Research Paper

Effect of Hydrophilic-Hydrophilic Interactions between the Foulant and Membrane Surface on the Fouling Propensity of Different Foulants

Saeid Rajabzadeh [1], Hiroki Awaji [1], Yuchen Sun [1], Daisuke Saeki [2,3], Noriaki Kato [1], Hideto Matsuyama [1,*]

[1] Research Center for Membrane and Film Technology, Department of Chemical Science and Engineering, Kobe University, Rokkodaicho 1-1, Nada, Kobe 657-8501, Japan
[2] Research Initiative for Supra-Materials (RISM), Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan
[3] Department of Materials Chemistry, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

Article info

Keywords

Highlights

- PES membrane surface grafted by poly sulfobetaine methacrylate (pSBMA)
- Membrane surface hydrophilicity enhanced by grafting
- Three different foulants were evaluated for anti-fouling propensity
- Hydrophilic interaction between membrane and foulant pronounced the fouling
- Fouling mechanism was discussed based on the interactions of the molecules

Graphical abstract
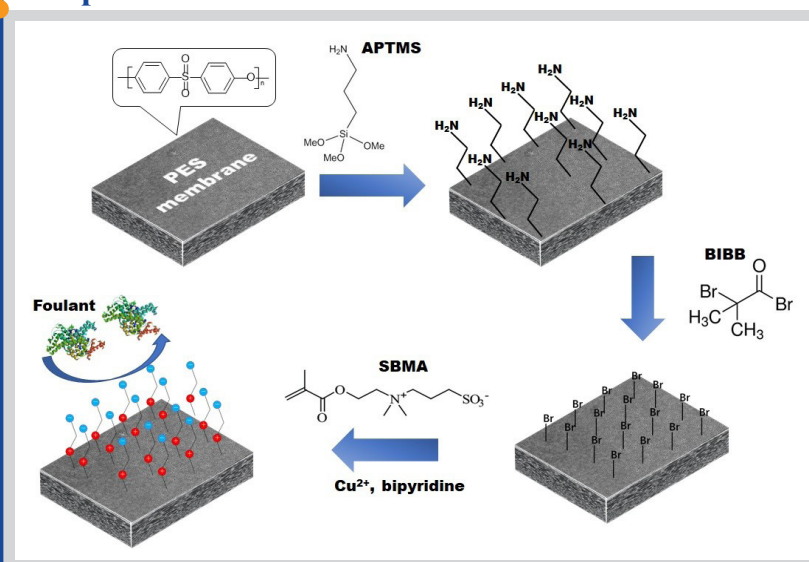
Abstract

Polyethersulfone (PES) membrane was grafted with sulfobetaine methacrylate (SBMA) zwitterion to obtain a membrane surface with improved hydrophilicity. Successful grafting was confirmed by FTIR-ATR, and grafting density was controlled by adjusting the 3-aminopropyltrimethoxysilane (APTMS)/trimethoxy(propyl)silane (TMPS) ratio. The interactions between different foulants with the membrane surface were evaluated. Three different foulants, namely, humic acid (HA), bovine serum albumin (BSA), and sodium alginate (SA) were used to evaluate the anti-fouling properties of the grafted PES membrane. It was expected that increasing the surface hydrophilicity would decrease membrane fouling. However, a completely different trend of fouling propensity was observed for the three different foulants. For the grafted membrane with higher hydrophilicity, a considerable anti-fouling phenomenon property was observed when it was exposed to BSA. In contrast, when SA was used as the foulant, there was a slight increase in the anti-fouling propensity, and surprisingly, when HA was used, the modified hydrophilic membrane showed higher fouling than that of the pristine membrane. These results propose that the different trends of fouling are related to the interactions of the foulant molecules with the membrane material. Considering the hydrophilic nature of the HA and SA, and SBMA grafted on the membrane, it was concluded that the conventional approach of making a membrane surface hydrophilic by grafting to avoid its fouling by protein-type foulants may result in even worse results for some types of foulants such as SA and especially HA.

1. Introduction

Membrane fouling is considered as the major drawback in water treatment applications [1-4]. Many studies have been conducted to address this undesirable phenomenon of membrane fouling during the water treatment process. Although noticeable development was done in understanding the fundamentals of the fouling phenomenon, it is quite complicated and cannot be clarified sufficiently yet. In the case of proteins, e.g., bovine serum albumin (BSA), the fouling mechanism is explained by the hydrophobic-hydrophobic interaction of the foulant molecules with the membrane polymer

molecules [5,6]. In reality, the water that requires treatment includes several kinds of foulants such as natural organic material (NOM), polysaccharides, and BSA and other proteins. It is known that except some proteins such as BSA, pollutants such as NOM can potentially foul the membrane [7].

Although fouling of membranes with non-protein-type foulants has been investigated, the main focus in previous studies has been on process conditions such as transmembrane pressure, membrane pore size, and initial permeability of water [8]. The effect of the constituents of treated water on fouling is not as well-studied [9]. Some simplistic modeling of membrane fouling has also been carried out, but such studies do not consider the interactions between the foulant and membrane materials [8].

Typically, several different materials with hydrophilic and hydrophobic fractions constitute NOM. It is a mixture of different types of non-biodegradable materials with an extensive size distribution ranging from nanometer to micrometre [10]. The hydrophilic fraction is rich in aliphatic carbons and hydroxyl groups [10]. Most researchers ignore the effect of the hydrophilic part of NOM, mainly humic and fulvic acids. It is known that the commercially available humic acids (HA) are mainly composed of hydrophilic components [11]. Yamamura et al. [9] have evaluated the fouling by the fractionated hydrophilic and hydrophobic parts of HA obtained from different river water samples on the polyacrylonitrile (PAN), polyethene (PE) and polyvinylidene difluoride (PVDF) membranes. They concluded that while the hydrophilic part of the HA fouled commercial PVDF and PE membranes significantly, the PAN membrane was not fouled. The authors mainly focused on the properties and filtration conditions of HA, and the interaction of HA with the membrane was considered completely marginally. Although Yuan et al. reported that hydrophilic HA could potentially cause noticeable fouling when the UF and MF membranes were used, they simply assessed the effect of the filtration conditions and the fouling mechanism was not considered [7].

