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Novel nanofiltration membranes with tunable permselectivity by polymer mediated phase separation in polyamide selective layer☆

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ABSTRACT

Microstructure in selective layer has played a decisive role in permselectivity of nanofiltration (NF) membranes, and nanomaterials were well-known additives that had been applied to mediate the microstructure and permeability of polyamide NF membranes. However, nanoadditives generally displayed a poor dispersion in membranes or in fabrication process. To solve this problem, we showed an interesting concept that novel NF membranes with hybrid selective layer consisting of flexible polyisobutylene (PIB) and rigid polyamide could be fabricated from well-defined interfacial polymerization. The hydrophobic polymer mediated phase separation and microdomains formation in polyamide layer were found. The immiscibility between the rigid polyamide and flexible PIB as well as the resultant interface effect was interpreted as the reason for the polymer enhanced permselectivity, which was similar with the well-known thin film nanocomposite (TFN) membranes that nanoparticles incorporated contributed significantly to membrane permeability and rejection performance. Our results have demonstrated that novel NF membranes with enhanced performance can be prepared from immiscible polymers, which is a new area that has not been extensively studied before.

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1. Introduction

It is reported that 50% of global population will face water scarcity by 2030, and more than 40% of population will live within 100 km away from the ocean by the time [1]. It is foreseeable that water scarcity will become a major crisis that will show great impacts on our further life. Although lots of methods have been developed to produce clean and drinking water, fresh water produced by traditional strategies such as the distillation and flocculation is generally energy-intensive and inefficient. In contrast, membrane separation is devised to be a green and energy-saving method to solve the problem of growing water scarcity, and much effort has been devoted to developing advanced materials for membrane separation [2].

Nanofiltration (NF) membranes that show a selective removal of minerals are good candidate for salted and brackish water desalination, and great achievements have been made [3–7]. Generally, interfacial polymerization (IP) is as effective as many other methods that can be applied to prepare NF membranes with both high permeability and high retentions. However, in comparison with methods of grafting, surface coating, and layer by layer (LBL) assembly, the interfacial polymerization is more easily to be scaled up, and membranes meeting

the requirements of practical desalination can be prepared largely from the well-defined IP process [2]. Moreover, the IP strategy has shown a strong designability that is hard to be achieved by aforementioned methods, and functional additives and monomers that are compatible with IP process has been developed for new IP processes [8–11]. Besides monomers and oligomers that have been widely investigated as useful additives for IP process, nanomaterials also attract much attention in fabricating of NF membranes with strengthened performance [9]. Depending on containing or not containing nanoparticles, NF membranes with polyamide as selective layer can be classified into thin film composite (TFC) membrane and thin film nanocomposite (TFN) membrane, respectively [4,12,13]. In comparison with TFC membranes, TFN membranes have shown a 10%–30% increase in water permeability without compromise of salt rejection, and trade-off effect that is generally encountered by TFC membranes has been partly solved by TFN membranes [9,12]. Nanomaterials of different properties and topologies have been found to contribute positively to membrane permselectivity [14–19]. However, agglomeration of nanoadditives in membranes and in fabrication has been universally inspected, and membrane permselectivity is significantly deteriorated when nanoadditives are fed inappropriately. To prevent nanoadditives from agglomeration within the PA layer, nanoadditives in solutions are usually remained at an extremely low concentration where the aggregation is restrained [9, 16,18]. However, this strategy usually suffers from a low efficiency that only a small part of nanoadditives can be polymerized into membranes, and much nanoadditive is reserved in solutions. Although great effort has

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been devoted to improving the dispersion of nanomaterial in membrane and in solutions, the agglomeration of nanomaterial remains a great problem that has not been completely solved until now [12,13].

The microdomains and interface effect arose from incompatibility between nanoadditive and polymer matrix had been deduced as the reason for the unique permselectivity of gases through hybrid membranes containing nanoadditives [18], and similar reasons can be ascribed to TFN membranes prepared from interfacial polymerization. To mimic the microdomains formation of nanoadditives in polyamide layer, we design a novel interfacial polymerization by using flexible polyisobutylene as the additive that is immiscible with hydrophilic and rigid polyamide. Obviously, unlike the nanoadditives that are inclined to aggregate in solutions and in membranes, polymer additive can molecularly dissolve in solution during the fabrication, and *in-situ* formation of microdomains in selective layer will be constructed if incompatibility between additive and polyamide exists. This designing can solve the agglomeration problems of nanomaterials at the beginning of fabrication. It was interesting to find that the phase separation of PIB from polyamide layer has been truly induced when PIB was properly feed, and microdomains of PIB in polyamide layer had been established smoothly. More interestingly, the water flux of fabricated NF membrane showed a strong dependence on the feed concentration of PIB. This observation is close to the finding that is commonly inspected in TFN membranes. The comparable performance of our NF membranes with several representative hydrophilic NF membranes indicates that performance enhanced NF membranes can be practically prepared from novel interfacial polymerization by using immiscible polymer as additive. Obviously, the dissolubility rather than dispersion of polymer in fabricating solvents makes them easily deal with in comparison with nanoadditives. Our results have demonstrated that many new NF membranes with better performance can be prepared when polymer additives are properly designed.

