Ionic strength- and thermo-responsive polyethersulfone composite membranes with enhanced antifouling properties†

Tao Xiang, Ting Lu, Wei-Feng Zhao and Chang-Sheng Zhao†

Smart materials with controllable responses to various stimulations offer considerable potential in many applications. Herein we report a simple and efficient method to fabricate ionic strength- and thermo-responsive polyethersulfone composite membranes using zwitterionic copolymers of sulfobetaine methacrylamide (SBMI) and sulfobetaine methacrylate (SBMA). The permeability of the modified membranes could be adjusted by varying the ionic strength from 0 mol kg\(^{-1}\) to 1.0 mol kg\(^{-1}\) and/or varying the surrounding temperature from 15 °C to 90 °C, and both the responses were reversible. The thermo-response transition temperature could be regulated by changing the chemical compositions of the zwitterionic copolymers. Furthermore, the zwitterionic copolymer modified membranes exhibited excellent antifouling resistances to protein solutions and surfactant-stabilized oil-in-water emulsions. Their ionic strength- and thermo-responsive flux, separation ability, and excellent antifouling properties endowed the membranes with a wide range of applications in the field of separation.

1. Introduction

Stimuli responsive membranes can change their physicochemical properties in response to external stimuli in the environment,\(^\text{1-3}\) and have been extensively applied in fields such as advanced separation, drug delivery, and biosensors.\(^\text{4,5}\) Their conformation, interfacial properties such as hydrophilic/hydrophobic properties and charges can vary with external stimuli, resulting in changes in the pore size and permeability properties of the membranes.\(^\text{6}\) The environmental stimuli include pH, temperature, light, ionic strength, electric fields, magnetic fields, and so on.\(^\text{1,2}\) Compared with single-stimulus responsive membranes, dual- and multi-stimuli-responsive membranes, which can respond to more than one stimulus, possess more regulation modes and broader applications.\(^\text{1,2}\) As ionic strength and temperature are common and easily controlled stimuli, it is of great importance to develop ionic strength- and thermo-responsive membranes to broaden the application of responsive membranes, which have rarely been reported. Polymeric materials including polyethersulfone (PES), cellulose acetate (CA), polyacrylonitrile (PAN), polyvinyl alcohol (PVA) and polysulfone (PSf) are widely used in biomedical devices and the separation field, and the modifications to endow them with multi-responsive functions are significant.\(^\text{3,7}\)

Thermo-responsive polymers have been widely studied, for which the conformational change occurs due to the variation in reversible solubility upon changing the temperature.\(^\text{8-10}\) Thermo-responsive membranes can be fabricated by introducing thermo-responsive polymers in the substrates.\(^\text{11,12}\) Poly(N-isopropylacrylamide) (PNIPAAm), as the most widely used polymer with a lower critical solution temperature (LCST) around 32 °C, has been used to modify poly(vinylidene fluoride) (PVDF),\(^\text{13,14}\) polysulfone (PSf),\(^\text{15}\) and chitosan\(^\text{16}\) with adjusted permeability properties. Sulfobetaine-based zwitterionic polymers, bearing both positive ammonium and negative sulfonate charges on the repeat unit, exhibited an upper critical solution temperature (UCST), below which the zwitterionic polymers were poorly soluble due to attractive inter-chain electrostatic interactions.\(^\text{17-21}\) Thermo-responsive membranes can show thermoresponsivity by changing their permeability properties, which has not been reported yet.

Ionic strength-responsive or salt-responsive polymers mainly contain a charged polyelectrolyte.\(^\text{23,24}\) Zwitterionic polymers always...
exhibit improved solubility when salts are added to the aqueous solution, since the salts reduce the inter-chain interaction, leading to chain expansion and then water-solubility.25,26 As for negatively and positively charged polyelectrolytes, the added salt could screen the electrostatic interaction within the polymer, leading to a conformational change from the stretched form to a collapsed one.27

As mentioned above, the inter-chain interaction and solubility of zwitterionic polymers can vary with both the temperature and ionic strength of the solution. Yet, the previously studied ones mainly focused on the solubility and conformational change in solutions.17,25,26 What if we introduce zwitterionic polymers in membranes? In our previous study,28 we prepared poly(sulfobetaine methacrylate) (PSBMA) modified polyethersulfone (PES) ultrafiltration membranes, which exhibited adjusted water flux by changing the ionic strength of the solution. Zwitterionic polymer modified membranes exhibited excellent resistance to proteins, platelets and cell adhesion, which was attributed to the decent hydrophilic hydration layer formed by the high density of PSBMA segments on the membranes.29–31 Herein, we propose to fabricate zwitterionic polymer modified membranes with both adjusted thermo-responsive and ionic strength-responsive properties along with the antifouling properties.

