Composite ultrafiltration membranes from polymer and its quaternary phosphonium-functionalized derivative with enhanced water flux

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Abstract

Novel ultrafiltration (UF) membranes were prepared by blending brominated poly(phenylene oxide) (BPPO) and its quaternary phosphonium derivative (TPPOQP-Br) as additive using a phase inversion method. The chemical structure and microstructure of the membranes were characterized by ATR-IR spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The XPS results indicated that the BPPO/TPPOQP-Br composite membranes exhibited an increase in the concentration of TPPOQP-Br from the top surface to the bottom surface. In contrast, the composite membranes prepared from BPPO and its quaternary ammonium derivative (TPPOQA-Br) showed an opposite concentration gradient of TPPOQA-Br. This was attributed to the difference in wettability and hydration
rate between TPPOQP-Br and TPPOQA-Br, leading to different membrane microstructure and chemical composition distributions. BPPO membrane showed a water flux of 215 L m\(^{-2}\) h\(^{-1}\) at 100 kPa and its molecular weight cut-off of PEG is 93.8 kDa; the corresponding values of the optimal BPPO/TPPOQP-Br membrane are 873 L m\(^{-2}\) h\(^{-1}\) and 111.3 kDa, both of which are better than those of BPPO/TPPOQA-Br with the similar additive loading (381 L m\(^{-2}\) h\(^{-1}\) and 150.2 kDa). Therefore, the addition of TPPOQP-Br significantly enhances the water permeability while maintaining the excellent rejection properties in the resultant UF membranes. This work extends the choice of the additives in the UF membrane fabrication, and further proves that the addition of hydrophobic and charged polymer with slow hydration property is an effective strategy for improving flux and anti-biofouling properties of UF membranes.

**Keywords:** Ultrafiltration membrane, Poly(phenylene oxide), Quaternary phosphonium, Quaternary ammonium, Additive gradient

1. Introduction

Ultrafiltration (UF) membranes have gained considerable attention in the field of waste water treatment [1-3], food processing [4, 5] and protein separation [6, 7], etc. Over the past half century, the non-solvent induced phase inversion technique has been widely used for preparing UF membranes [8]. Typically, the resultant asymmetrical membranes have a very thin, dense skin layer and a thick, macro-porous supporting layer. Until now, many different polymers such as polysulfone (PSf) [9], polyethersulfone (PES) [10], polyacrylonitrile (PAN) [11], cellulosics [12] and poly(vinylidene fluoride) (PVDF) [13] are used in the fabrication of UF membranes. To better meet the application needs, these membranes are required to possess high water permeability, excellent separation properties and good anti-fouling properties. To this end, many techniques have been developed, most of which focus on the
surface enrichment of the hydrophilic materials, including: (a) surface modification such as physical coating [14] or chemical [15] and photo-induced [16, 17] grafting functional materials especially containing hydrophilic groups onto the top surface of the pre-formed UF membranes, (2) addition of some hydrophilic modifiers in the casting solution that tend to segregate on the top surface during the phase inversion process [18-22]. Despite the fact that the anti-fouling properties can be improved after modification, it is still challenging to achieve both high water permeability and separation property.

Unlike the common modification via hydrophilization of UF membrane top surface, we have previously developed a new methodology of designing high-performance UF membranes for improving water permeability without losing separation properties [23]. In particular, composite membranes were prepared by blending polyethersulfone (PES) and tris(2,4,6-trimethoxyphenyl) polysulfone-methylene quaternary phosphonium chloride (TPQP-Cl). Because of the abundant benzene ring around the charged quaternary phosphonium, TPQP-Cl exhibited higher hydrophobicity and lower hydration than PES, and then it was pushed down to the bottom layer during the phase inversion process. Consequently, the resulting membrane showed an increase in TPQP-Cl concentration from the top surface to the bottom surface along with a unique macro-porous structure at the cross-section, both of which would positively affect the membrane water flux. To further explore this new methodology, it is important to investigate the membrane formation and properties using different polymer backbones; and it is also necessary to understand the effects of quaternary phosphonium functionalized additive in comparison with additives with other charged groups.