2. Materials and Method

2.1. Reagents and materials

The support polysulfone membrane with molecular weight cut-off in range from 30000 to 50000 was provided by Hangzhou Water Treatment Technology Development Center. Piperazine (99% +), trimesoyl chloride (TMC, 98% +), sodium chloride (NaCl, 99% +) and sodium sulfate anhydrous (Na_2SO_4 , 99.4%) were obtained from Sigma-Aldrich. Polyisobutylene (PIB, B80) with number averaged molecular weight of 200000 $\text{g} \cdot \text{mol}^{-1}$ was purchased from the BASF chemical company. Poly(ethylene glycol)s (PEG200, PEG400 and PEG600) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were used as received without further purification unless noted otherwise. Ultrapure water used in this work was produced by Millipore-Q Academic system and the resistance was higher than 18.2 $\text{M}\Omega \cdot \text{cm}$.

2.2. Membrane preparation

The support PSf membranes were first immersed into ultrapure water for 24 h to remove the chemicals adsorbed onto membranes during the storage. The cleaned membranes were then dipped into phosphate buffer solution (PBS, pH = 10) containing piperazine (0.2 wt%) for 30 s. The resulting membrane was taken out and excessive aqueous solution on membrane surface was removed using a squeegee roller, and the support was dried in the air for about 3 min. The membrane was then immersed into the *n*-hexane solution containing 0.1 wt% TMC and different amounts of PIB for 10 s. The resultant membrane was drained and dried at 80 °C in an oven for 10 min. This membrane was finally kept in de-ionized water for storage for further characterization.

2.3. Permeability and rejection determination

The permeability and retention performance of as-prepared membranes were evaluated using a self-designed RO water permeation apparatus that was shown in our previous work [20]. Membrane with an effective area of 20 cm^2 was loaded into a circular stainless steel cell for permselectivity measurement. The solutions of 2000 $\text{mg} \cdot \text{L}^{-1}$ NaCl and 1000 $\text{mg} \cdot \text{L}^{-1}$ Na_2SO_4 were prepared as the feed solutions and their retentions were determined, respectively. The operating temperature was maintained at 25 °C by a thermal set system, and the transmembrane pressure was controlled at 999.74 kPa (145 psi). The flux was obtained by weighing the permeate water collected over a period of time, and the salt rejection (R_s) was determined according to the following equation:

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

where C_p and C_f are the salt concentrations of the permeate and feed solutions, respectively, which were determined by a conductivity meter. The water flux and salt rejection were recorded after its performance reached the steady state.

The rejections to polyethylene glycol (PEG200, PEG400 and PEG600) oligomers were determined following a similar process, and the concentration of PEG in feeding solution was set at 100 $\text{mg} \cdot \text{L}^{-1}$ in all determinations. The PEG rejection (R_{PEG}) was determined according to the following equation:

$$R_{\text{PEG}} = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

where C_p and C_f are the PEG concentrations of the permeate and feed solutions, respectively, which were determined by a total organic carbon analyzer.

2.4. General characterizations

The surface morphologies of the fabricated membranes were visualized by a field emission scanning electron microscope (FESEM, Hitachi S4700) that was operated at a voltage of 15 kV, and membranes were sputtered with a thin Pt layer (~1.5 nm) to eliminate charging before SEM observation. Surface compositions of membranes were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000 C ESCA system, PHI Co., USA), and composition within 5 nm (corresponded to the take-off angle of 60°) in outer surface was determined. The surface composition of as-prepared membrane was also characterized by an attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR), and spectra were collected from 64 scans with a resolution of 4 cm^{-1} . Surface roughness and morphologies of membranes were determined from dimensions of 10 × 10, 5 × 5 and 2 × 2 μm^2 by the atomic force microscope (AFM) in a tapping mode, and roughness was calculated. Zeta potentials of membranes were determined following the process showed in literature [21]. Water contact angles and surface energy were determined by a contact angle analyzer (Dataphysics, OCA20, Germany).

3. Results and Discussion

3.1. Effect of PIB on membrane permeability

Polyisobutylene (PIB) is a well-known rubbery polymer that shows the glass transition temperature of about −70 °C. The low-polarity of PIB makes it dissolved easily in many organic solvents including the benzene (BZ), hexane, gasoline and chloroform [22], and *n*-hexane soluble PIB is therefore a good polymer additive that is compatible with well-defined interfacial polymerization. It can be anticipated that

novel TFC membranes containing hydrophobic polymer additive can be prepared following the well-defined interfacial polymerization when the synthesis process is carefully designed.

The pure water flux against the feed concentration of PIB in organic phase is firstly investigated, and the effect of PIB on membrane permeability is studied. Interestingly, it is found from Fig. 1 that the permeability of fabricated membranes shows a close relationship with the concentration of PIB. Considering the phase separation is more easily induced at higher PIB concentrations, the membranes prepared from PIB with concentrations larger than 0.12 wt% are mainly focused. Obviously, the permeability of membranes prepared at this condition increases firstly and then decreases with an increasing concentration of PIB, and the maximum flux obtained at a PIB concentration of 0.24 wt% is cal. 50% higher than that of membranes prepared with PIB concentration of 0.12 wt%. The value is also 3 times higher than that of membrane prepared with a PIB concentration of 0.98 wt%. Clearly, our observation strongly indicates that PIB applied in interfacial polymerization will bring membrane good permeability before the additive is excessively fed, and the reliability of this observation is repeatedly found when membranes are prepared with much lower TMC concentrations. The relationship between permeability and PIB concentration becomes even more obvious in comparison with that of TFC membranes prepared with much higher TMC concentration. Typically, lower TMC concentration in organic phase will offer membrane lower degree of cross-linking and therefore much higher permeability. The permeability decreases in range of 0–0.12 wt% is not clear, but the obvious increase of membrane hydrophobicity might be the reason responsible for it, and the explanation will be showed later in following sections.