The aim of this study is to fabricate ionic strength- and thermo-responsive PES membranes using sulfobetaine-based zwitterionic copolymers, poly(sulfobetaine methacrylamide-co-sulfobetaine methacrylate) (PSBMI-co-PSBMA), which are synthesized via in situ cross-linked free radical copolymerization. As PSBMI and PSBMA have different transition temperatures of about 30 °C and 80 °C,32,33 respectively, we anticipate regulating the permeability properties by controlling the chemical compositions of the zwitterionic copolymers (Scheme 1a).

Composite membranes were then fabricated using the obtained solution by spin casting coupled with a liquid-liquid phase separation technique. The permeabilities of the membranes were evaluated by measuring the water flux as a function of ionic strength and temperature. At temperatures lower than the transition temperature, the zwitterionic polymers are in a shrunken state because of inter-chain electrostatic interactions, so the membrane pores are “OPEN”2 on the other hand, at temperatures higher than the transition temperature, the zwitterionic polymers are in a swollen state, due to the decreased inter-chain electrostatic interactions, so the membrane pores are “CLOSED”. Similarly, by changing the ionic strength of the solution, the zwitterionic polymers can be transformed between shrunken and swollen states, resulting in the membrane pores being “OPEN” and “CLOSED”, respectively. Their antifouling properties towards protein solutions and surfactant-stabilized oil-in-water emulsions were also studied.

2. Materials and methods

2.1. Materials

2-(Dimethylamino)ethyl methacrylate (DMAEMA, 99%, Aladdin), dimethylamino propyl methacrylamide (DMAPMA, 99%, Aladdin), 1,3-propanesulfonate (99%, Aladdin), N,N'-methylenebisacrylamide (MBA, 99%, Aladdin), dimethyl sulfoxide (DMSO), sodium chloride (NaCl, 99%, Kelong), n-hexane (99%, Aladdin), polyethersulfone (PES, Ultrason E6020P, BASF), n-hexane (98%, Aladdin), Tween-80 (Aladdin), bovine serum albumin (BSA, fraction V, Sigma) and bovine serum fibrinogen (BFG, Sigma) were used as received. 2,2’-Azobis(2-methylpropionitrile) (AIBN, 98%, Aladdin) was purified by recrystallization. Micro BCA™ protein assay reagent kits (Thermo Co.) were used as received. Phosphate buffered saline solution (PBS, 0.01 mol L⁻¹, pH 7.4) was prepared before use. Deionized water was used throughout the study.

2.2. Membrane preparation

Zwitterionic monomers sulfobetaine methacrylamide (SBMI) and sulfobetaine methacrylate (SBMA) were first synthesized by the reaction between 1,3-propanesulfonate and DMAPMA or DMAEMA, respectively.34 and the synthesis process is shown in the ESI.† The result of 1H NMR spectra verified the successful synthesis of the monomers (Fig. S1, ESI†). The copolymers poly(sulfobetaine methacrylamide-co-sulfobetaine methacrylate) (PSBMI-co-PSBMA) were synthesized by in situ cross-linked copolymerization of SBMI and SBMA in PES solution. The method is simple without processes like precipitation and dialysis, and the structure of the membranes was stable since cross-linkers were added into the reaction solution with the monomers.35–37 The membrane fabrication process is as follows: PES and SBMI and SBMA monomers were dissolved in DMSO to get a homogeneous solution, and the solution was bubbled with nitrogen to remove oxygen. Then a mixture of AIBN and MBA in DMSO was added into the above solution under a nitrogen atmosphere. The details of the compositions of the reaction solutions are shown in Table 1. The polymerization was carried out at 75 °C with a stirring speed of 400 rpm for
16 h. After being cooled and vacuum degassed, the solution was prepared into membranes by spin casting coupled with a liquid–liquid phase separation technique at room temperature. The membranes were rinsed in deionized water thoroughly to remove the residual solvent. All the prepared membranes had a uniform thickness of about 55 ± 3 μm. For comparison, a pristine PES membrane without the zwitterionic copolymer was also fabricated using the same procedure.

