

## Charged Membranes Prepared by SPEEK of Very Low Degree of Sulfonation

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**ABSTRACT:** Novel charged membranes were prepared with sulfonated poly(ether ether ketone) (SPEEK). Methylsulfonic acid was used as solvent to accommodate the very low degree of sulfonation of the SPEEK. Membranes were prepared by immersion phase inversion method, using coagulation baths of different composition and temperature. Low molecular weight and negatively charged dye molecules were used as model solutes to test the nanofiltration (NF) performance of the membranes. Higher than 93% rejection of the two dye molecules, Rose Bengal and Reactive Brilliant Red, was observed at normal operating temperature. A permeate flux as high as  $497 \text{ L m}^{-2} \text{ h}^{-1}$  and higher than 90% of solute rejection at  $80^\circ\text{C}$  was achieved in the NF of Reactive Brilliant Red aqueous solution, in contrast to a flux of  $226 \text{ L m}^{-2} \text{ h}^{-1}$  and about 78% of solute rejection at the same temperature in the case of Rose Bengal solute. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** membranes; phase separation; morphology

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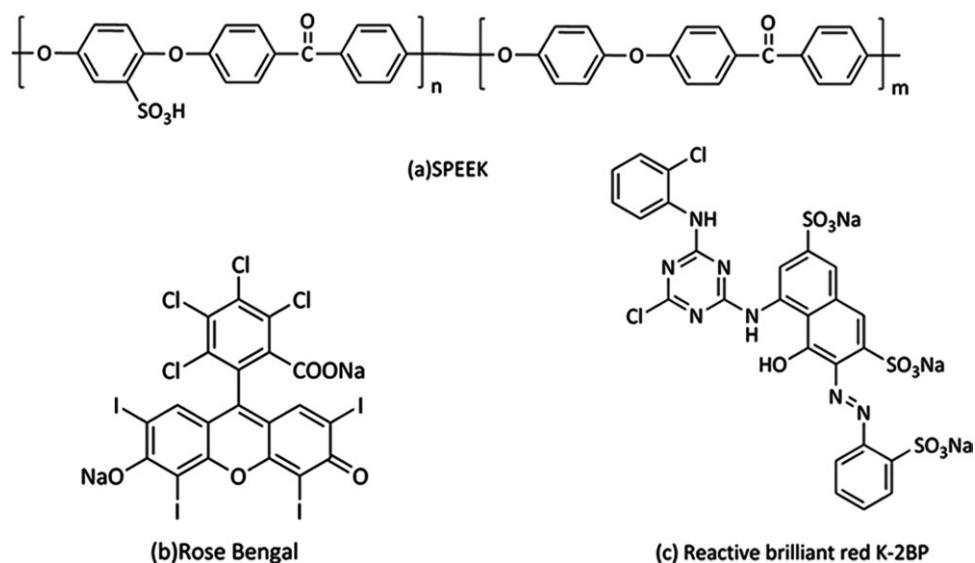
### INTRODUCTION

Nanofiltration (NF) is a pressure-driven membrane process which has found wide application in diverse industrial sectors, including water treatment,<sup>1–5</sup> chemical production,<sup>6</sup> food processing,<sup>7</sup> biotechnology,<sup>8</sup> etc. Charged NF membranes have been extensively researched and practically used to reduce fouling, increase water permeability, and enhance solute retention. Different methods can be employed to introduce charges into a membrane. The most often adopted method is polymer blending,<sup>9–12</sup> i.e., mixing a charged polymer with another polymer in the solution during membrane preparation. Other methods include interfacial polymerization,<sup>13–15</sup> plasma modification,<sup>16</sup> photochemical modification,<sup>17</sup> and surface modification by UV irradiation<sup>18,19</sup> or layer-by-layer deposition.<sup>20,21</sup>

Among the available charged polymers, sulfonated poly(ether ether ketone) (SPEEK) [Figure 1(a)] was often chosen to bring negative charges to NF membranes due to its high thermal and mechanical stability, as well as good miscibility with several important membrane forming polymers. In the past decade, many researches on SPEEK containing NF composite membranes were reported. These include membranes of SPEEK compounding with polysulfone (PS or PSf),<sup>10–12</sup> polyethersulfone (PES),<sup>9,22,23</sup> polyetherimide (PEI),<sup>24</sup> cellulose acetate (CA),<sup>25</sup> and so on.

To prepare SPEEK composite membranes, the sulfonation degree of the SPEEK material employed usually needs to be well above 30%, so that it can dissolve in commonly used organic solvents, e.g. dimethylformamide (DMF) or dimethylsulfoxide (DMSO).<sup>26</sup> Also, a high content of sulfonate groups in the SPEEK is often required to equip a membrane with enough charges, as SPEEK is usually not a major component of the whole membrane. However, the more sulfonate groups SPEEK has, the more likely this material tends to dissolve in aqueous solutions, especially at elevated temperature.<sup>26,27</sup> So membranes containing SPEEK of high degree of sulfonation are not suitable for higher temperature use. Such membranes can even deteriorate at room temperature as a result of SPEEK escaping with time from the membranes. It would be desirable to fabricate NF membrane wholly with SPEEK, so that its sulfonation degree can be low enough to avoid over swelling or dissolution and yet the charge content in the membrane is high enough to facilitate its performance of separation. So far, such membrane has not been reported to our best knowledge.