3.2. Surface composition and chemistry

Surface compositions of polyamide NF membranes prepared from interfacial polymerization are investigated consecutively by FTIR-ATR and XPS, respectively, and the results are showed in Fig. 2 as well as in Table 1. Although both technologies will show the results that are thickness-dependent, penetrating thickness of FTIR-ATR is much deeper and chemical composition spanning the whole thin film layer (100–200 nm) can be detected. However, XPS generally gives precise surface composition that does not exceed 10 nm on outer surface.

Fig. 2 has shown the FTIR-ATR spectra of PSf support membrane, control polyamide membrane prepared without feeding of PIB, and NF membrane prepared with 0.72 wt% PIB. The characteristic vibrations at 2961, 2885 and 1581 cm^{-1} from PSf support membranes serve as internal standard, and intensity changes from these vibrations are effective indicators displaying compositional changes of membranes prepared under different conditions. For control TFC polyamide membrane prepared without feeding of PIB, the newly appeared adsorption at 1627 cm^{-1} (close to 1581 cm^{-1}) can be assigned to well-defined amide bonds ($-\text{NH}-$) that are associated with the polymerization between the TMC and *m*-phenylene diamine (MPD). The

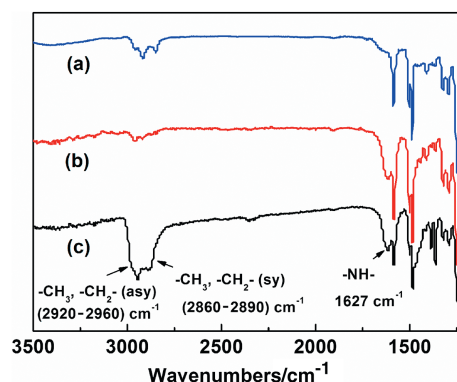


Fig. 2. FTIR-ATR spectra of support membrane (a), control NF membrane prepared without feed of PIB (b), and NF membrane prepared with feed of 0.72 wt% PIB (c).

Table 1
Compositions of polyamide thin film layer determined by XPS

Membranes	Atomic composition				
	C/%	O/%	N/%	O/C	N/C
0 wt%-PIB	61.6	24.6	13.8	0.4	0.225
0.12 wt%-PIB	89.1	7.1	3.8	0.08	0.043
0.48 wt%-PIB	89.9	6.6	3.5	0.07	0.039
0.72 wt%-PIB	90.0	6.5	3.4	0.07	0.038

obviously weakened adsorptions at 2961 and 2885 cm^{-1} that are ascribed to support membranes demonstrate the successful construction of polyamide layer on PSf substrate. When PIB was used as an oil phase additive, spectra of fabricated membrane show much stronger adsorption at 2961 (asymmetric stretching vibration) and 2885 cm^{-1} (symmetric stretching vibration) than that of the control membrane, indicating the successful incorporation of PIB into polyamide network during the interfacial polymerization. It is needed to pay attention to that the adsorption (1627 cm^{-1}) from polyamide thin layer remains unchanged when PIB is incorporated, which indicates that the reaction of interfacial polymerization has not been obviously affected by feeding of this hydrophobic additive to oil phase. This explanation can be further interpreted that unreactive PIB does not participate in the well-defined interfacial polymerization. However, the effect of PIB on internal structure and cross-linking degree of polyamide cannot be detected by FTIR, and Fig. 2 showed herein just demonstrates that PIB has been tethered onto polyamide layer successfully.

In addition to the chemical composition of PA layer determined by FTIR-ATR, the constitution within 5 nm on outer surface is inspected by XPS, and the results are shown in Table 1. It can be clearly found that the additive of PIB in oil phase has significantly altered the

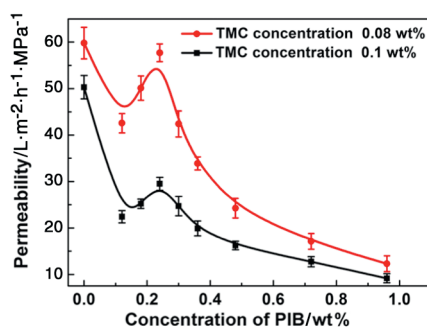


Fig. 1. Permeability of the TFC membranes prepared at different PIB concentrations. Images on the right hand showed the molecular structure as well as the properties of PIB.