2.3. Characterization

$^1$H NMR spectra were recorded on a Bruker AVII-400 MHz spectrometer (Bruker Co., Germany). Fourier transform infrared spectra (FTIR) were obtained using a Fourier-transform infrared spectrometer (Nicolet 560, USA). Each spectrum was collected at a resolution of 4 cm$^{-1}$ and the reflectance spectra were scanned over the 675–4000 cm$^{-1}$ range. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS ULTRA DLD XPS Instrument, employing Al Kα excitation radiation. Thermogravimetric analysis (TGA) was performed on a TG209F1 TG instrument (Netzsch, Germany) at a heating rate of 10 °C min$^{-1}$ under a N$_2$ atmosphere. The surface and cross-sectional morphologies of the membranes were characterized using a desktop scanning microscope (SEM, Phenom Pure, FEI) with a voltage of 5 kV. The hydrophilicity of the membrane surface was characterized on the basis of contact angle measurements. The contact angles (DCAs) were measured and calculated on a contact angle goniometer (DataPhysics OCA20, Germany) equipped with video capture at ambient temperature. One drop of water (3 μL) was dropped onto the surface of the membrane with an automatic piston syringe and photographed. The contact angles at every five seconds were determined from these images using calculation software. The porosities ($\phi$), mean pore sizes ($r_m$) and water uptakes (WU) of the membranes were measured using the methods in our previous study, and the details are shown in the ESL.$^\dagger$

2.4. Ultrafiltration experiments

Ultrafiltration experiments were utilized to investigate the ionic strength- and thermo-dependent permeability performances using the apparatus as described in our previous study. The antifouling properties were also evaluated and expressed in terms of the flux recovery ratios before and after ultrafiltration of BSA solution. In addition, oil-in-water emulsions with varying ionic strength were also applied to the membranes.

A dead-end ultrafiltration cell with an effective membrane area of 3.9 cm$^2$ was used. The test membrane was pre-compacted with deionized water at a pressure of 0.1 MPa for 30 min to achieve steady filtration, and then the flux was measured at a pressure of 0.05 MPa.

2.4.1. Ultrafiltration of pure water. The water flux of the membrane was measured by collecting the permeated water, and calculated using the following equation:

$$\text{Flux} = \frac{V}{S \cdot t \cdot P}$$

where $V$ (mL) is the volume of the permeated solution; $S$ ($\text{m}^2$) is the effective membrane area; $t$ (h) is the time for collecting the permeated solution; and $P$ (mmHg) is the applied pressure of the membrane.

2.4.2. Ultrafiltration of salt solution at varying temperatures. To study the ionic strength- and thermo-responsivity, both the ionic strength and temperature of the inlet solution were carefully controlled by adding sodium chloride and using a water bath, respectively. For the ionic strength-responsivity, the temperature of the inlet solution and ultrafiltration cell was controlled at a certain value, with the ionic strength ranging from 0 to 1.0 mol kg$^{-1}$. For the thermo-responsivity, the ionic strength of the inlet solution was maintained at a certain value, with the temperature ranging from 15 to 90 °C. The fluxes under various ionic strengths and temperatures were also calculated using eqn (1) after the flux became steady.

2.4.3. Ultrafiltration of BSA solution. To investigate the antifouling properties, BSA is used as a model foulant with a concentration of 1 mg mL$^{-1}$ (dissolved in PBS). The BSA solution and PBS were alternately applied to the membranes at a pressure of 0.05 MPa for three cycles, and the fluxes were calculated using eqn (1). For each cycle, the BSA solution was first applied to the membranes, then the membranes were cleaned with deionized water for each cycle. The flux of PBS was then measured. The antifouling properties were expressed in terms of the flux recovery ratio ($F_{RR}$) of PBS, which was calculated by the following equation:

$$F_{RR}(\%) = \left(\frac{F_1}{F_2}\right) \times 100$$

where $F_1$ and $F_2$ (mL m$^{-2}$ h$^{-1}$ mmHg) are the PBS fluxes before and after protein ultrafiltration, respectively.