In this article, we report our work on preparing charged membranes merely with SPEEK of very low sulfonation degree and present their performance in the NF of charged dye solutes from water.



**Figure 1.** The chemical structure of (a) SPEEK, (b) Rose Bengal and (c) Reactive Brilliant Red K-2BP.

## EXPERIMENTAL

### Materials

Poly(ether ether ketone) (PEEK) (Victrex<sup>®</sup>, Grade 450 P,  $M_w = 38,300$ ), in the form of pellet, was purchased from Nanjing Yuanbang Engineering Plastics, Rose Bengal (RB,  $M_w = 1017.65$ ) [Figure 1(b)] was supplied by Alfa Aesar China (Tianjin). Reactive Brilliant Red K-2BP (RBR,  $M_w = 808.48$ ) [Figure 1(c)] was purchased from Tianjin Tianshun Chemical Dyestuff. Methylsulfonic acid (MSA), sodium hydroxide, hydrochloric acid, absolute ethyl alcohol, and concentrated sulfuric acid (95–98%) were purchased from Kewei Chemistry. Deionized water having a conductivity of less than  $10 \mu\text{S cm}^{-1}$  was produced by means of reverse osmosis in our laboratory.

### SPEEK Preparation and Characterization

SPEEK was prepared in our laboratory in the way similar to that described in Ref. 26. PEEK was dried in a vacuum oven at  $100^\circ\text{C}$  overnight. After that, PEEK (10 g) was dissolved in 150 mL of concentrated sulfuric acid (95–98%) and vigorously stirred at  $35^\circ\text{C}$  for 3 h to yield SPEEK. Then the resultant solution was poured into ice cold water to precipitate SPEEK which was then rinsed and dried for later use. The degree of sulfonation of SPEEK was 7% as determined by back-titration, in which 1–2 g of SPEEK was kept in 0.5 M aqueous NaOH for 24 h and then was back titrated with 1 M HCl using phenolphthalein as the indicator. More details of the titration method were described in Ref. 28.

The obtained polymer was characterized via Fourier transform infrared spectroscopy (FTIR) in absorbance mode, using an FTIR spectrometer (Bio-RAD FTS 6000). Prior to FTIR measurement, the samples were dried at  $80^\circ\text{C}$  for 24 h. Thermogravimetric analysis (TGA) was carried out using a thermal balance (TA-50 Instrument Shimadzu TGA) at a heating rate of  $10^\circ\text{C min}^{-1}$  over the range of  $50\text{--}800^\circ\text{C}$  under a nitrogen atmosphere.

### Membrane Preparation

SPEEK membranes were prepared by immersion phase inversion method. Similar method to prepare porous SPEEK membranes

in fuel cells had been reported,<sup>29</sup> but in this research we chose MSA as solvent in order to properly dissolve SPEEK of very low degree of sulfonation. Casting solution was obtained by stirring the mixture of SPEEK and MSA vigorously for 6 h at room temperature. The resultant solution was kept for 48 h to completely release air bubbles. Then it was poured onto a glass plate and spread over the plate surface with a doctor blade at  $25^\circ\text{C}$  and the humidity of  $60 \pm 5\%$ , forming a liquid film of  $160 \pm 10 \mu\text{m}$  in thickness. The liquid film, together with the glass plate, was then immediately immersed in a coagulation bath, where a membrane was formed through the process of phase inversion. Subsequently, the membrane was washed with deionized water to remove residual MSA and kept in deionized water before testing.

The membranes obtained using  $25^\circ\text{C}$  deionized water as coagulation medium and casting solution with 7, 9, and 11 wt % SPEEK in MSA will be later referred to as M-7, M-9, and M-11, respectively.

Post-treatment of M-9 membranes was carried out by immersion in boiling water for 10 or 30 min. These membranes will be referred to as M-P10 and M-P30, while the pristine M-9 membrane will be renamed as M-P0 when it is compared with the post-treated membranes.

The membranes prepared using 9 wt % SPEEK casting solution and water coagulant of 3, 25, 40, and  $60^\circ\text{C}$  will be referred to as M-T3, M-T25, M-T40, and M-T60, respectively.

Membranes were also prepared using  $25^\circ\text{C}$  coagulation baths of different compositions, i.e. pure water,  $2 \text{ molL}^{-1}$  NaOH aqueous solution and 30 wt% ethanol aqueous solution. These membranes will be referred to as M-W, M-NaOH/W, and M-EthOH/W, respectively.