PIB				Physical property		
				T_g	-70 °C	
				δ	16.6 MPa ^{0.5}	
				M_n	200000 g·mol ⁻¹	
Solubility				Tolerance		
BZ	Hexane	Methanol	Acetone	Acid	Alkali	Oxidation
Yes	Yes	Swollen	Swollen	Yes	Yes	No

composition of as formed TFC membranes, and the atomic fractions of the oxygen and nitrogen that are associated with the polyamide decrease by more than 70%, indicating that PIB has been hybridized into polyamide layer during membrane formation. This obvious change of surface composition can be readily inspected at the lowest PIB concentration of 0.12 wt% (the ratio of PIB to MPD is 0.6:1). However, it is also found that further increasing the PIB concentration from 0.12 wt% to 0.48 wt% and 0.72 wt% does not lead to a continuous change of chemical compositions in polyamide layer, and the TFC nanofiltration membrane prepared from 0.48 wt% and 0.72 wt% shows similar compositions with that of membranes prepared from 0.12 wt% PIB.

PIB is a petrochemical polymer that shows the strong hydrophobicity, and TFC membranes will show an obvious change in surface wettability if PIB has been incorporated into membranes. Therefore, contact angle measurement is another effective method to prove the successful incorporation of PIB into membranes. Contact angles showed in Table 2 confirm this expression and TFC membranes prepared from 0.12 wt% have showed a water contact angle of 94.6° , which is almost 60° higher than that of control membranes (without PIB). The CA determination indicates that our membranes become hydrophobic when PIB has been incorporated. This result becomes more persuasive when the contact angles are determined with the CH_2I_2 which is commonly adopted to evaluate the nonpolarity of membranes. For the same membrane prepared from 0.12 wt% PIB, the CA to CH_2I_2 shows a value of 47° and it is nearly two times larger than that of reference membrane. Similar results are further determined for other hydrophobic membranes prepared from higher concentrations of PIB. The surface energy as well as dispersive and polar component calculated from these two related CA results indicates that the polarity of as prepared membranes decreases by an order of magnitude when PIB is incorporated. It is worth noting that the CA determination has shown an interesting phenomenon consisting with the results inspected by XPS, and they both imply that further increase of the feed concentration of PIB by 4 or 6 times to 0.48 wt% and 0.72 wt% does not lead to obvious changes of surface wettability and compositions. This result is beneficial for us to compare the membrane performance with each other under the same hydrophilicity (or hydrophobicity).

3.3. Permeability of membranes containing PIB

The rejection performance of as-prepared TFC membranes to NaCl, Na_2SO_4 , MgCl_2 , MgSO_4 and charge neutral PEG oligomer is determined. As displayed by Fig. 3(a) and (b), it is easily found that permeability for both saline solutions of NaCl and Na_2SO_4 increases firstly and then decreases with an increasing feed of PIB, and the permeability consists well with the result that pure water permeability has showed the maximum value at a moderate PIB concentration of about 0.24 wt%. Although similar permeability has been determined for both salts, different rejection tendency to NaCl and Na_2SO_4 has been found. For NaCl, the rejection keeps increasing with an increasing feeding of PIB. Combined with permeability results, the finding can be interpreted that both permeability and rejection keep increasing when PIB feeding concentration is remained lower than 0.24 wt%. However, further increasing the PIB concentrations to 0.48 wt% and higher will lead to an

obvious trade-off effect, and the permeability decreases significantly although retentions keep increasing. This condition will become entirely different for the Na_2SO_4 , and salt retentions keep decreasing with an increasing feeding of PIB. In this region the permeability increases by 50% with only slightly compromising of Na_2SO_4 rejection. Similar permeability and rejection performance with that of the results found for NaCl and Na_2SO_4 has also been determined for MgCl_2 and MgSO_4 , respectively. These results can be found in Fig. 3(c) and (d). Our membranes can be classified into well-defined nanofiltration membranes when the rejections to NaCl and MgCl_2 have been taken into account.

The permselectivity performance of as prepared membranes to different salts can be understood from a combined mechanism of ion exclusion and steric effects. From zeta potential determination (Fig. 4(b)), we find that the incorporation of PIB onto thin film layer decreases the charge property of the fabricated membranes obviously. The steric effect that is associated with pore size is next determined with charge neutral PEG oligomers as the solutes. It is easily found that as prepared membranes show nearly 100% rejection to the PEG oligomer with molecular weights of 400 and 600, indicating that the pore size of as-prepared nanofiltration membranes is much smaller than the hydrated radius of PEG400 which is calculated to be 0.56 nm. Further determination indicates that the molecular weight cut-off (MWCO) of our NF membranes is around 200, and 90%–92% of PEG200 is rejected. Therefore, the pore sizes of as prepared TFC membranes are equivalent to molecular size of PEG 200 that is calculated to be 0.4 nm, which consists well with the result that the MgSO_4 is nearly 100% rejected by our membranes (Table 3). It is needed to pay attention that the rejections determined for three PEG oligomers are reliable since the result determined for individual PEG has been confirmed by the other two solutes. Under this condition, it can be interpreted that the pore sizes of TFC membranes have not been obviously alternated by PIB, and pore size of TFC membranes containing different amounts of PIB remains unchanged (Fig. 4(a)). Since the similar pore size for all the TFC membranes, it is easily understood that our membranes with increasing PIB will show decreased salt retentions when zeta potential results have been taken into account. The steric effect on salt retention can be further learned from Table 3 which lists the molecular characteristics of the solutes used in this work, and passage of NaCl and Na_2SO_4 through our membranes will be very easy if charge property is disregarded.

