Gao, Purification and concentration of collagen by charged ultrafiltration membrane of hydrophilic polyacrylonitrile blend, *Separation and Purification Technology*, 66 (2009) 257-262.
- [4] S. Mozia, D. Darowna, R. Wróbel, A.W. Morawski, A study on the stability of polyethersulfone ultrafiltration membranes in a photocatalytic membrane reactor, *Journal of Membrane Science*, 495 (2015) 176-186.
- [5] G.R. Guillen, G.Z. Ramon, H.P. Kavehpour, R.B. Kaner, E.M.V. Hoek, Direct microscopic observation of membrane formation by nonsolvent induced phase separation, *Journal of Membrane Science*, 431 (2013) 212-220.
- [6] A. Rahimpour, S.S. Madaeni, S. Ghorbani, A. Shockravi, Y. Mansourpanah, The influence of sulfonated polyethersulfone (SPES) on surface nano-morphology and performance of polyethersulfone (PES) membrane, *Applied Surface Science*, 256 (2010) 1825-1831.
- [7] X. Li, S. De Feyter, I.F.J. Vankelecom, Poly(sulfone)/sulfonated poly(ether ether ketone) blend membranes: Morphology study and application in the filtration of alcohol based feeds, *Journal of Membrane Science*, 324 (2008) 67-75.
- [8] M. Kumar, D. McGlade, M. Ulbricht, J. Lawler, Quaternized polysulfone and graphene oxide nanosheet derived low fouling novel positively charged hybrid ultrafiltration membranes for protein separation, *RSC Adv.*, 5 (2015) 51208-51219.
- [9] C. Zhao, J. Xue, F. Ran, S. Sun, Modification of polyethersulfone membranes – A review of methods, *Progress in Materials Science*, 58 (2013) 76-150.

- [10] L. Wang, Y. Lin, B. Peng, Z. Su, Tunable wettability by counterion exchange at the surface of electrostatic self-assembled multilayers, *Chemical communications*, (2008) 5972-5974.
- [11] O. Azzaroni, A.A. Brown, W.T.S. Huck, Tunable Wettability by Clicking Counterions Into Polyelectrolyte Brushes, *Advanced Materials*, 19 (2007) 151-154.
- [12] L. Wang, B. Peng, Z. Su, Tunable wettability and rewritable wettability gradient from superhydrophilicity to superhydrophobicity, *Langmuir : the ACS journal of surfaces and colloids*, 26 (2010) 12203-12208.
- [13] C. Yao, X. Li, K.G. Neoh, Z. Shi, E.T. Kang, Surface modification and antibacterial activity of electrospun polyurethane fibrous membranes with quaternary ammonium moieties, *Journal of Membrane Science*, 320 (2008) 259-267.
- [14] F. Yao, G. Fu, J. Zhao, E. Kang, K. Neoh, Antibacterial effect of surface-functionalized polypropylene hollow fiber membrane from surface-initiated atom transfer radical polymerization, *Journal of Membrane Science*, 319 (2008) 149-157.
- [15] Q. Zhang, Q. Zhang, J. Wang, S. Zhang, S. Li, Synthesis and alkaline stability of novel cardo poly(aryl ether sulfone)s with pendent quaternary ammonium aliphatic side chains for anion exchange membranes, *Polymer*, 51 (2010) 5407-5416.
- [16] Q. Zhang, S. Zhang, L. Dai, X. Chen, Novel zwitterionic poly(arylene ether sulfone)s as antifouling membrane material, *Journal of Membrane Science*, 349 (2010) 217-224.
- [17] Y. Wang, Y. Su, Q. Sun, X. Ma, X. Ma, Z. Jiang, Improved permeation performance of Pluronic F127–polyethersulfone blend ultrafiltration membranes, *Journal of Membrane Science*, 282 (2006) 44-51.
- [18] V. Vatanpour, S.S. Madaeni, R. Moradian, S. Zinadini, B. Astinchap, Novel antibifouling nanofiltration polyethersulfone membrane fabricated from embedding TiO₂ coated multiwalled carbon nanotubes, *Separation and Purification Technology*, 90 (2012) 69-82.
- [19] P. Zhong, X. Fu, T.S. Chung, M. Weber, C. Maletzko, Development of thin-film composite forward osmosis hollow fiber membranes using direct sulfonated

polyphenylenesulfone (sPPSU) as membrane substrates, *Environmental science & technology*, 47 (2013) 7430-7436.