In this paper, we synthesized tris(2,4,6-trimethoxyphenyl) poly(phenylene oxide) methylene quaternary phosphonium bromide (TPPOQP-Br) and then prepared the BPPO/TPPOQP-Br composite UF membranes by blending TPPOQP-Br with BPPO. BPPO has good thermal and mechanical properties, and abundant highly reactive –CH₂Br groups [24], and it is commonly
available and has been used to prepare UF membranes with good performance [25].
Moreover, we also synthesized triethyl poly(phenylene oxide) methylene quaternary ammonium and then prepared BPPO/TPPOQA-Br UF membranes for comparison. The structures and filtration performance of membranes were investigated in detail.

2. Experimental

2.1. Materials

Brominated poly(phenylene oxide)BPPO (Mw= 60,500) with a benzyle substitution ratio of 0.57 was provided by Tianwei Membrane Co. Ltd. China. 1-methyl-2-pyrrolidone (NMP, 99.5%), tris(2,4,6-trimethoxyphenyl)-phosphine (TTMPP), triethylamine and polyethylene oxide (PEG) with difference molecular weight (35, 100, 200 kDa) were purchased from Sigma-Aldrich, Australia, and used without further purification.

2.2. Synthesis of tris(2,4,6-trimethoxyphenyl) poly(phenylene oxide)-methylene quaternary-phosphonium-bromide (TPPOQP-Br) [24]

To synthesize TPPOQP-Br, BPPO (1.72 g, an equivalent of 5 mmol –CH₂Br groups) and TTMPP (3.19 g, 6 mmol) were firstly dissolved in 80 mL NMP at room temperature. The mixture was kept stirring at 50 °C for 24 h, and then the resultant solution was cast onto a pre-cleaned glass plate for solvent evaporation at 40 °C. After being dried under vacuum at 40 °C for 48 h and washed thoroughly with water, the final TPPOQP-Br powder was obtained. The molecular structures of BPPO and TPPOQP-Br are shown in Figure 1.

2.3. Synthesis of triethyl poly(phenylene oxide) methylene quaternary ammonium-bromide (TPPOQA-Br)

TPPOQA-Br was prepared by the reaction of BPPO with triethylamine. 2 g of BPPO was firstly dissolved in 20 ml NMP and then 0.51g of triethylamine was added. After stirring for
24 h at room temperature, the solution was dried at 40 °C under vacuum for solvent evaporation, followed by washing with deionized water thoroughly to get the final TPPOQA-Br, whose molecular structure is shown in Figure 1.

2.3. Preparation of membranes

Commercial BPPO was used as the main component for membrane casting. 50 mL of polymer casting solution was prepared by blending 15wt% BPPO/NMP solution and 15wt% TPPOQP-Br/NMP solution (BPPO/TPPOQP-Br weight ratio are: 10/0, 9/1, 8/2 and 7/3, see Table 1). After ultrasonication the blending solution was left to stand overnight until no bubbles were observed. The membranes were prepared by using a Gardco® adjustable micrometer film applicator with a stainless steel blade (Paul N. Gardner Company, Inc. USA). 5 mL of the polymer solution was cast on a clean glass plate with a gap of 200 µm. Afterwards the membrane was solidified in a coagulation bath of deionized water for several minutes. The resulting membranes was washed thoroughly and soaked in the double deionized (DDI) water overnight before use. For comparison, the BPPO/TPPOQA-Br 8/2 was also prepared using the same procedures (see Table 1).

2.4. Membrane characterization

The membrane morphologies were observed by scanning electron microscopy (SEM). For the surface morphology observation, the membranes were fixed on a carbon tape and then sputter coated with roughly 0.5 nm iridium (Ir) layer and the images were recorded using a FEI Magellan 400 450 instrument at an accelerating voltage of 5 kV with different magnifications. For the cross-sectional morphology observation, the membrane samples were firstly immersed in DDI water for 24 h, then water on their surface was removed by filter paper carefully. Afterwards the samples were fractured in liquid nitrogen, followed by drying and
coating with Pt for SEM observation. Their images were then recorded using a FEI Nova NanoSEM instrument at an accelerating voltage of 5 kV with different magnifications.