3.4. Permselectivity comparison of PIB coating layer with polyamide

From the aspects of chemical composition of as-prepared TFC membranes, the upper selective layer is consisted of polyamide and PIB, and the permselectivity should be determined by these two components. Permselectivity comparison of control TFC membranes prepared by coating PIB on support membranes (100 wt%-PIB) and by interfacial polymerization of piperazine and TMC (0 wt%-PIB) is showed in Table 4. It is easy to learn from Table 4 that TFC membrane prepared by coating PIB on PSf support membranes shows a very low flux, which is only 5% in value in comparison with that of control membrane. This experimental designing is useful and it is understood that the polyamide layer prepared from interfacial polymerization of TMC and piperazine is 20 times more permeable than that of PIB coating layer. Therefore, it is

Table 2
Contact angle and surface energy of fabricated TFC nanofiltration membranes

Membranes	CA/(°)		Dispersive component	Polar component	Total ^① /J·m ⁻²
	H ₂ O	CH ₂ I ₂			
0 wt%-PIB	32.6 ± 2.8	22.0 ± 0.9	32.08	32.45	64.53
0.12 wt%-PIB	94.6 ± 3.1	47.0 ± 1.3	34.62	0.92	35.53
0.24 wt%-PIB	95.2 ± 1.7	48.3 ± 2.1	33.95	0.88	34.83
0.48 wt%-PIB	95.7 ± 2.0	50.3 ± 3.7	32.79	0.92	33.71
0.72 wt%-PIB	97.5 ± 1.8	51.4 ± 0.8	32.55	0.67	33.22
0.96 wt%-PIB	98.5 ± 3.4	52.5 ± 0.3	32.09	0.57	32.66

^① Calculated from averaged contact angles.

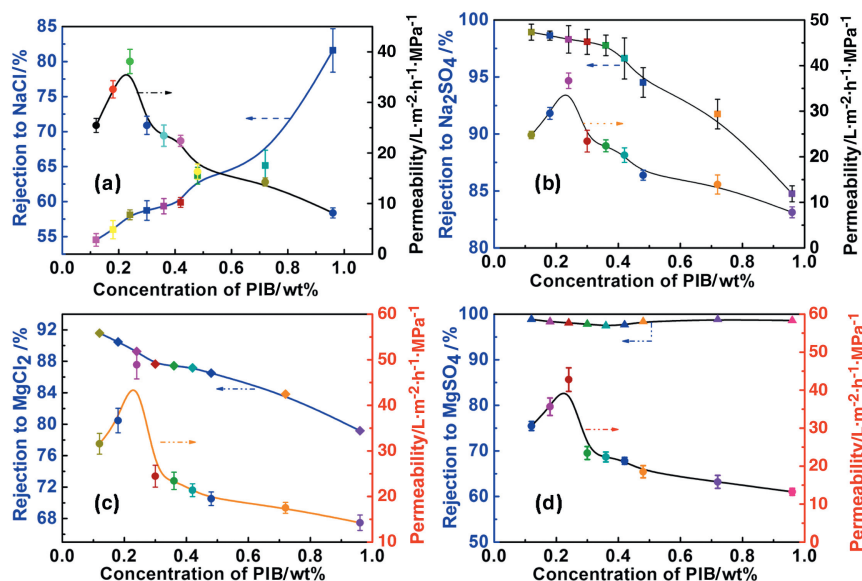


Fig. 3. The rejection performances of as-prepared TFC nanofiltration membrane to NaCl (a), Na₂SO₄ (b), MgCl₂ (c) and MgSO₄ (d).

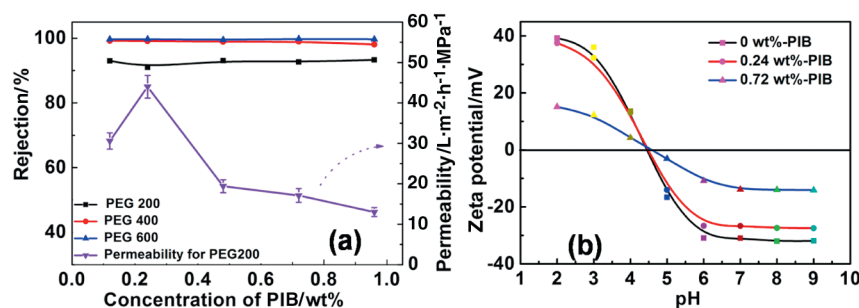


Fig. 4. The rejections to PEG oligomer (a) and zeta potential of TFC membranes (b).

not different to understand that the permeability of as-prepared membranes containing PIB will be polyamide-dominated if PIB is the dispersed phase in thin film layer. This expression can explain the result that the permeability keeps increasing with an increasing of PIB from 0.12 wt% to 0.24 wt%. However, this condition will be reversed and the permeability becomes PIB-determined when the PIB on membranes is the major and continuous phase. This explanation corresponds to the second stage that the permeability decreases with an increasing feeding of PIB. Besides the obviously different permeability of PIB coating layer and polyamide, it is additionally found that PIB show less selectivity than that of polyamide layer. The PIB coating layer shows similar rejections (~80%) to NaCl and Na₂SO₄ that is associated with pore size sieving instead of the ion extrusion. However, polyamide (PA) layer shows

obviously different rejection to NaCl and Na₂SO₄ and displays a strong selectivity to mono and divalent cations, and combined mechanisms of pore sieving as well as ion repulsion is responsible for the different permeability found for the polyamide.