Qu et al. [12] evaluated the fouling of commercial cellulose acetate (CA) and PES membranes using extracellular organic matter (EOM) and found that the fouling of hydrophilic CA membrane was higher than that of the PES membrane. The authors mainly focused on the effect of pore size and porosity of the membrane on the fouling propensity. The microscopic and detailed mechanism of fouling by considering the interaction of the foulant with the membrane polymer was not evaluated. Lee et al. [13] used several kinds of UF and MF membranes with different river water samples to assess the river water foulants. After the analysis of river water and the fouled membrane, they found that it was not only hydrophobic membranes but also hydrophilic membranes that play a notable role in membrane fouling. Although the authors used different commercial hydrophobic and hydrophilic membranes, the effect of the membrane material and its interaction with the foulant was not investigated. These authors mainly focused on the membrane characteristics, i.e., membrane pore size and porosity.

In the last decade, many types of zwitterions have been used as novel materials owing to their remarkable anti-fouling properties [14-21]. By definition, a zwitterion is a molecule with an equal number of positively and negatively charged functional groups in its structure. Zwitterionic materials are novel materials for anti-fouling membranes. It has been reported that zwitterions can potentially outperform poly(ethylene glycol) derivatives as conventional anti-fouling materials. This is because zwitterions form stronger bonds with water molecules on the membrane surface and produce a hydrated layer that can prevent the fouling [15]. Sulfobetaine methacrylate (SBMA) has been reported as an excellent non-fouling material. Zwitterions as anti-fouling materials are mainly used to prevent non-selective protein adsorption and to prepare anti-biofouling surfaces for many applications, including the membranes.

Although there are several methods to modify the surface of the hydrophobic membranes, surface grafting is considered as the most versatile method with the long-term stability of the grafted moieties on the surface of the membrane [22]. Surface-initiated atom transfer radical polymerization (SI-ATRP) is a widely used method to graft zwitterionic molecules on the membrane surface [23]. In this study, we used a two-step modified SI-ATRP method to graft the SBMA molecules on the less reactive surface of the commercial PES membrane [24]. 3-Using aminopropyltrimethoxysilane (APTES) the surface of the PES membrane was aminated to improve the α-bromoisobutyryl bromide immobilization (BIBB). After BIBB immobilization, SBMA was grafted on the membrane surface via SI-ATRP.

In this study, commercial PES membrane was used as the pristine hydrophobic membrane, and the PES membrane surface was grafted by SBMA to make it hydrophilic. The effect of the different foulants, i.e., BSA as a protein foulant, HA as a NOM foulant, and sodium alginate as a representative of polysaccharide foulants, were used to measure the fouling tendency of both pristine and grafted membranes. On modification of the membrane by SBMA, BSA fouling decreased considerably. However, SA and HA fouling propensity did not decrease and in fact, worsened as compared to the pristine membrane. As the grafted membrane fouling experiment was performed with the feed hydrodynamic condition similar to that of the pristine membrane, we concluded that the difference in the fouling propensity might be attributed to the interaction of the foulant molecules with the functional groups of the membrane.

2. Materials and methods

2.1. Materials and reagents

A commercial polyethersulfone (PES) membrane (PBMK07610, Millipore, MWCO: 300 kDa) was used as the starting membrane for modification, and a PES membrane with MWCO of 30 kDa from the same company was used as a pristine membrane. The fouling results of the surface grfated membranes were compared with those of the pristine commercial PES membrane in similar pure water permeability. Hexane, methanol, L(+)-ascorbic acid, and lyophilized BSA were purchased from Wako Pure Chemical Co., Japan. α-Bromoisobutyryl bromide (BIBB), copper bromide (CuBr$_2$), and HA sodium salt were purchased from Sigma-Aldrich Co., LLC, Germany. 3-Aminopropyltrimethoxysilane (APTMS), trimethoxy(propyl)silane (TMPS), and 2,2-bipyridine were purchased from Tokyo Kasei Co., Japan. [2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium (SBMA) was purchased from Millipore. Dextran was purchased from Nacalai Tesque, Inc., Japan. The pure water used in this study was produced by a Millipore Milli-Q unit (Millipore, USA). All the chemicals and reagents were uses as received from the company without any purification.

2.2. Procedure for ATRP reaction

A schematic illustration of the zwitterion modification is shown in Figure 1. To introduce reaction sites for ATRP, the PES membranes were first functionalized with amino groups using APTMS/TMPS solutions. The membrane coupons were immersed in an aqueous solution containing APTMS/TMPS with various ratios for 30 min. The total volume fraction of the two components was fixed at 1.5%. The density of the reaction sites was controlled by adjusting the APTMS/TMPS ratio, and three different recipes were used to modify the membrane. These details are given in Table 1. When the APTMS/TMPS ratio is higher, more amino groups are formed on the membrane, resulting in a higher SBMA grafting density. The details of the grafting method used in this study have been reported previously [24,25].

The obtained membranes were dried under vacuum for 10 min to remove moisture. Next, the initiator BIBB was immobilized onto the membranes by immersing them in a hexane solution containing 3 wt% of BIBB for 2 min. The membranes were carefully cleaned with hexane and water and stored in pure water until required.

Atom transfer radical polymerization (ATRP) method was used to graft the pSBMA chain onto the initiator-immobilized PES membranes. Two solutions were prepared. Solution 1 was a solution of ascorbic acid (1.76 g, 0.01 mol) in a 20 mL mixture of water and methanol (1/1, v/v). Solution 2 was prepared by dissolving CuBr$_2$ (22.3 mg, 0.1 mmol) and 2,2′-bipyridine (31.2 mg, 0.02 mmol) in a 20 mL mixture of water and methanol (1/1, v/v). Subsequently, the ATRP reaction was conducted using the following procedure. The solution of SBMA monomer (2.79 g, 0.01 mol) in 14.4 mL of water/methanol mixture (1/1, v/v) was added to a round-bottom flask. Next, 1.6 mL of stock solution 1 was added and the flask was sealed and purged with nitrogen for 10 min to remove any residual air. The polymerization reaction was initiated by adding 4 mL of stock solution 2 to the flask and allowed to continue for 40 min. Subsequently, the poly SBMA (pSBMA)-grafted membrane was taken out and cleaned by washing with Milli-Q water. Finally, the membranes were stored in fresh Milli-Q water. The grafted membranes are named PES_C1, PES_C2, and PES_C3, based on the different APTMS/TMPS ratios used for amino group introduction shown in Table 1. An unmodified PES membrane with 30 kDa of MWCO was also used as a pristine membrane because its water permeability was similar to that of the grafted membrane.