2.4.4. Ultrafiltration of oil-in-water emulsions. The oil-in-water emulsion was prepared as follows: 10 mL of n-hexane was added into 490 mL of deionized water with 15 mg of Tween-80 as the emulsifier, and the solution was stirred at 1200 rpm for 5 h. NaCl was also added to the water to control the ionic strength with 0.1 mol kg$^{-1}$. Then the fluxes for the emulsions were also calculated using eqn (1).

2.5. Blood compatibility

2.5.1. Protein adsorption. BSA or BFG was dissolved in PBS with a concentration of 1 mg mL$^{-1}$. The membrane with an area of 1 × 1 cm$^2$ was incubated in PBS at 37 °C for 1 h and immersed in the protein solution at 37 °C for 2 h. The membrane
was then gently rinsed with PBS and then immersed in 2 wt% aqueous SDS solution at 37 °C for 1 h under agitation to remove the protein adsorbed onto the membrane. The protein concentration was measured using a UV-vis spectrophotometer (UV-1750, Shimadzu, Japan) at a wavelength of 562 nm using Micro BCA™ protein assay reagent kits, then the protein adsorption amounts were calculated.

2.5.2. Platelet adhesion. Fresh human blood (man, 24 years old) was collected using vacuum tubes (5 mL, Terumo Co.), containing a citrate/phosphate/dextrose/adenine-1 mixture solution (CPDA-1) as the anticoagulant (anticoagulant to blood ratio, 1:9). To eliminate the interference of other components in blood, such as erythrocytes and leucocytes, platelet-rich-plasma (PRP) was used for the platelet adhesion experiment. The blood was centrifuged at 1000 rpm for 15 min to obtain PRP. All the blood compatibility experiments were performed in compliance with the relevant laws and institutional guidelines, as per Chinese clinical trials of the medical device regulation (01.04.2014) and methods of ethical review of biomedical research involving human beings (01.12.2016), and the protocol was approved by the Institutional Ethical Committee (IEC) of Sichuan University (11.05.2016), China, and all participants provided written informed consent.

The membrane with an area of 1 × 1 cm² was incubated in PBS at 37 °C for 1 h. Then the PBS was removed and 1 mL of fresh PRP was added and incubated with PRP at 37 °C for 2 h. Afterward, the membrane was gently rinsed three times with PBS and treated with 2.5 wt% glutaraldehyde in PBS at 4 °C for at least 1 day for curing platelets. To observe the morphology of the platelets on the surface, the membrane was washed with PBS, and subjected to a drying process by immersing it in a series of graded alcohol–PBS solutions (25%, 50%, 70%, 75%, 90%, 95% and 100%) and isoamyl acetate–alcohol solutions (25%, 50%, 75% and 100%) for 15 min each time. The critical point drying of the specimens was done with liquid CO₂.

The number of the adherent platelets on the membrane was calculated according to five SEM images from different places on the same membrane.

3. Results and discussion

3.1. Morphologies of the membranes

SEM images for the upper surface and glass side surface are shown in Fig. 1(a) and (b). It was observed that the surface of the pristine PES membrane was smooth and there were no obvious pores on the surface. Yet, pores were obvious on the upper surface and glass side surface of the zwitterionic copolymer modified membranes. The cross-sectional images are shown in Fig. 1(c), and large amounts of macrovoids were observed for the PES membrane. After the zwitterionic copolymers were introduced, the macrovoids disappeared and a spongy structure was observed, due to the liquid–liquid exchange between non-solvent (water) and the solvent (DMSO), and the phase separation of polymers.

3.2. Chemical compositions of the membranes

The surface chemical compositions of the membranes were analyzed by ATR-FTIR and XPS. The ATR-FTIR spectra are shown in Fig. 2(a) and Fig. S2 (ESI†). The absorption peaks at 1643 cm⁻¹ and 1726 cm⁻¹ were ascribed to the –CONH– and –COO– groups, which belonged to SBMA and SBMI in the copolymer, respectively. To analyze the chemical compositions of the zwitterionic copolymers in the membranes, the integral area ratios of the peaks of –CONH– and –COO– (\( \text{A}_{1672-1614}/\text{A}_{1751-1700} \)) were also calculated and are shown in Fig. 2(b). The integral area ratios were very close to the ratios of SBMI to SBMA added into the reaction solutions, indicating that the chemical compositions of the zwitterionic copolymers could be controlled by altering the
ratios of SBMI to SBMA in the reaction solutions. The results of XPS are shown in Fig. 2(c) and Fig. S3 (ESI†). The peak of 401.9 eV for the N 1s scan was ascribed to the N⁺ in the polymer of PSBMA. When the SBMI were copolymerized with SBMI, a new peak of 399.1 eV appeared, which belonged to the –CONH– group. By comparing the integral areas of the peaks of 401.9 and 399.1 eV, the ratios of SBMI to SBMA in the membranes could also be calculated as shown in Fig. S4 (ESI†).