### Membrane Characterization and Nanofiltration

Zeta potential of the membranes was obtained by an electrokinetic analyzer (SurPASS, Anton Paar, GmbH, Austria), with the

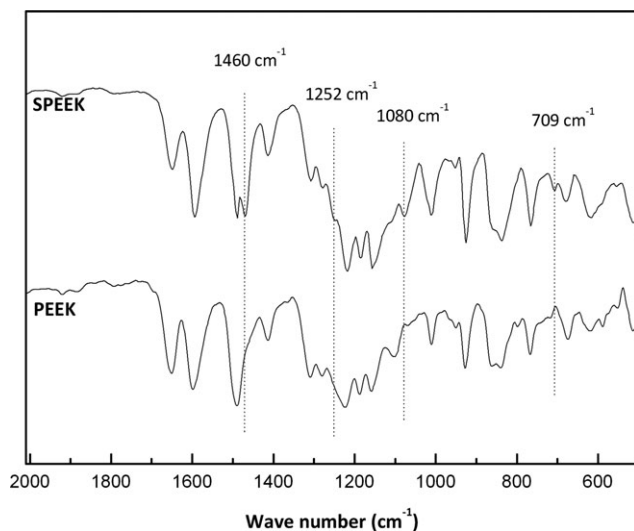


Figure 2. FTIR spectra of the PEEK and SPEEK.

same procedure described in previous literatures.<sup>30,31</sup> The membranes were immersed in a background electrolyte prior to measurements, which were then conducted in the background electrolyte solution at room temperature.

The morphological information of the resulting SPEEK membranes was obtained via scanning electron microscope (SEM, Nanosem 430, USA). Membrane cross-sections were revealed through breaking the membrane in liquid nitrogen. The samples were sputtering coated with gold before SEM imaging.

The tensile strength and breaking elongation of the membranes were measured in dry state using an electronic universal testing machine (DMA-Q800, TA Instruments, USA).

The water uptake (WU) of the membranes at room temperature was obtained through measuring the weight of water saturated membrane sample  $W_w$  and the dry weight of the same sample  $W_d$ . WU was calculated using the equation:

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

NF was carried out via an in-house experimental set up with a cross-flow configuration. The feed solution was pumped from the feed tank to a stainless steel membrane cell accommodating a round membrane of 52 mm in diameter. While the feed stream coming out of the cell went back to the tank, permeate was collected to a beaker. The change of permeate weight with time was recorded. Samples of feed and permeate were analyzed via a UV-Visible light spectrometer (HP 8453 E UV-Vis).

The membranes to be tested were first pressurized with pure water at a trans-membrane pressure (TMP) of 0.4 MPa until a steady state flux was reached. Nanofiltration was normally operated at 0.16 MPa, unless otherwise mentioned. Aqueous solutions of RB and RBR, both having a solute concentration of 0.1 g L<sup>-1</sup>, were used as model feed solutions to test the membranes.

The flux of permeate, PF, was obtained by measuring the effective membrane area  $A$ , the total volume of the permeate  $Q$  as a function of time  $t$  and using the equation:

$$PF = \frac{Q}{At} \quad (2)$$

The rejection of solute,  $R$ , was calculated using the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (3)$$

where  $C_p$  and  $C_f$  are the solute concentration in the permeate and feed solution, respectively.

## RESULTS AND DISCUSSION

### Sulfonate Groups in the Membranes

Pristine PEEK and sulfonated PEEK to be used as the membrane material were characterized by FTIR spectroscopy. The spectra of both polymers were put together for comparison, as shown in Figure 2. The split peak at wave number 1460 cm<sup>-1</sup> is the absorption due to varied aromatic rings in SPEEK.<sup>28</sup> While the absorption at 709, 1080, and 1252 cm<sup>-1</sup> are assigned to the sulfonate groups in SPEEK, corresponding to the S—O stretch, the symmetric O=S=O stretch and the asymmetric O=S=O stretch, respectively.<sup>28,32</sup> Thus, the FTIR results confirm the existence of sulfonate groups in the sulfonated PEEK polymer.

The TGA curves of PEEK and SPEEK were also obtained, as shown in Figure 3. As expected, the PEEK is very thermal stable that the onset of its weight loss is until about 550°C. Whereas in the TGA curve for SPEEK, weight loss begins at about 100°C, presumably due to the evaporation of water attracted by the sulfonate groups. Then there are two more obvious weight loss steps at around 350 and 550°C, respectively. The first step of weight loss can be attributed to the decomposition of the sulfonate groups,<sup>33</sup> and the second one the breakdown of the polymer backbones. The amount of weight loss at the 350°C step agrees approximately with the degree of sulfonation measured by the titration method.

