

Vertically Oriented Microporous Membranes Prepared by Bidirectional Freezing

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Electronic Supplementary Information

Abstract Polystyrene membranes with precisely controlled and vertically oriented pores are fabricated by a bidirectional freezing process. In this process, the influence of polymer in growth of diphenyl sulfone (DPS) crystals has been demonstrated by XRD and simulated by DFT based on the interaction between DPS crystal faces and polystyrene (PS). The influence of temperature gradient on membrane structures is also elucidated. Compared to the original membrane and modified traditional membranes, modified PS membranes with vertically oriented pores show large and stable fluxes in the processes of multiple oil and water separation.

Keywords Separation membrane; Vertical pores; Bidirectional freezing; Oil separation

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INTRODUCTION

Polymer membranes have been widely used in filtration processes such as wastewater treatment, blood dialysis, and beverage clarification. The membranes are usually fabricated *via* phase separation including non-solvent induced phase separation (NIPS)^[1–3] and thermally induced phase separation (TIPS)^[4–7]. Such membranes are generally characterized by tortuous porous structures and broad pore size distributions. Recently, the preparation of membranes with aligned pores has received great attention because of their wide applications in precise separation^[8], organic electronics^[9], molecular filtration^[10], microfluidics^[11], and tissue engineering^[12].

In the preparation of aligned porous membranes, directional freezing is often used which utilizes oriented solvent crystallites as templates to produce flow passages (or pores) of micron-scale size^[13–20]. Water-soluble polymers have been used to prepare aligned porous structures *via* directional freezing^[13, 14, 20]. For example, aligned poly(vinyl alcohol) (PVA) structures were produced by slowly lowering an aqueous solution of PVA into liquid nitrogen^[13]. The frozen solution was then freeze-dried to yield a 94% porous cylindrical monolith. Wu *et al.* prepared poly(ethylene glycol) (PEG) cryogels with oriented porous structures by

unidirectional freezing^[14]. However, the use of ice crystals as templates for the preparation of separation membranes is limited because membrane-forming polymers are often insoluble in water. This method has been significantly extended when organic solvents are used to prepare such porous structures. Organic solvents that are frequently used include benzene^[15], 1,4-dioxane^[16–18], and dimethyl sulfoxide (DMSO)^[19]. Kim *et al.* reported that poly(L-lactic acid) (PLLA) monoliths with aligned pores can be obtained by directional freezing of PLLA solutions in 1,4-dioxane^[16]. Wang *et al.* used 20 wt% PVDF/DMSO solution to fabricate aligned membrane *via* directional freezing^[19]. The membrane shows superior water flux compared with traditional membranes with similar average pore size. Whether water or organic reagents are used as solvents, relatively low freezing temperature is necessary for orientation of the crystallized templates because of their relatively low melting points (*e.g.*, water: 0 °C; 1,4-dioxane: 11.8 °C; DMSO: 18.4 °C). Also, the solvents need to be extracted at lower temperature in order to avoid redissolution of the polymer. Solvents with high melting points may dissolve polymers at high temperature, and can be extracted at room temperature. In our previous works, we used dimethyl sulfone (DMSO) as the solvent of PVDF to prepare membranes with vertically oriented pores *via* bidirectional freezing^[21].

In this study, we investigated polystyrene (PS) solutions with different concentrations in diphenyl sulfone (DPS), which has a melting point of 128 °C, to demonstrate the influence of polymer concentration and temperature gradient

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on membrane structures generated *via* bidirectional freezing. Vertically oriented porous PS membranes with pore size ranging from 0.27 μm to 1.8 μm were prepared. The interactions between PDS crystal faces and PS were simulated by density functional theory (DFT). The membranes were further modified by surface deposition of dopamine and polyethyleneimine (PEI) for oil/water separation.