To investigate the bulk chemical compositions of the modified membranes, TGA was carried out from 20 to 800 °C under a N₂ atmosphere (Fig. 2(d)). The PES membrane showed a weight loss in the 380–680 °C range, which was ascribed to the decomposition of PES. The modified membranes showed a weight loss of about 14% in the 250–380 °C range and a weight loss of about 45% in the 380–680 °C range, which were ascribed to the decomposition of the zwitterionic copolymer and PES, respectively. TGA results indicated that there were about 23 wt% of zwitterionic copolymers in the modified membranes.

### 3.3. Wettability measurements

The water contact angle (WCA) is used to characterize the hydrophilicity of membrane surfaces, providing the wettability properties of the material surface. The initial WCA of the PES membrane was 82.8° and decreased by about 6° in 200 s as shown in Fig. 3. For the zwitterionic copolymer modified membranes, the initial WCAs of the modified membranes were 40–60° and decreased by about 15° in 200 s. We also found that the PSA membrane showed better hydrophilicity than the PSI membrane, which might have resulted from the shorter alkyl chain. These results indicated that the hydrophilicity of the

---

**Fig. 2** (a) ATR-FTIR spectra of zwitterionic copolymer modified membranes in the 1610–1880 cm⁻¹ region, in which the peaks at 1643 cm⁻¹ and 1726 cm⁻¹ represent the characteristic absorption peaks of –CONH– and –COO–, respectively. (b) Integral area ratios of the peaks of –CONH– and –COO– in the 1672–1614 cm⁻¹ and 1751–1700 cm⁻¹ regions, respectively. (c) XPS spectra of N 1s scan for PSI, PSI₁SA₁ and PSA membranes. (d) TGA curves for the PES, PSI, PSI₁SA₁ and PSA membranes.

**Fig. 3** Water contact angles (WCAs) decaying with time for the pristine and modified PES membranes at room temperature.
modified membranes was improved compared to the pristine PES membrane. The increased hydrophilicity may have a positive influence on the antifouling properties, which will be discussed below.

The wettability of the bulk membrane was then measured in terms of water uptake, which was calculated by the weight change before and after the membranes were fully wetted. As shown in Table 2, the water uptake of the PES membrane was 47.66%.

After the zwitterionic copolymers were introduced in the membranes, the water uptakes were increased to above 120%. Thus, the wettability of the modified membranes was significantly improved.

### 3.4. Porosities, pure water fluxes and mean pore sizes of the membranes

Membrane porosity is significant for investigating the relationship between membrane structure and membrane permeability, and

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Membrane porosity (%)</th>
<th>Pure water flux (mL·m⁻²·h⁻¹·mmHg)</th>
<th>Mean pore size (nm)</th>
<th>Water uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>76.73</td>
<td>242.91</td>
<td>20.19</td>
<td>47.66</td>
</tr>
<tr>
<td>PSI</td>
<td>69.85</td>
<td>145.75</td>
<td>17.01</td>
<td>125.40</td>
</tr>
<tr>
<td>PSI₁SA₁</td>
<td>70.47</td>
<td>303.64</td>
<td>24.37</td>
<td>131.37</td>
</tr>
<tr>
<td>PSI₁SA₁</td>
<td>69.37</td>
<td>429.15</td>
<td>29.37</td>
<td>146.86</td>
</tr>
<tr>
<td>PSI₁SA₃</td>
<td>68.59</td>
<td>566.80</td>
<td>34.08</td>
<td>139.62</td>
</tr>
<tr>
<td>PSA</td>
<td>69.65</td>
<td>781.38</td>
<td>39.48</td>
<td>136.41</td>
</tr>
</tbody>
</table>

Fig. 4 Fluxes as a function of temperature for (a) PES, (b) PSI, (c) PSI₁SA₁, (d) PSI₁SA₁, (e) PSI₁SA₃ and (f) PSA membranes. The ionic strengths of the solutions were controlled at 0 mol kg⁻¹ and 1.0 mol kg⁻¹ by adding NaCl.
the results are shown in Table 2. To eliminate the effect of temperature on membrane structure, the water flux was measured at room temperature. The porosity of the PES membrane was 76.73%, which was greater than those of all the modified membranes. The result coincided with the SEM images, in which large amounts of macrovoids were obvious.