2.3. Characterization of the membranes

Fourier-transform infrared spectroscopy (FTIR-ATR, ALPHA, Bruker, USA) together with X-ray photoelectron spectroscopy (XPS, JPS-9010 MC, JEOL Co. Ltd, Japan) were used for assessment of the surface chemical composition of the prepared membranes. The XPS machine was included an Al Kα radiation source, and the 45° was considered as the take-off angle of photoelectron. Membrane surface chemical compositions were calculated based on the surface areas of the pertinent atomic peaks.
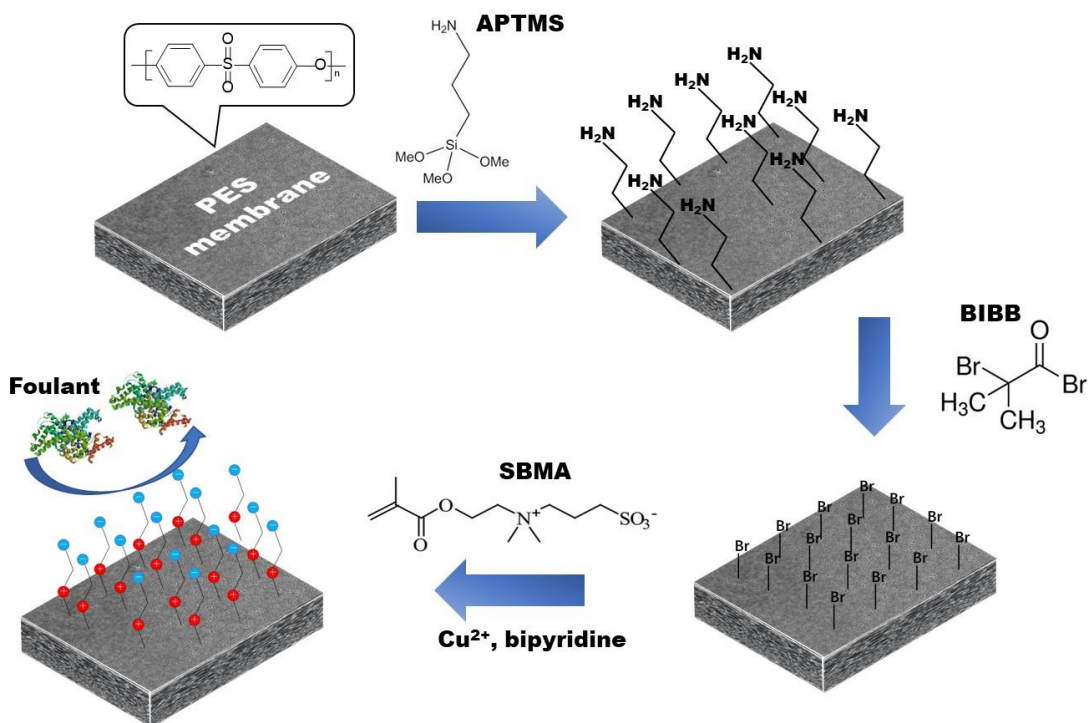
Fig. 1. Schematic illustration of the zwitterion modification on PES membrane. (Note: Me refers to a methyl (CH$_3$) group).

Table 1
APTMS/TMPS ratios used to prepare modified PES membranes.

Membrane	APTES/TMPS	APTES (mL)	TMPS (mL)	Water (mL)
PES_C1	1:2	0.1	0.2	19.7
PES_C2	2:1	0.2	0.1	19.7
PES_C3	3:0	0.3	0.0	19.7

A static contact angle, CA, (Drop Master 300, Kyowa Interface Science Co.; Japan) used to evaluate the hydrophilicity of the surface of the prepared membrane. To avoid the effect of moisture and/or other solvents, the membranes were dried in an oven at 50 °C for three days, and the dried membranes were used for CA evaluations. For CA measurements, 0.5 µL water drops were placed on the prepared membrane surface from the machine needles that is connected to a plastic syringe, and the images were taken immediately when the water drops met the membrane surface. At least five parallel measurements were carried out in different positions, and the average value was reported.

The morphologies of the prepared membranes were evaluated by scanning electron microscopy (SEM) (JSM-7500F, JEOL Co. Ltd., Japan). Prepared membranes were dried for 24 hours in a freeze drier (FD-1000, EYELA; Japan) to remove any moisture from membrane structure. Subsequently, the samples were coated with an osmium layer with thickness

around 10 nm (Neoc-STB, MEIWAFOSIS Co. Ltd., Japan) before starting the observation.

The pure water permeability (PWP) of the membranes was measured by a cross-flow cell with an active area of 8.04 cm^2 (setup is shown in Figure 2). The membrane was placed on a metal plate, and a rubber ring was used to seal the water leakage from the cell. Pure water was flown into the cell with a pump at the flow rate of 0.6 L h^{-1}. Hydraulic pressure of 1 bar was applied, and the permeate was collected and weighed. The PWP was calculated using the following formula:

$$PWP = \frac{V}{A.\Delta t.\Delta P} \tag{1}$$

where in this equation V (L) is the volume of the permeated water, A (m^2) is the membrane active area, Δt (h) is the filtration operation time, and ΔP (bar) is the transmembrane pressure.

2.4. Evaluation of anti-fouling performance

The anti-fouling performance of the membranes was evaluated using 1000 ppm BSA, 20 ppm HA, and 10 ppm SA solutions. The BSA solution was prepared by first adding 9.46 g (0.067 mol) of Na$_2$HPO$_4$ and 4.00 g (0.033 mol) of NaH$_2$PO$_4$ to 1 L of Milli-Q water to obtain a phosphate buffer solution with pH of 7.4, followed by the addition of 1 g of BSA. HA and SA solutions were prepared by dissolving the corresponding amount of solid powders (0.02 g HA, or 0.01 g SA) in 1 L of Milli-Q water. The above solutions were stirred until no solid residues were visible.
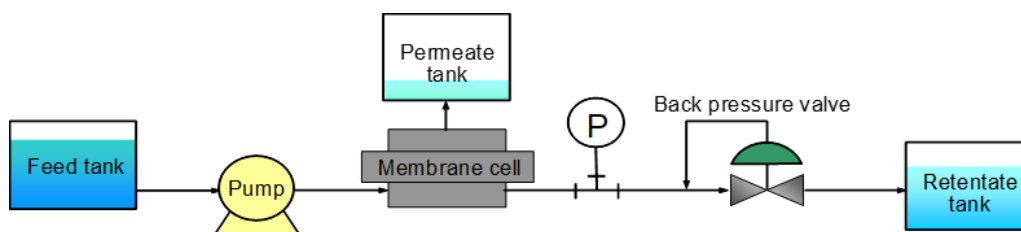

Fig. 2. Schematic illustration of the filtration apparatus.