X-ray photoelectron spectroscopy (XPS) was conducted with a Thermo Fisher X-ray photoelectron spectroscopy system (ESCALAB250). The X-ray radiation source was monochromatic Al Kα (1486.7 eV) and an incident angles and electron take-off angle of 54° and 90° respectively relative to the sample plane was employed, the elemental analysis from survey scans was used. The content of P or N element was used to determine the amount of quaternary phosphonium or quaternary ammonium groups, which were used to calculate the polymer compositions on the top and bottom surfaces on the basis of TPPOQP-Br and TPPOQA-Br. FTIR spectra of the membranes were measured using an ATR-FTIR (Perkin Elmer, USA) spectrometer in the range of 500-4000 cm⁻¹ at an average of 32 scans with a resolution of 4 cm⁻¹. The static contact angles of the dried and wet membranes were measured at room temperature using an OCA 15 EC contact angle measuring instrument (Dataphysics, Germany). A water drop with a volume of 5 µL was dropped onto the membrane with a microsyringe in air. At least 3 contact angles at different locations for each membrane were recorded with time. For wet membrane samples, they were firstly immersed in DDI water for 24 h. Then the membrane was cut into the desired shape and fixed on the glass, after that, the water on the surface of the membrane will be remove by the filter carefully. Then the test would be carried out immediately.

2.5. Pure water flux and molecular weight cut off experiments

Pure water flux of the membranes was tested at room temperature using a Sterlitech HP4750 dead-end stirred cell (Sterlitech Corporation, USA) with an inner diameter of 49 mm and an effective membrane area of 14.6 cm². The cell volume capacity is 300 ml and attached to a 5.0 L dispensing vessel. The membrane sample was first pre-compacted at 250 kPa for 1-2 h
until it reached a constant flux. Then the water flux was determined at different feed pressures (100, 150 and 200 kPa) by measuring the weight change with the time of the permeate water on a digital balance (PA2102C, Ohaus) interfaced with a computer. The data from the balance was logged to a computer using a program in LabView.

Polyethylene glycol (PEG) with molecular weights of 35, 100, 200 kDa were dissolved in deionized water to prepare 1 g L⁻¹ aqueous solutions to determine the molecular weight cut off (MWCO) and solute rejection. Rejection measurements were performed at a pressure of 100 kPa using the PEG solution as the feed solution. Thereafter, the concentrations of permeate and feed solution were measured via a total organic carbon analyzer (TOC-LCSH, Shimadzu, Japan) and the PEG rejection was calculated with the measured feed (Cᵢ) and permeate (Cᵢ) concentrations by the following equation (1):

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

(1)

All the samples were tested under the same conditions twice times. The pore size of the membrane was defined as the hydrodynamic diameter of PEG, which can be calculated from the MWCO of the membrane by the following equation (2) [26]:

\[ r = 0.0262(nm) \sqrt{MW \left( \frac{g}{mol} \right)} - 0.3(nm) \]  

(2)

where MW is the lowest molecular weight of the PEG molecule at a rejection of 90% in the measurements.