The pure water fluxes were then measured. The water flux of the pristine PES membrane was 242.91 mL m⁻² h⁻¹ mmHg, and the fluxes of the modified membranes ranged from 145.75 to 781.38 mL m⁻² h⁻¹ mmHg and showed a relationship with the chemical compositions of the zwitterionic copolymers. The reason might be that the hydrophilicity of the membranes had a critical effect on the water flux. As shown in Fig. 3, the hydrophilicity of the modified membranes increased with the increase of the SBMA amount in the zwitterionic copolymer.

The mean pore sizes (rₚ) of the membranes were then calculated using the Guerout–Elford–Ferry equation on the basis of pure water flux and porosity. Since the porosities of all the membranes showed little difference, the pore sizes were mainly affected by the pure water flux. The pore sizes of all the membranes ranged from 17.01 to 39.48 nm.

### 3.5. Ionic strength- and thermo-responsive properties of the membranes

The swelling and shrinking of the zwitterionic polymers could be altered by changing the ionic strength or temperature, which could be explained by the antipolyelectrolyte effect. The performance of the zwitterionic copolymer modified membranes with varying temperature and ionic strength is interesting. The fluxes as a function of temperature for the membranes are first investigated. When the temperature was elevated from 15 to 90 °C, the water fluxes for all the modified membranes showed a good linear trend. The fluxes started to decrease at about 30 °C, 45 °C, and 55 °C for the PSI, PSI, SA, and PSA membranes, respectively. At these points, the inter-chain electrostatic interactions of the zwitterionic copolymers were weakened and the polymer chains swelled, resulting in flux decrease. For example, the fluxes of the PSI, SA membrane decreased between about 30 and 55 °C, between which the zwitterionic copolymer chains swelled. When the temperature increased above 55 °C, the fluxes increased again, similar to that for the pristine PES membrane.

When the inlet solution was 1.0 mol kg⁻¹ NaCl solution, the fluxes for all the modified membranes showed a good linear relation to the increase of temperature, which was similar to that for the pristine PES membrane. The reason was that when the 1.0 mol kg⁻¹ NaCl solution was applied, the zwitterionic copolymer chains were fully swollen, and changed little upon increasing the temperature. The results indicated that when the inlet solution was DI water, all the modified membranes showed thermo-responsivity, and the transformation temperature was adjustable by controlling the temperature on membrane structure, the water flux was measured at room temperature. The porosity of the PES membrane was 76.73%, which was greater than those of all the modified membranes. The result coincided with the SEM images, in which large amounts of macrovoids were obvious.

The pure water fluxes were then measured. The water flux of the pristine PES membrane was 242.91 mL m⁻² h⁻¹ mmHg, and the fluxes of the modified membranes ranged from 145.75 to 781.38 mL m⁻² h⁻¹ mmHg and showed a relationship with the chemical compositions of the zwitterionic copolymers. The reason might be that the hydrophilicity of the membranes had a critical effect on the water flux. As shown in Fig. 3, the hydrophilicity of the modified membranes increased with the increase of the SBMA amount in the zwitterionic copolymer.

The mean pore sizes (rₚ) of the membranes were then calculated using the Guerout–Elford–Ferry equation on the basis of pure water flux and porosity. Since the porosities of all the membranes showed little difference, the pore sizes were mainly affected by the pure water flux. The pore sizes of all the membranes ranged from 17.01 to 39.48 nm.

### 3.5. Ionic strength- and thermo-responsive properties of the membranes

The swelling and shrinking of the zwitterionic polymers could be altered by changing the ionic strength or temperature, which could be explained by the antipolyelectrolyte effect. The performance of the zwitterionic copolymer modified membranes with varying temperature and ionic strength is interesting. The fluxes as a function of temperature for the membranes are first investigated. When the temperature was elevated from 15 to 90 °C, the water fluxes for all the modified membranes showed a good linear trend. The fluxes started to decrease at about 30 °C, 45 °C, and 55 °C for the PSI, PSI, SA, and PSA membranes, respectively. At these points, the inter-chain electrostatic interactions of the zwitterionic copolymers were weakened and the polymer chains swelled, resulting in flux decrease. For example, the fluxes of the PSI, SA membrane decreased between about 30 and 55 °C, between which the zwitterionic copolymer chains swelled. When the temperature increased above 55 °C, the fluxes increased again, similar to that for the pristine PES membrane.