The same apparatus used to evaluate PWP was employed again to evaluate anti-fouling propensity. The membranes were first treated with pure water for 30 min until the flux became constant. It is known that the membrane PWP, pore size, and initial flux influence membrane fouling [26]. Therefore, to evaluate fouling propensity, all membranes in this study were adjusted to have ~100 LMH of initial flux by adjusting the pressure. As the membrane pore size and PWP decreased considerably after grafting, 30 kDa PES with much smaller pore size and PWP similar to those of the modified membranes was used as a pristine membrane. Its fouling propensity was compared to that of the modified membranes in fair condition to mainly assess the efficacy of the membrane material against fouling. After 30 min of flowing pure water for compaction and stabilization of the water permeability, the water was replaced with the foulant solutions to evaluate anti-fouling performance. The filtration of model foulants lasted for 60 min, and the change in water permeability was monitored using a balance connected to the computer. For easier comparison of the decrease in water permeability, the ratio J/J_0 was used, where J_0 denotes the PWP and J represents the water permeability of the foulant solution at each time of the filtration.

3. Results and discussion

3.1. Surface chemical analysis of the membranes

To confirm the existence of pSBMA chains on the surface of the modified membranes, their FTIR spectra were obtained and analyzed. The results are shown in Figure 3. The FTIR spectrum of the PES membrane showed several sets of important peaks. The peaks at 1410, 1483 and 1575 cm^{-1} corresponded to the benzene ring in the PES backbone. The ether functional groups were identified by a set of peaks appearing at 1298 cm^{-1} and 1325 cm^{-1}, corresponding to their vibrational stretching modes. The stretching peaks of the sulfone groups were identified at 1105 cm^{-1} and 1141 cm^{-1}. In the pSBMA-grafted PES_Cx membranes, several new peaks were observed. The peak at 1039 cm^{-1} corresponded to the sulfonate group. The two new peaks at 1508 and 1736 cm^{-1} indicated the presence of quaternary ammonium groups and carbonyl groups, respectively. The appearance of these new peaks clearly proved the success of pSBMA grafting. A wide peak with weak intensity at 3429 cm^{-1} was attributed to the small amount of water molecules absorbed on the pSBMA-grafted membranes. Since pSBMA is highly hydrophilic and PES is relatively hydrophobic, the peak for the water molecule is another evidence of the successful modification.

As FTIR is mainly qualitative analysis rather than quantitative analysis and deep penetration of IR radiation this method does not provide the precise concentration of the element on the membrane surface, XPS measurement was performed for the analysis of the amount of each element. The chemical compositions of the membranes' surface were further analyzed by using XPS, and the molar ratios of the elements were calculated (Table 2). After membrane modification, new signals for Si, Br, and N were detected, corresponding to the introduction of APTMS/TMPS, BIBB, and pSBMA, respectively. Thus, the successful modification by pSBMA was also confirmed by XPS. Table 1 shows that the content of N increased from 2.11 to 5.67 with an increase in the APTMS/TMPS ratio, which implies that more pSBMA chains were introduced onto the modified membranes. As TMPS does not contribute to the immobilization of BIBB, and PES_C2 contains less APTMS and more TMPS than PES_C3, fewer reaction sites were available on these membranes, leading to a lower amount of grafted pSBMA. This was confirmed by the results summarized in Table 2, which show that by decreasing the APTMS/TMPS ratio (on increasing the TMPS amount), the Br and thus N contents decreased, indicating a decrease in the extent of grafted pSBMA.

3.2. Surface water contact angle of the prepared membrane

The surface hydrophilicity of the prepared membranes was evaluated by water CA (WCA) measurements, and the results are shown in Figure 4. The unmodified PES membrane is relatively hydrophobic with a WCA of 78°. It is widely known as a material with insufficient hydrophilicity [27] owing to the large number of benzene rings in its backbone. This property renders PES vulnerable to various kinds of organic fouling. After grafting of pSBMA, the modified membranes demonstrate noticeable improvement in membrane surface hydrophilicity by a considerable decrease in CA from 78° for pristine PES membrane to ~56° for grafted membranes. As a widely used zwitterion, SBMA is highly hydrophilic, which is responsible for the considerably lower CA. Curiously, although PES_C3 has the highest amount of pSBMA chain on its surface (as discussed in Section 3.1), its CA is not so different from the other two modified membranes. From the results shown in Figure 4, it appears that the WCA of the grafted membrane did not change to any

significant extent. Although a higher APTMS ratio is helpful for introducing more pSBMA (resulting in a higher N ratio in XPS analysis), the hydrophilicity has already reached its limit and will not improve further. It is worth mentioning that although CA is a good index for evaluation of the membrane surface hydrophilicity, it is affected by other parameters such as membrane surface roughness, porosity and pore size as well. Thus, although based on the XPS results (Table 2), the grafting amount changed on alteration of the APTES/TMPS ratio, the WCA did not change noticeably. Therefore, we hypothesize that the membrane structure (pore size, porosity and roughness) affects the CA. As a dried membrane was used for CA evaluation, the CA was higher than in the case of a wet membrane.
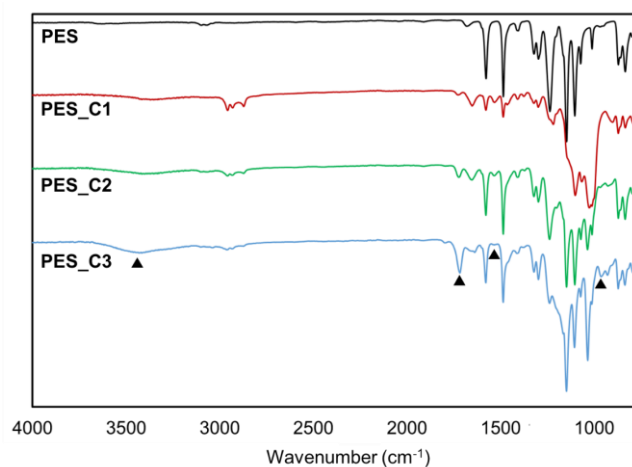

Fig. 3. ATR-FTIR spectra of the pristine and grafted PES membranes.