3. Results and discussion

3.1. FT-IR

Fig. 2 shows the FT-IR spectra of BPPO, TPPOQP-Br and the BPPO/TPPOQP-Br composite membranes. As the precursor, BPPO (Fig. 2 (a)) shows the characteristic band at 593 cm⁻¹ attributing to the C–Br stretching [27]. After reaction with TTMPP, two characteristic bands
of quaternary phosphonium groups at 920 and 950 cm\(^{-1}\) can be found in the spectrum of TPPOQP-Br (Fig. 2 (e)), indicating the successful introduction of quaternary phosphonium groups into the TPPOQP-Br membrane. Moreover, the band at 593 cm\(^{-1}\) disappears, indicating the ca. 100% conversion from BPPO to TPPOQP-Br. In their mixture, the characteristic peaks at 593, 920 and 950 cm\(^{-1}\) can be observed as expected in the spectrum of BPPO/TPPOQP-Br membrane (Fig. 2 (b)-(d)). From Fig. 2(b) to Fig. 2(d), the intensities of the 920 and 950 cm\(^{-1}\) bands increase while that of 593 cm\(^{-1}\) decreases, which agrees well the increasing TPPOQP-Br content from BPPO/TPPOQP-Br 9/1 to BPPO/TPPOQP-Br 7/3.

### 3.2. Scanning electron microscopy (SEM)

SEM was used to investigate the microstructure of membranes. Generally, a typical asymmetrical membrane structure with a thin nanoporous top layer, a macrovoid sub-layer and a macroporous bottom layer can be observed for all BPPO/TPPOQP-Br membranes (Fig. 3-5). However, it is obvious that the membrane microstructure is affected by the addition of TPPOQP-Br significantly. As shown in Fig. 3, at 10% TPPOQP-Br loading, the membrane surface pore size becomes larger on the top (skin) layer and the top layer becomes more porous as compared with the pristine BPPO. However, with increasing the amount of TPPOQP-Br from 10% to 30%, the membrane surface porosity and pore size decrease especially for the membrane with 30% TPPOQP-Br. For the cross-sectional morphology (Fig. 4), BPPO/TPPOQP-Br 9/1 membrane exhibits a closely connected finger-like macrovoids with large sizes as compared with the BPPO membrane. With further increasing the content of TPPOQP-Br, a cellular sponge-like structure with larger macrovoids is produced. Moreover, it can be seen from Table 3 that the thickness of the active layer and membrane themselves increase with increasing the TPPOQP-Br content. The similar phenomena were also observed in our previous work [23], which should be due to the different hydration rate
between BPPO and TPPOQP-Br. The hydrophobic TPPOQP-Br with slower hydration rate in the casting solution would be pushed down to the bottom layer during the phase inversion process as compared with BPPO, resulting in greater thicknesses of the membrane and the active layer. For the bottom layer morphology, all the BPPO/TPPOQP membranes show the large pore size as compared with BPPO membranes, resulting from the slow hydration rate of TPPOQP as mentioned above. In contrast, the morphology of the BPPO/TPPOQA-Br 8/2 membrane is different from that of BPPO/TPPOQP-Br 8/2 membrane, especially in the cross-sectional microstructure. Compared with BPPO/TPPOQP-Br 8/2, BPPO/TPPOQA-Br 8/2 membrane shows a more porous top surface and the surface pore size is larger. Moreover, the pore at the cross-section of BPPO/TPPOQP-Br 8/2 is cellular sponge-like while that of BPPO/TPPOQA 8/2 is still finger-like, which is similar to that of the pristine BPPO. Such difference should be due to the difference in the wettability and hydration rate between the two polymers, and redistribution of these polymers during the membrane formation.

3.3. XPS analysis

BPPO, TPPOQP-Br 8/2 and TPPOQA-Br 8/2 membranes were selected for XPS analysis. Their spectra are shown in Fig. 7 and the actual contents of the polymer additives at the active and bottom layer calculated from to the XPS data are summarized in Table 2.

For BPPO/TPPOQP-Br 8/2, the P element content at the bottom surface is higher than that at the top surface. The corresponding actual contents of TPPOQP-Br additive at the top and bottom surface are calculated to be 11.3% and 28.8%, respectively. Despite the actual component content obtained from XPS being the average values within a couple of microns thickness from the surface, the XPS result clearly indicates that there is a TPPOQP-Br concentration gradient in the membrane. The similar phenomena were also observed in our previous work [23]. In contrast, in BPPO/TPPOQA-Br 8/2 membrane with TPPOQA-Br as additive, there is an opposite concentration gradient from the top to bottom surface [23]. The
actual TPPOQA-Br content at the top and bottom surface is 21.7% and 18.3%, respectively. Such a difference can be explained by the surface segregation phenomena and the hydration rate of the two different additives. During the phase inversion process, hydrophilic TPPOQA-Br tends to be hydrated more quickly than BPPO prior to precipitation, resulting in surface enrichment of the hydrophilic TPPOQA-Br [28]. On the contrary, TPPOQP-Br is slower in hydration and pushed down by the coagulant (water) to the bottom layer, thereby increasing the concentration gradient of TPPOQP-Br from the top layer to the bottom layer.