The different permselectivity of PA layer from that of PIB shows in Table 4 explains the salt rejections appeared in Fig. 3. At the first stage that the permeability is PA dominated, the NaCl retention is determined by PA layer and therefore the much lower NaCl retention. At the second stage that is PIB-dominated, the NaCl retention is determined by PIB layer and therefore the much higher NaCl retention. This assumption can explain the result that why NaCl rejection keep increasing with an increase feeding of PIB in membranes. Actually, the above explanation also explains the rejection result inspected for Na₂SO₄.

Table 3

Molecular and atomic characteristics of solute used in this work [23]

Ion/molecule	Atomic/molecular weight	Diffusion coefficient $\times 10^9/\text{m}^2 \cdot \text{s}^{-1}$	Non-hydrated radius/nm	Hydrated radius/nm
Na ⁺	39	1.33	0.107	0.28
Mg ²⁺	24.3	0.706	0.072	0.36
Cl ⁻	35.5	2.03	0.184	0.28
SO ₄ ²⁻	96	1.07	0.222	0.30
PEG200 ^①	180–220	0.693	0.270	0.40
PEG400 ^①	360–440	0.495	0.396	0.56
PEG600 ^①	540–660	0.402	0.495	0.69

^① The diffusion coefficients were theoretically calculated from Stokes–Einstein equations with the PEG radius showed in literature [24]. Nonhydrated radius was calculated from equation showed in literature [25].

Table 4

Performance comparisons of control membranes prepared from coating PIB on support membranes and by interfacial polymerization of piperazine and TMC monomers

	Performance	PIB coated	PIP/TMC
NaCl	Flux ^① /L·m ² ·h ⁻¹	2.2 ± 0.12	43.5 ± 0.3
	Rejection/%	82.1 ± 0.7	42.5 ± 0.9
Na ₂ SO ₄	Flux ^① /L·m ² ·h ⁻¹	2.1 ± 0.1	44.1 ± 0.34
	Rejection/%	84.2 ± 1.1	99.1 ± 1.4

^① Flux determined at the trans-membrane pressure of 999.74kPa (145 psi).

Because PIB coating layer shows much lower Na₂SO₄ retention than that of PA layer, the PIB contained TFC membranes will show decreasing retention with an increasing feed of PIB in membranes, and the salt retention will be PIB dominated when PIB becomes the continuous phase. It is interesting to find that NaCl and Na₂SO₄ retentions of the TFC membrane prepared from the highest PIB concentration (0.98 wt%) do show the salt retention that is approaching to the performance for pure PIB coating layer, demonstrating the validity of our explanation showed above.

3.5. Surface structure and structure-performance relationship

Our assumption that PIB in membranes forms microdomains has been demonstrated by SEM and AFM, and results are showed in Fig. 5. Firstly, it is easily found from SEM images that PIB has alternated the surface morphologies of fabricated membranes obviously, and isolated PIB phase (*i.e.* sea island structure) on membranes is rather clear. This is an additionally important observation besides the contact angle and XPS analysis that proves the successful incorporation of PIB onto membranes. Excepting for the above results drawn from the SEM images, different segregated morphologies of PIB on membranes have been found. Typically, the cross-linked polyamide networking is the continuous phase with the PIB existing in discrete domains when feed concentration of PIB is lower than 0.24 wt%. However, continuous phase of PIB has been created when PIB in oil phase is increased to 0.48 wt%, and phase reversion is inspected. It is worth noting that the phase transition of PIB observed by SEM can be demonstrated by AFM. The morphological changes and phase transition of PIB domains inspected by SEM and AFM have demonstrated the idea we proposed in Section 3.4, and the performance is polyamide-dominated at lower PIB concentration where PIB is the minor and dispersion phase, but the performance will become PIB-dominated at higher PIB concentration where PIB merges into continuous phase.

Surface roughness has played a critical role on the permeability of NF and RO membranes. Hirose showed in his well-cited work that

polyamide composite membranes with larger roughness on skin layer would produce higher fluxes, and an approximately linear relationship between surface roughness and membrane flux has been proposed [26]. The roughness of our membrane is analyzed and the relationship between the root mean square (RMS) results and permeability is correlated, and results are shown in Table 5. Typically, it can be found that higher feed of PIB in membranes will lead to larger roughness, and RMS obtained from three different scanning dimensions demonstrates the same conclusion. However, we find that the permeability determined on our fabricated membranes does not show the linear increase with the RMS as the observation showed by the Hirose, indicating that the permeability of our membranes may be more determined by the internal cavities rather than the surface morphologies. The correlation between the flux and surface roughness found for homogeneous polyamide NF membranes without hybridization cannot explain the performance of our membranes well. Therefore, the AFM analysis showed herein supports our explanation that PIB enhanced permeability might be resulted from the internal structure and the loosely cross-linked networking that exists around the isolated PIB phases. This interface between rigid polyamide network and flexible PIB is different from previously observed interface that are entirely hydrophilic or hydrophobic, and the interface existed in our membranes is consisted of both the hydrophilic polyamide and hydrophobic PIB, which is proposed to be a special water channel that promises the passage of ions and molecules.