EXPERIMENTAL

Materials

Polystyrene (PS, $M_n = 2.35 \times 10^5$ g·mol⁻¹, MWD = 2.89, Zhenjiang Chiemei Chemicals) was dried to constant weight before use. Diphenyl sulfone (DPS, 99%, Aladdin Chemistry Co., Ltd.) was used as crystallizable solvent. Tris-(hydroxymethyl) aminomethane (Tris-HCl), ethanol, and *n*-hexane were purchased from Sinopharm Chemical Reagent Co. Ltd. Polyethyleneimine (PEI, $M_w = 600$ Da) was obtained from Aladdin. Dopamine hydrochloride (DA) was purchased from Sigma-Aldrich. All of the chemicals were used as received.

Fabrication of Membranes

Bidirectional freezing is used for preparing vertically oriented porous membranes. PS/DPS mixtures with different polymer concentrations were heated at 180 °C to form a homogeneous solution. After degassing air bubbles, the solution was quickly poured into a homemade mold preheated in an oven, which consists of two plates—one is made from stainless steel and the other is glass. A Teflon film with a circular opening (diameter = 10 cm) was inserted between the two plates to adjust membrane thickness. Then the mold was put into a container vertically, and water at different temperatures (20, 30 and 40 °C) was added into the container at a rate of 2.75 L·min⁻¹. After complete solidification, the nascent membrane was taken out of the mold and immersed into ethanol as the extraction solvent. When the diluent was completely extracted, the wet membrane was dried in vacuum for 24 h at room temperature. We denoted the membrane surface contacting the stainless steel plate as the bottom surface, and that contacting the glass plate as the top surface, because DPS crystals grow directionally from stainless steel plate to glass plate.

In the unidirectional freezing process, the same mold with solution was put vertically into a container which was filled with water. In addition, other operations were the same as bidirectional freezing.

Membrane Modification

DA (2 mg·mL⁻¹) and PEI (2 mg·mL⁻¹) were dissolved in Tris-HCl buffer solution (pH = 8.5, 50 mmol·L⁻¹). PS membrane was prewetted by ethanol before deposition. Then the membrane was floated on a DA/PEI solution surface under ambient temperature. The deposition time was 2 h. The membranes were then rinsed with deionized water and dried in a vacuum oven overnight.

Membrane Characterization

Morphologies of membrane cross-section and surface were examined by FESEM (SIRION-100) with an accelerating

voltage of 25 kV. Porosity and pore size were measured using a mercury injection apparatus (Auto Pore IV9500, Micromeritics). Temperature profiles of the mold were measured by a handheld multi-channel temperature measuring instrument (JK802, Jinke). X-ray powder diffraction (D/Max-2550PC, Panalytical) measurement was employed on a X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.54$ Å) irradiated at a scanning rate of 0.02 (°)·s⁻¹. The melting and crystallization temperatures of the polymer/diluent mixtures were determined by differential scanning calorimetry (DSC, Q20, TA instruments). The surface wettability was characterized by contact angle measurement using a contact angle system (MAIST Vision Inspection & Measurement Co. Ltd.).

Simulation

The simulation was carried out to illustrate the growth of DPS crystal. Geometries of intermediates were optimized using corrected PM6-D3 method^[22]. All calculations were performed using Gaussian 09 program. PS was modeled by a styrene trimer. The structure of crystal face was obtained from XRD single crystal data of DPS. The parameters of atoms on crystal face were fixed during the optimization.

RESULTS AND DISCUSSION

Membrane Preparation and Structures

PS membranes with vertically oriented pores were fabricated *via* bidirectional freezing (Fig. 1a). PS/DPS homogeneous solution at 180 °C was quickly poured into a homemade mold preheated in oven. Then the mold was put into a container vertically, and water at different temperatures (20, 30, and 40 °C) was added at a rate of 2.75 L·min⁻¹. As the amount of water increases, dual temperature gradients appear along the *y*-axis and *z*-axis directions, which is due to increasing addition of water and the difference in thermal conductivity of the mold between stainless steel and glass (Table S1, in electronic supplementary information, ESI). Typical temperature profiles are shown in Fig. 1, which show the variation of surface temperature of stainless steel plate and glass plate cooling by water at 30 °C. Obviously, the surface of stainless steel plate is cooled faster than the glass plate because of the higher thermal conductivity of stainless steel plate. The maximum temperature difference between the two plates reaches almost 15 °C. With water rising, the temperature gradient along the *z*-axis direction does not change significantly, which ensures a relatively constant solidification velocity for the polymer solution. In addition, a temperature gradient along the *y*-axis of the stainless steel plate is also established as water rises. Fig. 1(c) shows the temperature profile of two typical spots ($\Delta y = 2$ cm) at the stainless steel plate along the *y*-direction with gradual addition of water. The maximum temperature difference is about 67 °C when Δy is 2 cm. The temperature of line AC represents not only the crystallization temperature of 30 wt% PS/DPS solution (Fig. S1, in ESI) but also the ideal temperature of solid-liquid interface which parallels to the water. It is also found that Δt_{AC} (33 s) almost equals Δt (30 s), which means that the real solid-liquid interface almost