3.4. Contact angle

The water contact angles of membranes in the dry and wet states were determined to investigate the effect of the TPPOQP-Br concentration gradient on the membrane wettability (Fig. 8). For the dry membranes, the contact angles of BPPO/TPPOQP-Br membranes at the top are similar to that of BPPO; however, the contact angles of BPPO/TPPOQP-Br membranes at the top are greater than that of BPPO especially when the TPPOQP-Br content is high. It should be due to the higher wettability of TPPOQP-Br before hydration than BPPO. For the wet membranes, it can be seen that the contact angles of BPPO/TPPOQP-Br membranes are lower than those of BPPO at the top and bottom surfaces. It should be due to the higher wettability of TPPOQP-Br after hydration than BPPO. In addition, the decrease in the contact angle of the wet BPPO/TPPOQP-Br becomes more pronounced when more TPPOQP-Br is added. These results are consistent with our previous work [23], and they can be explained by the concentration gradient of the TPPOQP-Br from top to bottom surface identified by XPS. Therefore, it further proves that the unusual chemical gradient of the additive can be obtained by adding the quaternary phosphonium-based polymer. This strategy is not only applicable to the PES-based system, but also the BPPO-based system.

In addition, it can be found that the contact angle values of dry and wet BPPO/TPPOQA-Br 8/2 membrane at top and bottom surface are smaller than those of BPPO/TPPOQP-Br 8/2
membrane, because of higher wettability of TPPOQA-Br than TPPOQP-Br at dry and wet states.

3.5. Water permeability and molecular weight cut-off

Pure water flux and rejection are two most important parameters for ultrafiltration membrane applications. Fig. 9 shows the pure water flux of BPPO, BPPO/TPPOQP-Br and BPPO/TPPOQA-Br 8/2 membranes as a function of transmembrane pressure. It is expected that all the membranes show a linear increase in the water flux when the transmembrane pressure increases. The slopes of these straight lines correlate with the hydraulic resistance, which decreases as the slope increases [29, 30]. Specifically, BPPO membrane exhibits a pure water flux of 2.2 L m⁻² h⁻¹ kPa⁻¹, whereas the water flux for BPPO/TPPOQP-Br 9/1 and BPPO/TPPOQP-Br 8/2 membranes is 11.4 and 8.7 L m⁻² h⁻¹ kPa⁻¹, respectively. It should be noted that there is only a slight increase in the pore size and porosity at the top surface from BPPO to BPPO/TPPOQ-Br 9/1 and BPPO/TPPOQ-Br 8/2 membranes. The pore size calculated from molecular weight cut-off values of BPPO membrane and BPPO/TPPOQP-Br membranes with increasing TPPOQP-Br content are 16.0, 21.1, 17.8, 16.8 nm, which are in good agreement with the SEM observations. Note that the increase in pore size would lead to an increase in water flux according to Hagen Poiseuille equation. The theoretical flux, \( J \), was calculated based on the Hagen–Poiseuille model [31]:

\[
J = N d_p^4 \Delta P / (128 \mu l) = S d_p^2 \Delta P / (32 \mu l)
\]