Table 5

RMS results of TFC membranes prepared at different conditions

Membranes	Averaged RMS/nm			Permeability /L·m ⁻² ·h ⁻¹ ·MPa ⁻¹
	10 × 10 μm ²	5 × 5 μm ²	2 × 2 μm ²	
0.12 wt%-PIB	15.0	7.3	5.4	22.4 ± 1.3
0.24 wt%-PIB	19.9	11.5	9.6	29.5 ± 1.4
0.48 wt%-PIB	41.0	34.5	26.0	14.2 ± 0.9
0.72 wt%-PIB	49.7	36.7	27.1	13.8 ± 1.1
0.96 wt%-PIB	92.8	93.7	46.2	9.2 ± 1

Fig. 6 is provided to help understand this novel interfacial effect cause by immiscibility between PIB and polyamide layer. We formerly ascribe the PIB-enhanced permeability to the dispersion of PIB microdomains in selective layer. However, it still remained unsolved that why permeability can be enhanced by the dispersed PIB. To figure out this question, it is interesting to compare our results with that of the thin film nanocomposite (TFN) membranes developed by Hoek and co-

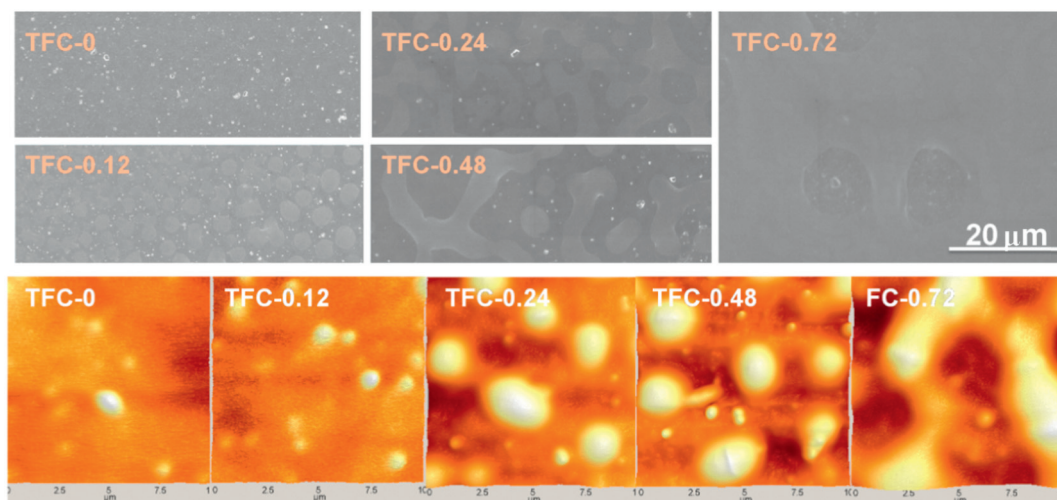


Fig. 5. Surface morphologies of fabricated membranes inspected by SEM (above) and AFM (below), scale bars in AFM images are 10 μm.

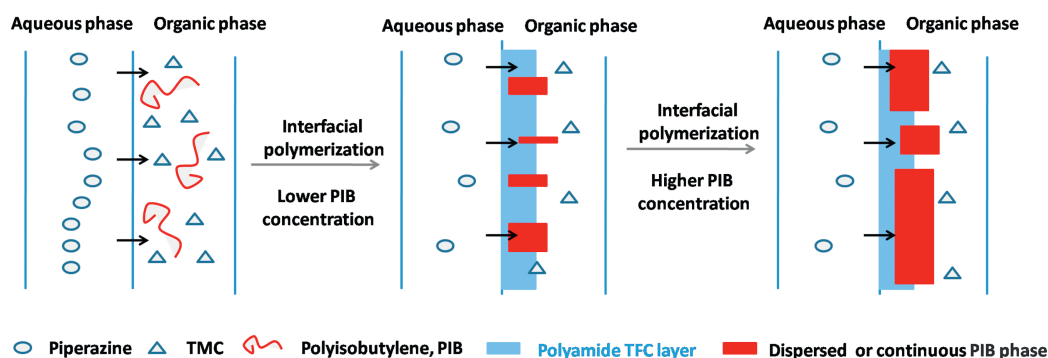


Fig. 6. Schematic illustration of the membrane formation and the dispersion of PIB in membranes.