Table 2
Surface elemental composition of the membranes as detected by XPS (data in mol %).

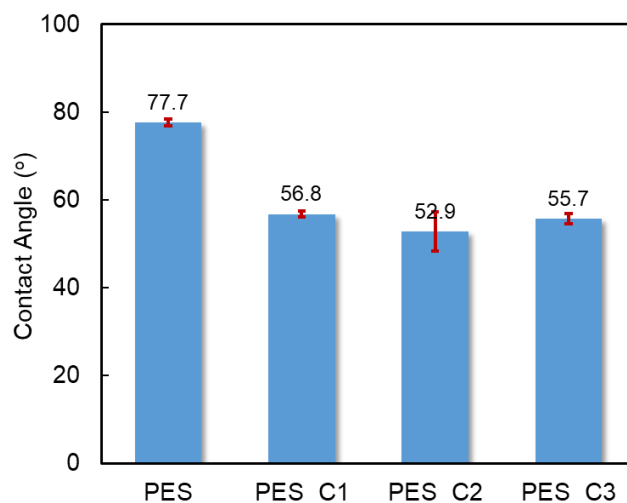| Membrane	C	N	O	Si	S	Br
PES	75.60	-	21.79	-	2.61	-
PES_C1	56.98	2.11	22.12	12.80	4.24	1.75
PES_C2	65.26	3.66	21.95	6.76	2.18	0.20
PES_C3	54.86	5.67	20.98	8.62	4.44	5.43

Fig. 4. Water contact angles of the pristine and grafted PES membranes.

3.3. Surface morphology of the membranes

The introduction of polymer chains by the grafting method is usually accompanied by densification of the membrane surface and decrease in permeability [28]. To confirm the effect of polymer chains on membrane morphology, we observed the outer surface of the membranes by SEM. The corresponding images of the membranes are shown in Figure 5. The pristine 30 kDa PES membrane revealed a porous surface with pore sizes of tens of nanometers, classifying it as an ultrafiltration membrane. The SEM image of the PES membrane with 30 kDa that was used as a pristine membrane with much lower water permeability and close to that of the grafted membrane, is also shown. After grafting pSBMA, the surfaces of PES_Cx became denser, with smaller pores and lower surface porosity. We hypothesize that some of the pores were blocked beneath the surface. Therefore, while the grafting of pSBMA provided better hydrophilicity, it also affected the permeability of the membrane as will be shown followingly in the next section of this study.

3.4. Pure water permeability of the membranes

The change in PWP is the most direct evidence of the membrane surface becoming dense upon grafting. It was expected that grafting would decrease the PWP of the membranes. Indeed, the PWP values of the pristine and modified membranes were measured, and interesting results were obtained (Figure 6). The unmodified PES 300 kDa membrane that was used as the base membrane for grafting was highly water-permeable, with a PWP of ~1500 L m^{-2} bar^{-1} h^{-1}. After pSBMA grafting, a sharp decline in the PWP of the grafted membranes was observed, which is consistent with the SEM observations (Figure 5). As expected, this decrease in water permeability is related to the densification of the grafted membranes. In Figure 6, it is evident that by increasing the grafting amount from PES_C1 to PES_C3, the water permeability decreased considerably. While PWP of PES_C1 was 481 L m^{-2} bar^{-1} h^{-1}, it decreased to 402 L m^{-2} bar^{-1} h^{-1} for PES_C2, and with further increase in grafting density, PWP for PES_C3 was the lowest at 206 L m^{-2} bar^{-1} h^{-1}. The PWP of the 30 kDa pristine PES membrane in the fouling region is also given in Figure 6. Its PWP of 478 L m^{-2} bar^{-1} h^{-1} was comparable with that of the grafted membrane and much lower than that of the 300 kDa PES. The SEM images in Figure 5 show a smaller pore size and lower porosity of the 30 kDa PES compared to that of 300 kDa PES. Thus, when pSBMA is grafted onto the PES membrane by ATRP, the polymer chains not only grow on the membrane surface but also inside the pores, including the bottleneck parts that are responsible for the membrane PWP. Therefore, a sharp decrease in PWP was observed. Considering that the CAs of all modified membranes were similar, PES_C1 showed higher PWP. Thus, PES_C1 was selected to assess the fouling propensity in this study as the membrane with optimized hydrophilicity and highest PWP.
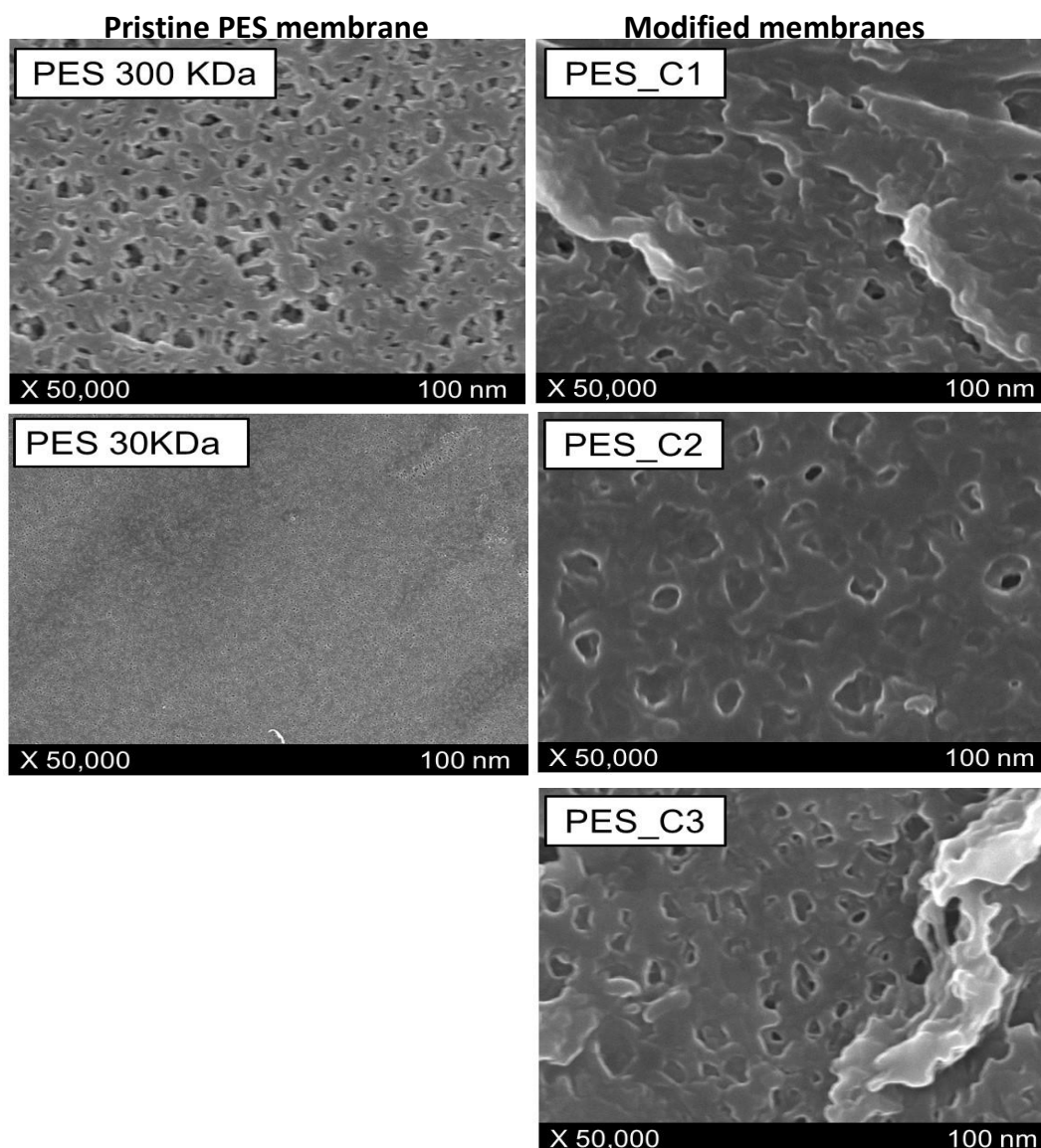