where \( N \) is the number of pores counted from high-resolution SEM image of the top surface of membrane, \( \Delta P \) is the pressure drop across the membrane (100 kPa), \( \mu \) is the viscosity of DDI water at room temperature (0.001 Pa s), and \( l \) is the thickness of the skin layer measured from the cross section of membrane and \( d_p \) is the diameter of the nanochannel defined as the calculated average surface pore diameter, and \( S \) is the surface porosity.
The results are shown in Table 4. The actual flux of the pristine BPPO is close to its theoretical flux. With the addition of TPPOQP-Br, the actual flux of the membrane is much greater than its theoretical flux; the ratio of the actual flux to theoretical flux of BPPO/TPPOQP-Br membrane increases from 2.6 to 4.2 and 16.2 as the TPPOQP content increases from 10% to 20% and 30%. In contrast, there is only a 30% increase when comparing the theoretical flux with the actual flux for BPPO/TPPOQA-Br 8/2 membrane. These results indicate TPPOQP-Br plays a crucial role in promoting water flux of BPPO-based composite membrane.

The results obtained in this study are consistent with our previous work where TPQP-Cl with the same quaternary phosphonium groups was used as an additive [23], the surface pore size change is one contributor to flux enhancement. The large increase in water flux may be attributed to the other effects resulting from the addition of TPPOQP-Br, including porosity changes in both active layer and supporting layer, and wettability gradient across membrane cross-section. As can be seen in the SEM section, the pores at the cross section become more connected and their sizes also increase significantly after addition of TPPOQP-Br. This change in microstructure would lead to a great enhancement in water flux, as indicated by our modelling results in our previous work [23]. In addition, the unique chemical gradient in the BPPO/TPPOQP-Br membranes could positively affect the water flow by promoting directional water movement [32, 33]. It is speculated that the resistance for water molecules may be reduced by the weak interactions between hydrophobic (aromatic rings around), charged (positive charged P core inside) structure and water molecules [34, 35]. With increasing the TPPOQP-Br content, the water flux of BPPO/TPPOQ-Br 7/3 is 5.4 L m⁻² h⁻¹ kPa⁻¹. As compared with BPPO/TPPOQ-Br 8/2, such a decrease should be due to the obvious decrease in the pore size and porosity at the top surface (see section 3.2 and Table 2).
In contrast, the BPPO/TPPOQA-Br 8/2 membrane exhibits a water flux of 3.8 L m⁻² h⁻¹ kPa⁻¹, which is only 43.7% of BPPO/TPPOQP-Br 8/2, even though the pore size at top surface of BPPO/TPPOQA-Br 8/2 is much greater. This should furthermore prove the benefits of the existence of large macrovoids at the cross section and the concentration gradient of TPPOQP-Br in the membrane in enhancing water permeability.

Fig. 10 shows the rejection of BPPO, BPPO/TPPOQP-Br and BPPO/TPPOQA-Br 8/2 membranes using PEG as a probe molecule. The 90% PEG rejection rate was taken as MWCO value for each membrane, which was used to calculate the pore size of the active layer of the membrane (see Table 3). It can be seen that the pristine BPPO membrane exhibits a MWCO of 93.8 kDa. Whereas the MWCO value of BPPO/TPPOQP-Br 9/1 is 162.2 KDa, that should be due to the increase in the pore size at the top surface compared with BPPO. With increasing the TPPOQP-Br content, BPPO/TPPOQP-Br 8/2 and BPPO/TPPOQP-Br 7/2 shows MWCO values of 111.4 kDa and 101.0 kDa, respectively. These results are consistent with the SEM observation, which clearly demonstrated that the top surface pore size decreased and the thickness of active layer increased o from BPPO/TPPOQP-Br 9/1 to BPPO/TPPOQP-Br 7/3 membrane. Considering both water flux and rejection, it can be concluded that BPPO/TPPOQP-Br 8/2 membrane exhibits the best performance among these BPPO/TPPOQP-Br composite membranes. In contrast, BPPO/TPPOQA-Br 8/2 exhibits the MWCO value of 150.2 kDa, which is about 50% higher than BPPO/TPPOQP-Br 8/2. Obviously, compared with BPPO/TPPOQA-Br 8/2, BPPO/TPPOQP-Br shows the improvement not only in water permeability but also in separation properties, resulting from the special structure of TPPOQP-Br and also proving its unique benefits as an additive used in UF membrane preparation.