[20] N.G. Lixin Xing, Yatao Zhang, Haoqin Zhang, Jindun Liu, A negatively charged loose nanofiltration membrane by blending with poly (sodium 4-styrene sulfonate) grafted SiO₂ via SI-ATRP for dye purification. , *Separation and Purification Technology*, (146 (2015) 50–59).

[21] K. Wang, X. Lin, G. Jiang, J.Z. Liu, L. Jiang, C.M. Doherty, A.J. Hill, T. Xu, H. Wang, Slow hydrophobic hydration induced polymer ultrafiltration membranes with high water flux, *Journal of Membrane Science*, 471 (2014) 27-34.

[22] A. Martín, J.M. Arsuaga, N. Roldán, J. de Abajo, A. Martínez, A. Sotto, Enhanced ultrafiltration PES membranes doped with mesostructured functionalized silica particles, *Desalination*, 357 (2015) 16-25.

[23] W.J. Lau, A.F. Ismail, Theoretical studies on the morphological and electrical properties of blended PES/SPEEK nanofiltration membranes using different sulfonation degree of SPEEK, *Journal of Membrane Science*, 334 (2009) 30-42.

[24] P. Qin, X. Hong, M.N. Karim, T. Shintani, J. Li, C. Chen, Preparation of poly(phthalazinone-ether-sulfone) sponge-like ultrafiltration membrane, *Langmuir : the ACS journal of surfaces and colloids*, 29 (2013) 4167-4175.

[25] A.L. Peiyong Qin, Cuixian Chen, Preparation of a poly(phthalazine ether sulfone ketone) membrane with propanedioic acid as an additive and the prediction of its structure., *Journal of Applied polymer science*, (2015, DOI: 10.1002/APP.41621).

[26] O.M.a.C.J. Barrett, Effects of Charge Density and Counterions on the Assembly of Polyelectrolyte Multilayers, *Journal of physics chemistry B*, 107 (2003) 2525-2530.

[27] W. Zhang, Y. Zhu, X. Liu, D. Wang, J. Li, L. Jiang, J. Jin, Salt-induced fabrication of superhydrophilic and underwater superoleophobic PAA-g-PVDF membranes for effective separation of oil-in-water emulsions, *Angewandte Chemie*, 53 (2014) 856-860.

[28] J.-F. Blanco, J. Sublet, Q.T. Nguyen, P. Schaetzel, Formation and morphology studies of different polysulfones-based membranes made by wet phase inversion

process, *Journal of Membrane Science*, 283 (2006) 27-37.

[29] A. Mehta, A.L. Zydney, Permeability and selectivity analysis for ultrafiltration membranes, *Journal of Membrane Science*, 249 (2005) 245-249.

[30] X. Fan, Y. Su, X. Zhao, Y. Li, R. Zhang, J. Zhao, Z. Jiang, J. Zhu, Y. Ma, Y. Liu, Fabrication of polyvinyl chloride ultrafiltration membranes with stable antifouling property by exploring the pore formation and surface modification capabilities of polyvinyl formal, *Journal of Membrane Science*, 464 (2014) 100-109.

[31] K. Zodrow, L. Brunet, S. Mahendra, D. Li, A. Zhang, Q. Li, P.J. Alvarez, Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal, *Water research*, 43 (2009) 715-723.

[32] P.F. Andrade, A.F. de Faria, S.R. Oliveira, M.A. Arruda, C. Goncalves Mdo, Improved antibacterial activity of manifestation polysulfone membranes modified with silver nanoparticles, *Water research*, 81 (2015) 333-342.

Graphical abstract

RMS=11.8

RMS=5.77

RMS=38.1