When the inlet solution was 1.0 mol kg⁻¹ NaCl solution, the fluxes for all the modified membranes showed a good linear relation to the increase of temperature, which was similar to that for the pristine PES membrane. The reason was that when the 1.0 mol kg⁻¹ NaCl solution was applied, the zwitterionic copolymer chains were fully swollen, and changed little upon increasing the temperature. The results indicated that when the inlet solution was DI water, all the modified membranes showed thermo-responsivity, and the transformation temperature was adjustable by controlling the chemical compositions in the zwitterionic copolymers; when a high ionic strength solution (like 1.0 mol kg⁻¹) was used, the thermo-responsivity would disappear.

![Fig. 5 Fluxes as a function of ionic strength, and the temperature was controlled at 15 and 50 °C, respectively.](image)

![Fig. 6 (a) Fluxes as the temperature was changed between 15 °C and 50 °C for PES, PSI, SA and PSA membranes. (b) Fluxes as the ionic strengths of the solutions were changed between 0 mol kg⁻¹ (“water” in the figure) and 1.0 mol kg⁻¹ (“salt” in the figure) for the PES, PSI, SA and PSA membranes.](image)
Then we investigated the water flux as a function of ionic strength as shown in Fig. 5. The fluxes of the pristine PES membrane at 15 °C or 50 °C did not change when the ionic strength was varied from 0 mol kg⁻¹ to 1.0 mol kg⁻¹. However, for the PSI₁SA₁ membrane, the fluxes sharply decreased from 0 mol kg⁻¹ to 0.1 mol kg⁻¹, and gradually decreased from 0.1 mol kg⁻¹ to 1.0 mol kg⁻¹. The variation trend was also remarkable when the temperature changed from 15 °C to 50 °C for the PSI₁SA₁ membrane. A similar consequence was also found for the other modified membranes. Thus, the modified membranes showed obvious ionic strength-responsivity for the zwitterionic copolymer modified membranes.

To assess the stability of the response to temperature and ionic strength, the reversibility of both thermo-responsivity and ionic strength-responsivity was then studied and the results are shown in Fig. 6. It was found that when the temperature or ionic strength was changed, the flux would become steady in less than 5 min. Meanwhile, the flux would attain the same values even after five cycles.

The above results indicated that the modified membranes exhibited excellent ionic strength- and thermo-sensitive properties, and the responses were reversible. When DI water was used as the inlet solution, the fluxes of the modified membranes could be adjusted by controlling the temperature, which showed an increase–decrease–increase trend. However, when a high ionic strength solution (1.0 mol kg⁻¹) was used, the response would disappear. From another perspective, the membrane pores and fluxes are mainly determined by electrostatic interactions of zwitterionic chains, which influence the swelling or shrinking of polymer chains. When a solution with low ionic strength (<0.1 mol kg⁻¹) was applied or the surrounding temperature was below the transformation temperature, the membrane fluxes could be adjusted by controlling the ionic strength or temperature, which was realized by weakening the inter-chain electrostatic interactions of the zwitterionic copolymers and enhancing the chain swelling. In contrast, when a high ionic strength (1.0 mol kg⁻¹) was applied or the surrounding temperature was above the transformation temperature, both the ionic strength- and thermo-sensitive properties would disappear, because the polymer chains were fully swollen.

3.6. Resistances to proteins and platelets
We first investigated the membrane resistance to proteins (BSA and BFG), and the results are shown in Fig. S5 (ESI†). The BSA and BFG adsorption amounts for the pristine PES were about 19.0 and 17.0 μg cm⁻², respectively. After the zwitterionic
copolymers were introduced into the membranes, the BSA and BFG adsorption amounts decreased to about 2–5 μg cm⁻².

Fig. 7 shows the typical SEM images of the platelets adhered on the pristine and modified PES membranes. Many platelets accumulated on the pristine PES surface (6.2 × 10⁶ cells per cm²), and the pseudopodia were obvious. After the membranes were modified with zwitterionic copolymers, the adhered platelet amounts were decreased and fewer pseudopodia were observed. The decreased amounts of the platelets indicated that the resistance to platelet adhesion was improved after the modification of the zwitterionic copolymers and the platelet morphology was better than that on the PES membrane.