Fig. 5. SEM images of the outer surface of the pristine and grafted PES membranes.
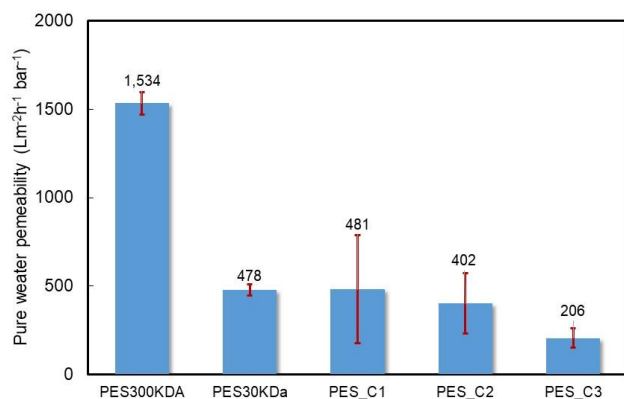
Fig. 6. Pure water permeability of the pristine and grafted PES membranes.

It is worth to mention here that the error bar for membranes PES_C1 and PES_C2 was noticeable. We hypothesize that this due to the presence of a considerable amount of TMPS chemical (Table 1). Basically, silane coupling agents are hydrophobic and easily form aggregates. Thus, it was hypothesized that some TMPS aggregates in the aqueous solution and adsorb onto the PES membrane surface. The adsorption of TMPS aggregates onto the PES membrane caused random membrane surface pores blocking that resulted in low reproducibility of the pure water permeability.

3.5. Anti-fouling properties of the membrane for different foulants

The anti-fouling performance of PES_C1 was evaluated using model foulants (BSA, HA, and SA) solutions, and pristine PES 30 kDa membrane was used for comparison as the control membrane. For each fouling experiment, pure water was filtered through until a stable water permeation was obtained, and subsequently, the pure water was replaced with the foulant solution. Figure 7 reveals that different foulants showed completely different trends in fouling. The BSA filtration results are plotted in Figure 7(a). As soon as the control membrane was subjected to the BSA solution, there was a drastic decrease in the water permeability (~80%) within 10 min of starting BSA filtration. Although the modified membrane PES_C1 showed a decline in the water permeability as the filtration progressed, the declining trend was much slower. For example, after 60 min of the BSA filtration, J/J_0 for the control membrane was 0.2, and that of the modified membrane was 0.5. Thus, the modified membrane persisted against BSA fouling considerably. This difference is caused by the hydrophilicity of the PES_C1 membrane. With the introduction of pSBMA chains, the PES_C1 membrane becomes hydrophilic owing to the water-capturing effect of the zwitterionic chains [15]. As BSA is intrinsically hydrophobic, the hydrophobic-hydrophobic interaction between the membrane and BSA was inhibited by the surface modification of the membrane. This is consistent with the results in the previous studies, especially relating to the anti-fouling property of zwitterionic membranes.

While the membrane surface became hydrophilic, the trend of HA fouling was in sharp contrast with those observed for BSA fouling (Figure 7(b)). Although the decreasing trend of J/J_0 for both membranes was lower than that of BSA for the control membrane, the grafted membrane (PES_C1) faced pronounced fouling as compared to the control membrane. It should be noticed that although the concentration of HA was merely 20 ppm (50 times lower than that of BSA), the J/J_0 of PES_C1 became 0.3 after 60 min of HA filtration while that of the control membrane was slightly higher at 0.4. As mentioned in the introduction, commercially available HA is mostly composed of hydrophilic components rather than hydrophobic components [11]. On the other hand, the grafted membrane surface is more hydrophilic than that the pristine PES membrane. Thus, the mechanism of the fouling cannot be explained based on hydrophobic-hydrophobic interactions, because in this case, the combination of the hydrophilic foulant and hydrophilic surface resulted in more fouling. Although not shown here, the acidic hydrogen of HA shows a strong tendency to approach oxygen with a negative charge in the structure of SBMA over other functional groups in SBMA. Thus, it may be that a hydrogen bond is formed between these two functional groups. As HA is hydrophilic, it can easily approach pSBMA and interact strongly with the negatively charged oxygen. It is plausible that this strong interaction is the reason for the pronounced fouling of the grafted membrane by HA. These interactions are currently being studied in our group.