It is also noted that all the BPPO/TPPOQP-Br membranes remain stable and fresh after being stored in water for about 11 months; in contrast, the pristine membrane becomes oily and the
water in the container becomes yellowish. These membranes were examined by SEM. The SEM images of top surfaces of BPPO and BPPO/TPPOQP membranes stored in water for about 11 months are shown in Figure 11. For BPPO membrane, there are many bacterial colonies on its top surface; whereas the amount of bacteria on the top surfaces of BPPO/TPPOQP membranes significantly decreases with increasing the amount of TPPOQP-Br. These results indicate that the addition of the charged TPPOQP-Br leads to an excellent improvement in anti-biofouling property.

**Conclusion**

Composite ultrafiltration membranes have been successfully prepared by blending BPPO and its quaternary phosphonium- functionalized derivative. Because of the different hydration rate of the two components during the phase inversion, the composite membranes show the unique charged gradient from the top to bottom membrane surface along with the asymmetrically porous channels with the larger pore size. Such special structure and chemical properties of the composite membranes have significant efforts on the membrane properties especially water permeability and separation properties. By controlling the amount of the functional charged groups in the membranes, the membranes properties can be effectively tailored. A comparison between the effects of the quaternary phosphonium- functionalized derivative and the typical quaternary ammonium- functionalized derivative is also made in this work. It is clear that the quaternary phosphonium-based membranes show much greater water permeability and separation properties than quaternary ammonium-based membrane under the same test conditions, suggesting the excellent effect of the addition of the quaternary phosphonium-functionalized additive.

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References


Figure captions

Fig. 1. Molecular structures of BPPO and TPPOQP-Br and TPPOQA-Br.

Fig. 2. FT-IR spectra of (a) BPPO, (b) BPPO/TPPOQP-Br 9/1, (c) BPPO/TPPOQP-Br 8/2, (d) BPPO/TPPOQP-Br 7/3 and TPPOQP membranes.

Fig. 3. The top-surface SEM images of (a) BPPO, (b) BPPO/TPPOQP-Br 9/1, (c) BPPO/TPPOQP-Br 8/2, and (d) BPPO/TPPOQP-Br 7/3 membranes.

Fig. 4. The cross-sectional SEM images of (a) BPPO, (b) BPPO/TPPOQP-Br 9/1, (c) BPPO/TPPOQP-Br 8/2, and (d) BPPO/TPPOQP-Br 7/3 membranes.

Fig. 5. The bottom-surface SEM images of (a) BPPO, (b) BPPO/TPPOQP-Br 9/1, (c) BPPO/TPPOQP-Br 8/2, and (d) BPPO/TPPOQP-Br 7/3 membranes.

Fig. 6. (a) Top-surface, (b) cross-sectional and (c) bottom-surface SEM images of TPPOQA-Br 8/2 membrane.

Fig. 7. XPS spectra of (a) BPPO, (b) BPPO/TPPOQP-Br 8/2 membranes at (b) active and (c) bottom layer, and BPPO/TPPOQA-Br 8/2 membrane at (d) active and (e) bottom layer.
Fig. 8. Contact angles of the dry and wet BPPO, BPPO/TPPOQP-Br and BPPO/TPPOQA-Br 8/2 membranes on the top and bottom surfaces.

Fig. 9. Pure water flux of BPPO, BPPO/TPPOQP-Br and BPPO/TPPOQA-Br 8/2 membranes as a function of transmembrane pressure.

Fig. 10. PEG rejection of BPPO, BPPO/TPPOQP-Br and BPPO/TPPOQA-Br 8/2 membranes.

Fig. 11. SEM images of top surface of (a) BPPO, (b) BPPO/TPPOQP-Br 9/1, (C) BPPO/TPPOQP-Br 8/2 and (d) BPPO/TPPOQP-Br 7/3 membranes after being stored for 11 months.