workers [27]. The finding showed by Hoek is rather amazing since these newly developed TFN membranes show obviously increased flux without substantial decrease of salt rejection, and nanomaterials with either porous or solid structure will all contribute positively to membrane permeability [9]. Although dispersed PIB in our membranes are soft phase that are different from the aggregated hard domains of nanomaterial in TFN membranes, it can be analogously interpreted that the disrupted polyamide networking around the microdomains should be also found in our membranes. This defect and loose cross-linking areas provide a fast flow for water molecules and ions. This condition corresponds to the graph showed in Fig. 6 (middle) which illustrates the random dispersion of minor PIB phase in polyamide layer, and perforation must be avoided to promise the rejection by remaining the PIB at a relative lower concentration. At this optimum condition, it is possible to increase the fast flow areas by increasing the concentration of PIB (lower than 0.24 wt%). However, the condition will be reversed and turned into the second stage when the PIB on TFC membranes merges into continuous phase (Fig. 6, right), where the performance of PIB containing NF membranes will be determined by PIB upper layer which covers the surface of as-prepared membranes. In comparison with fast diffusion of TMC monomer to the interface between organic and aqueous phases where the interfacial polymerization happens, the bigger molecular weight ($M_n = 20 \text{ kg} \cdot \text{mol}^{-1}$) and rather low diffusion rate of PIB polymer will deposit it slowly on polyamide layer which has been already established. This explanation is confirmed by SEM and AFM which show the clear location of PIB on film surface.

3.6. Performance comparison with other NF membranes

Finally, we make a short performance comparison of our NF membranes with that of representative hydrophilic NF membranes, and their permeability as well as salt rejections is showed in Table 6. Obviously, it can be found that our membrane shows a superior salt

rejection to some representative membranes showed in literature [16, 17, 28]. More interesting, our membrane shows superior performance in either the permeability or the salt rejections to the membranes that showed in Ref. [27], indicating that the hydrophobicity is not a decisive factor that determines the permselectivity of NF membranes. It is worth noting that these results cited from literature are all prepared from a self-designed interfacial polymerization process with new polymer/monomer as additives, and they are comparable in fabricating process to our membranes. In addition, we also find that our membrane have showed a superior performance to that of commercially available hydrophilic NF membrane (NF-40) produced by Film Tech., and our membranes is also comparable to performance of hydrophilic NF membrane produced by Toray (UTC-60). However, when the results from NF70 (Film Tech.) are taken into account, our membranes are much lower both in permeability and salt rejection, indicating that much work can be conducted to improve the performance of our membranes. Nevertheless, the result showed in this work has presented a new idea that the NF membranes can be prepared from polymer additives which induce phase separation and microdomains formation in selective layer, and membranes with better performance will be anticipated if the fabrication and the polymer additive are further optimized.

4. Conclusions

In summary, NF membranes with microdomains formation in selective layer had been successfully fabricated from a well-designed interfacial polymerization. It was interesting to find that the permeability of fabricated membrane increased firstly (dominated by polyamide layer) and then decreased (dominated by PIB layer) with an increasing feeding of PIB in oil phase, and our NF membrane prepared at the optimum condition shows a comparable permselectivity with that of representative hydrophilic membranes appeared in literature. The successful incorporation of PIB into upper selective layer and formation

Table 6

Performance comparison of typical NF membranes prepared by interfacial polymerization

Membrane	Contact angle	Permeability ^① /L·m ⁻² ·h ⁻¹ ·MPa ⁻¹	Rejections/%		Refs.
			NaCl	Na ₂ SO ₄	
0.24 wt%-PIB	95.2°	29.5 ± 1.4	75 ± 0.7	97 ± 1.2	This work
TEOA-6 wt%	Hydrophilic	5	42.2	82	[27] ^②
NF2	37°–42°	62.5	37.5	38.2	[28] ^③
NF5	Hydrophilic	41.5	61.2	70.5	[29] ^④
NF40	Hydrophilic	21.5	45	95	Film Tech. ^⑤
NF70	Hydrophilic	71.7	70	98	Film Tech. ^⑥
UTC-60	Hydrophilic	80	55	98	Toray ^⑤

^① Permeability was normalized from results following the equation of $J \propto \Delta P$, where ΔP is the trans-membrane pressure, and J is the water flux.

^② Rejections were determined at the salt concentration of 5 mmol·L⁻¹ under a pressure of 0.6 MPa. The pH and temperature were not specified.

^③ Testing was done with salts solution of 1000 mg·L⁻¹ at a pressure of 0.6 MPa. The pH and temperature were not specified.

^④ Testing was conducted with salt concentration of 1000 mg·L⁻¹ at pressure of 0.6 MPa. The temperature and pH were 25.0 °C and 6.2–6.5, respectively.

^⑤ Rejections were measured at the feed concentration of 30 mmol·L⁻¹ under a pressure of 0.5 MPa.

^⑥ Measurement was conducted at the feed concentration of 2000 mg·L⁻¹.

of viewable isolated PIB phase could be easily inspected by SEM or AFM. We deduced from this morphological observation that the interface between the rigid polyamide networking and the flexible PIB was an important reason for the aforementioned finding, and the reason of which was analogously interpreted as that found for TFN membranes containing nanoadditives. The as-prepared membrane exhibited typical nanofiltration characteristics, and the good retentions to NaCl, Na₂SO₄ as well as the PEG with molecular weights higher than 200 were determined. The hydrophilicity changed obviously and contact angle increased from 32° to 95° when PIB was added. The hydrophobicity was not a problem because the performance comparison of our membranes was conducted under similar hydrophobicity, indicating that the difference in permselectivity of prepared membranes was not the result from hydrophobicity changes but the evolution of internal structure. Our results have demonstrated that novel NF membranes with improved performance can be potentially prepared from immiscible polymers, which is a new area that has not attracted much attention until now.

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