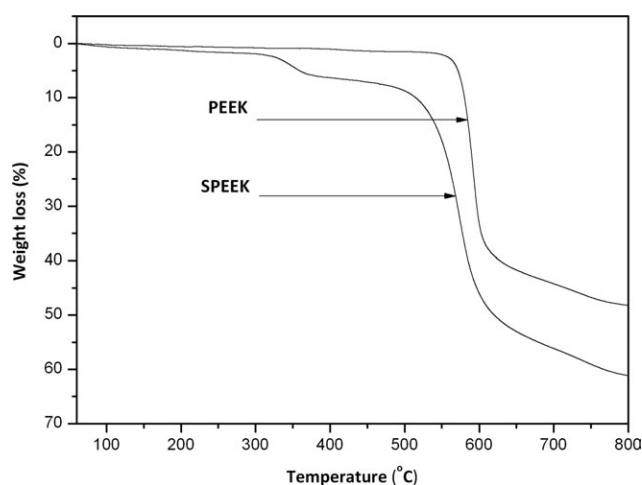


Figure 3. TGA curves of PEEK and SPEEK.

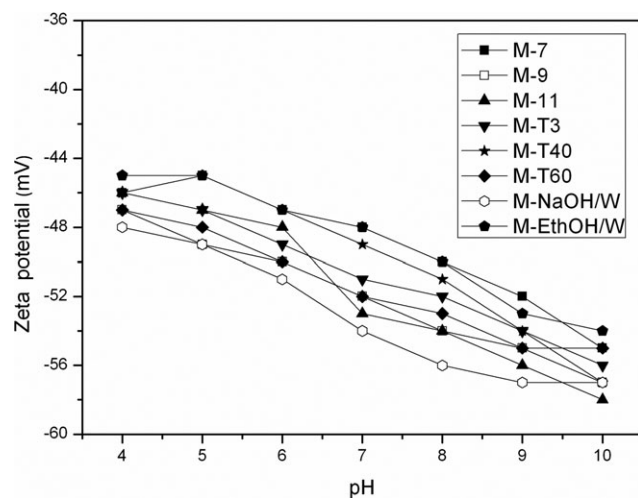


Figure 4. Zeta potentials of SPEEK membranes.

Because of their strong acidic sulfonate groups, the SPEEK membranes should be negatively charged, whenever there is disassociation of cations from the ionic groups. This is confirmed by zeta potential measurements (see Figure 4) which show that the SPEEK membranes bare negative charges at their surfaces. The absolute values of the potentials decrease with acidity in the range of pH 4–10, which is explainable in light of varying degree of disassociation of the sulfonate groups. It is also evident from Figure 4 that the preparing conditions of membranes have very little effect on their surface charges.

#### The Effect of SPEEK Concentration in Casting Solution

Membranes from casting solutions of different SPEEK concentration were prepared, using 25°C pure water as coagulation medium. While the external surfaces of these different membranes appear similar, their cross-section views differ markedly, as revealed by the SEM images shown in Figure 5. These membranes have the asymmetric structure consisting of a dense top-layer and a porous sublayer, which is typical of phase inversion membranes. A finger-pore layer and macro-void layer in the sublayers of the three membranes can be further distinguished, more conspicuously for M-7 than for M-9 and M-11 membranes.

With the increase of SPEEK concentration in casting solution, the chances of overlapping and entanglement between the polymer chains will increase, thus hindering their mobility. The viscosity of the solution also increases with the SPEEK concentration, which slows down the exchange between solvent and nonsolvent. These factors lead to decreased porosity in membranes.<sup>34,35</sup> Therefore, the pore volume decreased in both the finger-pore layer and the macro-void layer of the membranes in the order of M-7, M-9, and M-11.

The performances of the three membranes are summarized in Table I. As can be seen, the permeate fluxes of RB, RBR solutions and pure water decreased with increasing polymer concentration in the casting solution, indicating that higher polymer concentration are related to denser top-layer of the membrane.<sup>35</sup> For the same reason, the solute rejection by the

membranes increased with increasing SPEEK concentration in casting solutions.

However, M-7 membrane achieved higher rejection of RBR than that of RB, while the retention of RB by M-9 and M-11 membranes was higher than their retention of RBR (Table I). This suggests that the rejection rate is collectively determined by the relative sizes of membrane pores and solutes, as well as the number of charges carried by the solute molecules. If a charged membrane has relatively large pores on its top-layer, the charge number in the solute molecule will be more important to determine the extent of rejection, as is the case of M-7. When a membrane has small pores relative to the solute size, the effect of electrostatic repelling becomes less dominant, which might be the case of M-9 and M-11 membranes.

The difference of the mechanical properties of the three membranes is easily understandable when considering the variation of their porosity or density, whereas the change of water uptake (WU) appears counterintuitive at first glance. One would have expected invariant WU, for the degree of sulfonation of the SPEEK is identical for all the three membranes. However, the SPEEK used in this study is so low in the degree of sulfonation that the material itself can hardly be swollen by water. Instead, the WU data reflect basically the total pore volume of the corresponding membranes, and thus are in agreement with the information revealed by the SEM images (Figure 5).