As can be seen from Figure 7(c), when SA was used as the foulant, the

control membrane water permeability decreased sharply immediately after the membrane was subjected to SA, in a similar trend as with BSA, although the concentration of SA was merely 10 ppm (100 times lower than that of BSA). Although the grafted membrane showed less fouling than the control membrane, the fouling of the grafted membrane was considerable and J/J_0 reached to 0.36 after 60 min. SA includes hydrophilic groups such as COOH and Na^+ in its structure. As both the hydrophobic and hydrophilic membranes showed considerable SA fouling, and SA is not hydrophobic, we hypothesize that the fouling mechanism involves some other phenomenon than the hydrophobic-hydrophobic interaction. The reason for this occurrence is not clear and more detailed evaluation with considering the interaction of the SA with the membrane surface is needed. However, we speculate that the sodium cation in the SA structure tends to interact with the negatively charged functional groups in the modified membranes (i.e., negatively charged oxygen in the structure of the pSBMA and S=O groups in the pristine PES membranes). Since these interactions are electrostatic, we expect that there were strong interactions and led to severe fouling. From the fouling results summarized in Figure 7, it is evident that while pSBMA effectively resists the approach of BSA by forming a water layer on the membrane surface and avoiding hydrophobic-hydrophobic interaction, the same mechanism does not work for SA and especially HA. On treating the hydrophilic foulant solution using hydrophilic membranes, the hydrophilic interactions of the functional groups in the foulant and membrane molecules should be carefully considered.
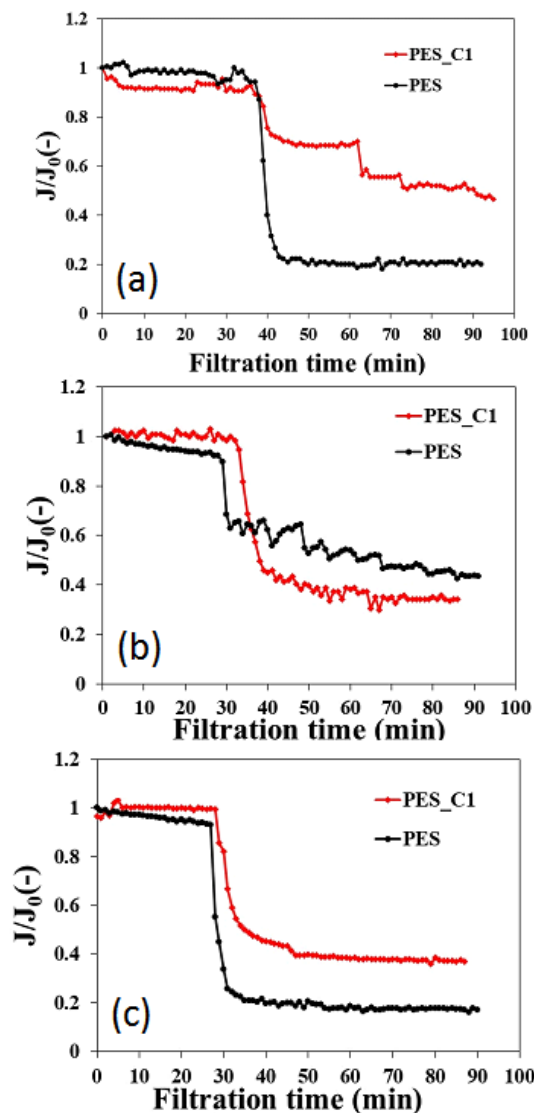

Fig. 7. Change in relative flux (J/J_0) versus time for PES and PES_C1 membranes, using (a) 1000 ppm BSA, (b) 20 ppm HA, and (c) 10 ppm SA as model foulants. Pure water was filtrated until a stable flux was obtained. After 30 min, foulant filtration was performed.

4. Conclusions

In this study, the effect of membrane surface hydrophilicity on the anti-fouling properties of the modified membranes and control membrane was investigated using different kinds of foulants. Using the SI-ATRP method, pSBMA was grafted on the PES membrane, and its grafting density was changed by adjusting the APTMS/TMPS ratio. The membrane surface hydrophilicity increased on grafting pSBMA, decreasing the CA from 78° for the pristine membrane to ~56° for the grafted membrane at the cost of decreasing the membrane PWP by covering the porous surface of the membrane.

As a general approach, it is expected that membrane fouling would decrease on increasing the membrane surface hydrophilicity by grafting with zwitterionic materials. This approach effectively decreased the fouling of the grafted membrane when 1000 ppm of BSA was used as foulant owing to a decrease in the hydrophobic-hydrophobic interaction. However, completely different trends were observed when 10 ppm of SA and especially 20 ppm of HA were used as the foulants. Surprisingly, when HA was used as foulant with 50 times lower concentration than that of BSA, the fouling of the hydrophilic membrane grafted with the zwitterion was more severe than that of the pristine PES membrane. This result implied that although both the membrane and HA were hydrophilic, the fouling propensity of the grafted membrane was higher than that of the pristine hydrophobic PES membrane. Hence, instead of the hydrophobic-hydrophobic interaction, it was another type of interaction between the membrane and foulant that was responsible for the membrane fouling. We concluded that the different trends in fouling are related to some specific interaction of the foulant molecules with the membranes. Based on our preliminary evaluation, it seems that for SA, and especially HA, a special kind of electrostatic interaction plays a role in making fouling more severe than in the case of the pristine membrane. It was concluded that except for the hydrophobic-hydrophobic interaction that is very well-studied as the main mechanism for membrane fouling, there is a possibility of other interactions such as electrostatic interactions between the hydrophilic membrane surface and hydrophilic part of the foulant that resulted in more serious fouling. The strong electrostatic interaction of the acidic hydrogen group of HA with the negatively charged oxygen of the zwitterion might be hydrogen bonding that causes severe fouling. When SA was used, the sodium cation in the structure of SA can have strong electrostatic interaction with the negatively charged oxygen of the zwitterion or S=O group of the pristine PES membrane, leading to severe fouling of SA even when a very low concentration of SA was used.