3.7. Antifouling properties of BSA solution and oil-in-water emulsions

The antifouling properties of the membranes were investigated by ultrafiltration of BSA solution, expressed in terms of flux recovery ratios (FRRs). The flux recovery ratios (FRRs) of the pristine PES membrane at 15 °C and 37 °C were about 70%. For all the zwitterionic copolymer modified membranes, the FRRs were above 92% as shown in Table 3. The flux curves during a process of three cycles of BSA solution and PBS were similar to those of our previous study. Thus, the modified membranes showed excellent antifouling properties with the BSA solution at both 15 °C and 37 °C with the FRRs greater than 92%.

To further study their antifouling properties, an oil-in-water emulsion was applied to the membranes at room temperature,

and the results are shown in Fig. 8. The fluxes of the PES membrane decreased with time. For the PSI membrane, when the inlet solution was an oil-in-water emulsion with an ionic strength of 0 mol kg⁻¹, the fluxes decreased with time; when the ionic strength was 0.1 mol kg⁻¹, the initial flux was smaller than in DI water, but the fluxes were stable over the test time and no decrease was found. The above results show that by increasing the ionic strength of the inlet solution, the stretched zwitterionic chains can effectively decrease the fouling of the oil-in-water emulsion.

4. Conclusions

Ionic strength- and thermo-responsive PES membranes modified with zwitterionic copolymers P(SBMI-co-SBMA) were fabricated by in situ cross-linked copolymerization of SBMI and SBMA in PES solution. The chemical compositions of the zwitterionic copolymers were adjustable by controlling the ratios of the monomers in the reaction solution. The modified membranes showed excellent reversible ionic strength- and thermo-sensitivity, which was mainly determined by the electrostatic interactions of zwitterionic chains, by influencing the swelling or shrinking of polymer chains. When the surrounding temperature was below the transformation temperature, the fluxes of the modified membranes sharply decreased from 0 mol kg⁻¹ to 0.1 mol kg⁻¹, and gradually decreased from 0.1 mol kg⁻¹ to 1.0 mol kg⁻¹; when the DI water was used as the feed solution, the membranes showed thermo-sensitivity and the transformation temperature could be adjusted by the chemical compositions of the zwitterionic copolymers. The results also revealed that when a high ionic strength (1.0 mol kg⁻¹) was applied or the surrounding temperature was above the transformation temperature, both the ionic strength- and thermo-sensitive properties would disappear, because the polymer chains were fully swollen. Meanwhile, the modified membranes showed good resistance to protein adsorption and platelets, and the antifouling in the ultrafiltration of BSA solution and oil-in-water emulsions was excellent. These results indicated that the P(SBMA-co-SBMI) modified membranes have potential to be used in the separation field.

Table 3 The antifouling properties of the membranes were investigated by ultrafiltration of BSA solution, expressed in terms of flux recovery ratios (FRRs) of the pristine PES membrane at 15 °C and 37 °C, respectively. Values are expressed as means ± SD, n = 3

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Flux recovery ratios (%)</th>
<th>15 °C</th>
<th>37 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>71.45 ± 5.21</td>
<td>73.21 ± 3.76</td>
<td></td>
</tr>
<tr>
<td>PSI</td>
<td>92.42 ± 6.15</td>
<td>92.21 ± 5.88</td>
<td></td>
</tr>
<tr>
<td>PSI₁SA₁</td>
<td>93.22 ± 5.76</td>
<td>92.41 ± 7.32</td>
<td></td>
</tr>
<tr>
<td>PSA</td>
<td>92.47 ± 6.91</td>
<td>93.35 ± 5.98</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8 Fluxes as a function of time for PES and PSI membranes at room temperature. The ionic strength was controlled at 0 mol kg⁻¹ and 0.1 mol kg⁻¹.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially sponsored by the National Natural Science Foundation of China (No. 51433007 and 51503125), and the Open Research Project of the State Key Laboratory of Molecular Engineering of Polymers, Fudan University (No. K2018-10). We also thank our laboratory members for their generous help, and gratefully acknowledge the help of Ms Hui Wang of the Analytical and Testing Center at Sichuan University for the SEM observation.
References