#### The Effect of Coagulation Medium

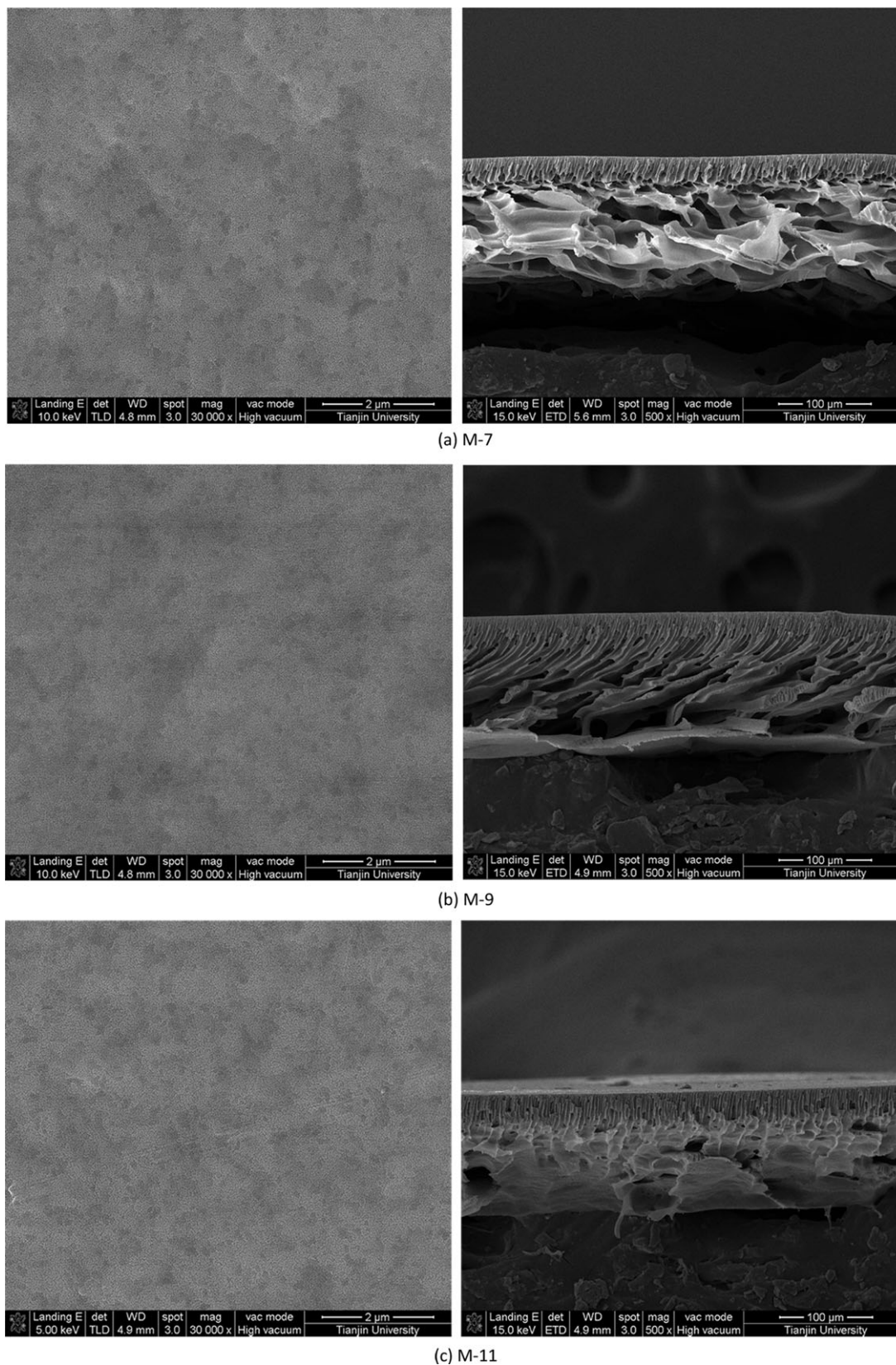
The temperature of coagulation medium is proven to be an impact on the dynamics of membrane formation.<sup>36</sup> In this study, the effects of its temperature were investigated using 9 wt % SPEEK casting solution and water coagulants of 3, 25, 40, and 60°C, respectively.

As shown in Table II, the permeate fluxes of the membranes increase as the temperature of the coagulation medium varying from 3 to 60°C, while the rejection decreased under the same variation of temperature. The change of both flux and rejection clearly indicate increment of pore size in the dense top-layer of membrane with rising water temperature. Higher temperature of coagulation medium not only can enhance the exchange of solvent and nonsolvent, but also decrease the saturation of polymer in the casting solution.<sup>35</sup> These factors speed up the phase separation and gelation processes in the casting solution and lead to membranes with coarse pores and high porosity. The above argument is supported by SEM evidence, which show larger slits on the surface of membrane M-T40 as opposed to M-T3 (Figure 6).

Higher temperature can also cause enhanced mobility of polymer in the casting solution, allowing more even packing of the polymer chains and thus facilitating fine pores to form. But in the present case, the influence of this factor seems very small.