References

[1] M. Mulder, Basic principles of membrane technology, Kluwer Academic Publishers, 1997. 10.1007/978-94-009-1766-8

[2] K.J. Howe, M.M. Clark, Fouling of microfiltration and ultrafiltration membranes by natural waters, Environ. Sci. Technol. 36 (2002) 3571–3576. doi.org/10.1021/es025587r

[3] N.H. Lee, G. Amy, J.P. Croue, H. Buisson, Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM), Water Res. 38 (2004) 4511–4523. doi.org/10.1016/j.watres.2004.08.013

[4] N. Porcelli, S. Judd, Chemical cleaning of potable water membranes: A review, Sep. Purif. Technol. 71 (2010) 137–143. doi.org/10.1016/j.seppur.2009.12.007

[5] K. Xiao, X. Wang, X. Huang, T.D. Waite, X. Wen, Combined effect of membrane and foulant hydrophobicity and surface charge on adsorptive fouling during microfiltration, J. Membr. Sci. 373 (2011) 140–151. doi.org/10.1016/j.memsci.2011.02.041

[6] J.A. Koehler, M. Ulbricht, G. Belfort, Intermolecular forces between proteins and polymer films with relevance to filtration, Langmuir, 13 (1997) 4162–4171. doi.org/10.1021/la970010m

[7] W. Yuan, A.L. Zydney, Humic acid fouling during ultrafiltration, Environ. Sci. Technol. 34 (2000) 5043–5050. doi.org/10.1021/es0012366

[8] A.W. Zularisam, A.F. Ismail, R. Salim, Behaviours of natural organic matter in membrane filtration for surface water treatment - a review, Desalination, 194 (2006) 211–231. doi.org/10.1016/j.desal.2005.10.030

[9] H. Yamamura, K. Okimoto, K. Kimura, Y. Watanabe, Hydrophilic fraction of natural organic matter causing irreversible fouling of microfiltration and ultrafiltration membranes, Water Res. 54 (2014) 123–136. doi.org/10.1016/j.watres.2014.01.024

[10] J.A. Leenheer, Systematic approaches to comprehensive analyses of natural organic matter, Ann. Environ. Sci., 3 (2009) 1–130.

[11] W. Yuan, A.L. Zydney, Humic acid fouling during ultrafiltration, Environ. Sci. Technol., 34 (2000) 5043–5050. doi.org/10.1021/es0012366

[12] F. Qu, H. Liang, J. Zhou, J. Nan, S. Shao, J. Zhang, G. Li, Ultrafiltration membrane fouling caused by extracellular organic matter (EOM) from Microcystis aeruginosa: Effects of membrane pore size and surface hydrophobicity, J. Membr. Sci. 449 (2014) 58–66. doi.org/10.1016/j.memsci.2013.07.070

[13] N. Lee, G. Amy, J.-P. Croué, H. Buisson, Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM), Water Res. 38 (2004) 4511–4523. doi.org/10.1016/j.watres.2004.08.013

[14] D.E. Heath, S.L. Cooper, Design and characterization of sulfobetaine-containing terpolymer biomaterials, Acta Biomater. 8 (2012) 2899–2910. doi.org/10.1016/j.actbio.2012.03.052

[15] A. Venault, Y. Chang, Designs of zwitterionic interfaces and membranes, Langmuir, 35 (2018) 1714–1726. doi.org/10.1021/acs.langmuir.8b00562

[16] L. Mi, S. Jiang, Integrated antimicrobial and nonfouling zwitterionic polymers, Angew. Chem. Int. Ed. 53 (2014) 1746–1754. doi.org/10.1002/anie.201304060

[17] S. Chen, S. Liang, An new avenue to nonfouling materials, Adv. Mater. 20 (2008) 335–338. doi.org/10.1002/adma.200701164

[18] P. Bengani-Lutz, E. Converse, P. Cebe, A. Asatekin, Self-assembling zwitterionic copolymers as membrane selective layers with excellent fouling resistance: Effect of zwitterion chemistry, ACS Appl. Mater. Interfaces 9 (2017) 20859–20872. doi.org/10.1021/acsami.7b04884

[19] J. Shaoyi, C. Zhiqiang, Ultralow-fouling, functionalizable, and hydrolyzable zwitterionic materials and their derivatives for biological applications, Adv. Mater. 22 (2010) 920–932. doi.org/10.1002/adma.200901407

[20] C.C. Chang, K.W. Kolewe, Y. Li, I. Kosif, B.D. Freeman, K.R. Carter, J.D. Schiffman, T. Emrick, Underwater superoleophobic surfaces prepared from polymer zwitterion/dopamine composite coatings, Adv. Mater. Interfaces 3 (2016) 1500521. doi.org/10.1002/admi.201500521

[21] J.B. Schlenoff, Zwitteration: Coating surfaces with zwitterionic functionality to reduce nonspecific adsorption, Langmuir 30 (2014) 9625–9636. doi.org/10.1021/la500057j

[22] C.S. Zhao, J.M. Xue, F. Ran, S.D. Sun, Modification of polyethersulfone membranes - A review of methods, Prog. Mater. Sci. 58 (2013) 76–150. doi.org/10.1016/j.pmatsci.2012.07.002

[23] W.W. Yue, H.J. Li, T. Xiang, H. Qin, S.D. Sun, C.S. Zhao, Grafting of zwitterion from polysulfone membrane via surface-initiated ATRP with enhanced anti-fouling property and biocompatibility, J. Membr. Sci. 446 (2013) 79–91. doi.org/10.1016/j.memsci.2013.06.029

[24] Z. Yang, D. Saeki, H. Matsuyama, Zwitterionic polymer modification of polyamide reverse-osmosis membranes via surface amination and atom transfer radical polymerization for anti-biofouling, J. Membr. Sci. 550 (2018) 332–339. doi.org/10.1016/j.memsci.2018.01.001

[25] Z. Yang, D. Saeki, H.-C. Wu, T. Yoshioka, H. Matsuyama, Effect of polymer structure modified on RO membrane surfaces via surface-initiated ATRP on dynamic biofouling behavior, J. Membr. Sci. 582 (2019) 111–119. doi.org/10.1016/j.memsci.2019.03.094

[26] X. Fu, T. Maruyama, T. Sotani, H. Matsuyama, Effect of surface morphology on membrane fouling by humic acid with the use of cellulose acetate butyrate hollow fiber membranes, J. Membr. Sci. 320 (2008) 483–491. doi.org/10.1016/j.memsci.2008.04.027

[27] B. Van der Bruggen, Chemical Modification of Polyethersulfone Nanofiltration Membranes: A Review, J. Appl. Polym. Sci. 114 (2009) 630–642. doi.org/10.1002/app.30578

[28] M. Birkner, M. Ulbricht, Ultrafiltration membranes with markedly different pH- and ion-responsivity by photografted zwitterionic polysulfobetain or polycarbobetain, J. Membr. Sci. 494 (2015) 57–67. doi.org/10.1016/j.memsci.2015.07.046