Besides pure water, other coagulation media with additional constituents were tried to learn the effects of bath composition on membrane performance. 2 molL<sup>-1</sup> NaOH aqueous solution and 30 wt% ethanol aqueous solution were chosen respectively. Membrane performances corresponding to the two compositions of coagulation medium were summarized in Table III,





**Figure 5.** SEM images of membranes casted from solutions of different SPEEK concentration, with 25°C pure water as coagulation medium. (a) M-7:7 wt %, (b) M-9: 9 wt %, (c) M-11:11 wt %.

**Table I.** Membrane Performance vs. Concentration of Casting Solution

Membrane	Pure water PF	RB solution		RBR solution		WU (%)	Tensile strength (MPa)	Elongation (%)
		R	PF	R	PF			
M-7	391 ± 19	75.2 ± 0.8	174 ± 9	82.8 ± 0.4	383 ± 19	90	1.22	9.65
M-9	189 ± 9	98.1 ± 0.3	91 ± 4	93.2 ± 0.4	176 ± 9	86	1.86	13.35
M-11	90 ± 4	98.3 ± 0.5	62 ± 3	96.1 ± 0.3	80 ± 4	83	2.04	13.67

PF, permeate flux in  $L m^{-2} h^{-1}$ ; R, rejection (%).

together with the results corresponding to the pure water medium for comparison.

It is seen from Table III that adding either NaOH or ethanol to the coagulation medium causes increased permeate flux and decreased dye rejection. Therefore, these two additives resulted in membranes with larger pores in their dense top-layer. But the two additives may work by different mechanisms.

Ethanol as a component of coagulant was frequently reported in previous literatures, showing diverse effects in different membrane systems.<sup>37,38</sup> Here, the coagulant of 30 wt% ethanol aqueous solution resulted in membrane with roughly more than 50% increase of permeate flux and less than 20% decrease of rejection compared with the membrane coagulated with pure water. Such variations suggest the addition of ethanol increased the exchange of the coagulant with the solvent MSA and resulted in more porous top-layer on the membrane. Presumably, the addition of ethanol to the nonsolvent water can lead to an increase of its affinity the solvent MSA.

Caustic alkali NaOH was chosen as an additive to the coagulation medium because it will react with the solvent MSA. The neutralization reaction should happen instantaneously at the interface of nascent membrane and coagulant solution, thus keeping almost zero MSA concentration outside the membrane. Consequently, the exchange of solvent and non-solvent becomes more rapidly because of higher driven force, leading to more porous top-layer on the membrane. The reaction between NaOH and MSA should also result in temperature increase due to the heat released, which might also contribute to the results shown in Table III.

### The Factors of Post-Treatment Temperature and Operation Temperature

Membranes formed from 9 wt % SPEEK casting solution were post treated with boiling water for different times. Considerable

decline of permeate flux was observed in comparison with the flux of pristine membrane, but the decline slowed down with the time of treatment (Table IV). Similar consequence of thermo treatment to other membranes was also reported.<sup>35</sup> The solidification of membrane along with phase inversion is so rapid that the polymer chains hardly have time to be arranged to their energy favorable state. Thermo post-treatment of the membrane provides its polymer chains with the chance of rearrangement, which can lead to denser top-layer of the membrane and thus lower permeate flux through it.

It is noted that the improvement of rejection due to the post-treatment was very limited, in contrast to the significant decrease of permeate flux (Table IV). It seems that the thermo treatment made the membrane denser more by reducing the number of nanopores than by reducing the pore size.

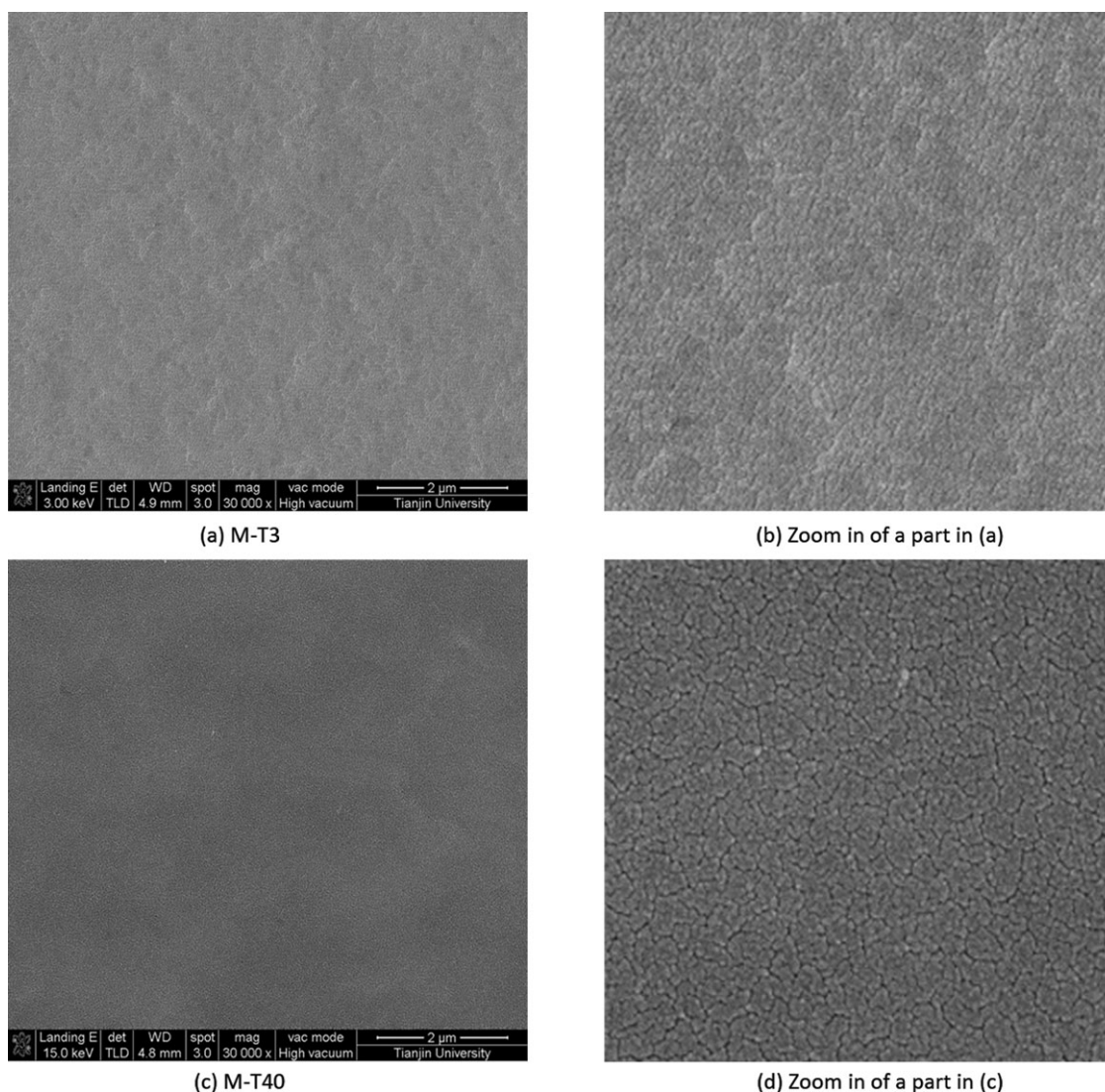
Membrane formed from 9 wt % SPEEK casting solution was also chosen to study the effects of operation temperature on the separation of RB or RBR solutions. The variation of permeate flux and solute rejection with the operation temperature is shown in Figure 7. Both fluxes showed significant and roughly linear increase with operation temperature at the range of 25–80°C, reaching to 226  $L m^{-2} h^{-1}$  and 497  $L m^{-2} h^{-1}$  respectively. Although quite different in the absolute value, the fluxes in the two cases are both tripled as the temperature rising from 25 to 80°C. The SPEEK membrane in RBR nanofiltration is especially good in that the large increase of flux was achieved at the expense of only slight rejection decline [Figure 7(b)].

The significant increase of permeate flux can be attributed to a number of factors originated from temperature rising. The polymer chains in the membrane will generally vibrate more vigorously with increased temperature, promoting the transport through the membrane. The viscosity of the feed solution will be smaller, so that resistance of transport will get lower. High temperature also facilitates dye solutes to diffuse from

**Table II.** Membrane Performance vs. Coagulation Bath Temperature

Membrane	Pure water PF	RB solution		RBR solution		WU (%)	Tensile strength (MPa)	Elongation (%)
		R	PF	R	PF			
M-T3	117 ± 6	99.1 ± 0.2	61 ± 3	95.1 ± 0.3	109 ± 5	85	1.56	13.4
M-T25	189 ± 9	98.1 ± 0.3	91 ± 4	93.2 ± 0.4	176 ± 9	86	1.86	13.35
M-T40	259 ± 13	97.3 ± 0.4	117 ± 6	90.2 ± 0.6	243 ± 12	88	1.31	12.71
M-T60	408 ± 20	71.6 ± 0.8	204 ± 10	83.4 ± 0.6	389 ± 19	89	1.28	14.96

PF, permeate flux in  $L m^{-2} h^{-1}$ ; R, rejection (%).



**Figure 6.** SEM images of the surfaces of membrane prepared using pure water coagulant of different temperature. (a) M-T3: 3°C, (b) Zoom in of a part in (a), (c) M-T40, (d) Zoom in of a part in (c).

membrane surface back to the bulk stream, thus weakening concentration polarization and enhancing permeation.

The differences in flux and rejection of RB and RBR nanofiltration under varying temperature may be partially explained by the fact that the charged groups in RBR outnumber that in RB [Figure 1(b, c)]. As SPEEK membrane is also negatively charged, higher repelling of RBR molecules by the membrane should be

expected. Concentration polarization in the case of RBR may also be lower as a consequence of stronger charge repulsion at the membrane surface. So both the rejection and the flux in RBR NF should be higher, which is in approximate agreement with the experimental results shown in Figure 7.

Poly (ether ether ketone) is known for its excellent thermo stability and mechanical properties. It is also not dissolvable by

**Table III.** Membrane Performance vs. Coagulation Bath Composition

Membrane	Pure water PF	RB solution		RBR solution		WU (%)	Tensile strength (MPa)	Elongation (%)
		R	PF	R	PF			
M-W	189 ± 9	98.1 ± 0.3	91 ± 4	93.2 ± 0.4	176 ± 9	86	1.86	13.35
M-NaOH/W	256 ± 13	96.7 ± 0.4	115 ± 6	92.6 ± 0.6	238 ± 12	87	2.07	14.57
M-EthOH/W	404 ± 20	77.6 ± 0.7	168 ± 8	80.2 ± 0.5	381 ± 19	87	1.83	12.12

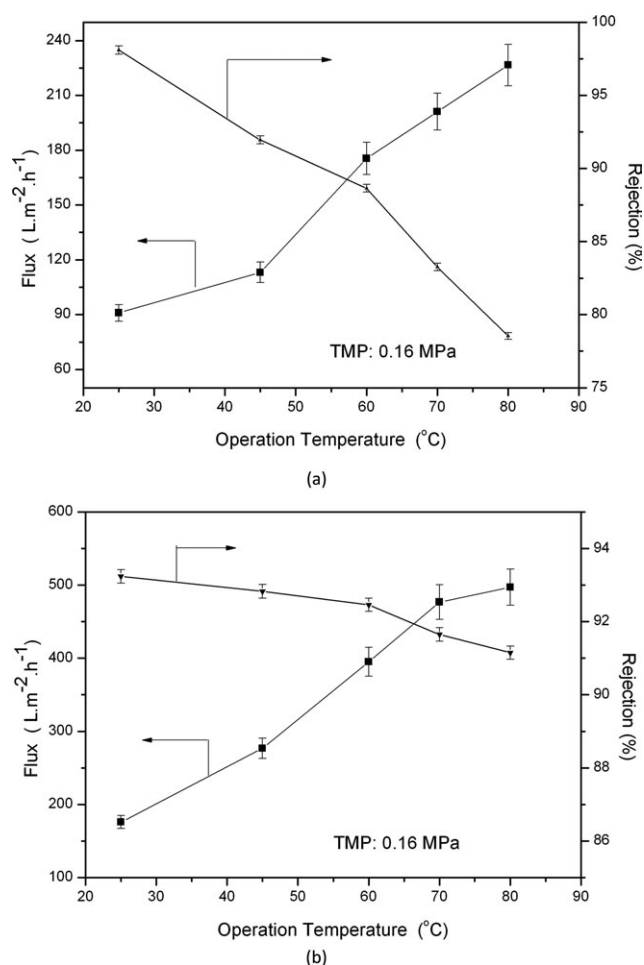
PF, permeate flux in  $L m^{-2} h^{-1}$ ; R, rejection (%).



**Table IV.** Membrane Performance Affected by Post Treatment with Boiling Water

Membrane	Pure water PF	RB solution		RBR solution	
		R	PF	R	PF
M-P0	189 ± 9	98.1 ± 0.3	91 ± 4	93.2 ± 0.4	176 ± 9
M-P10	81 ± 4	98.5 ± 0.2	74 ± 3	95.4 ± 0.6	77 ± 4
M-P30	68 ± 3	99.1 ± 0.2	59 ± 3	96.7 ± 0.5	65 ± 3

PF, permeate flux in  $\text{L m}^{-2} \text{h}^{-1}$ ; R, rejection (%).



**Figure 7.** The effects of operation temperature on the M-9 membrane separation of (a) Rose Bengal and (b) Reactive Brilliant Red K-2BP.

most solvents, even with slight sulfonation. While this research being very preliminary, certain essential aspects of SPEEK of very low degree of sulfonation as a membrane material have been demonstrated and looked promising. Further study of this membrane is certainly needed to fully reveal its potential as a high temperature membrane or as a solvent resistant nanofiltration (SRNF) membrane.

## CONCLUSIONS

Novel charged membranes were prepared with sulfonated poly(ether ether ketone) (SPEEK), using methylsulfonic acid as its

solvent to accommodate the very low degree of sulfonation of the polymer. Nanofiltrations of Rose Bengal and Reactive Brilliant Red aqueous solutions were carried out to test the performance of the membranes.

High permeate flux and high solute rejection can be achieved through proper choice of phase inversion process parameters including the concentration of casting solution, the temperature and composition of coagulation bath, and the temperature of post-treatment. High temperature operation resulted in significant increase of permeate flux and low decline of rejection.

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