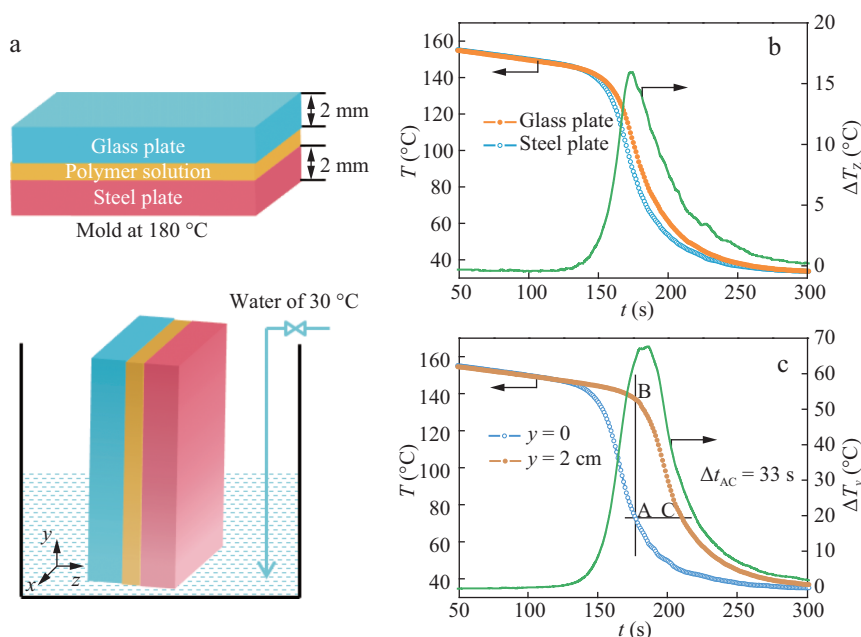


Fig. 1 (a) Preparation procedure for polymer membranes with vertical pores *via* bidirectional freezing; (b) Temperature profiles with time of the surfaces of stainless steel plate and glass plate; (c) Temperature profiles with time of two spots at the stainless steel plate along the *y*-direction ($\Delta y = 2$ cm). The water temperature is 30 °C and the flow rate is 2.75 L · min⁻¹. $\Delta t = 30$ s means the time required for water to rise by 2 cm.

parallels to the water. The line AB indicates that the temperature of the second test point is still much higher than the crystallization temperature of 30 wt% PS/DPS solution when water reaches the first test point. Therefore, the solvent crystals still grow directionally in the *z*-direction while the temperature gradient in the *y*-direction promotes the ordered nucleation of solvent crystals.

Fig. 2 shows SEM images of PS membranes with vertical pores prepared at different polymer concentrations *via* bidirectional freezing. Herein, three different concentrations of PS/DPS solutions were investigated. Figs. 2(a)–2(c) show cross-sectional SEM images of the membranes. With the increase of concentration, the vertical orientation of PS membrane is getting better. It can be observed that the membrane has an asymmetric structure with gradually open micro-channels when the concentration is 20 wt% (Fig. 2a). The same situation happens when the concentration is 25% (Fig. 2b). Nevertheless, vertically oriented cylindrical pores can be observed clearly when PS concentration increases to 30 wt%. This difference can be attributed to the Mullins-Sekerka instability^[13, 23, 24]. When a solution is frozen, crystals grow and solute molecules are excluded by these crystals due to a very low solubility of impurities in crystals, which causes both the loss of solvent in the liquid phase and the reduced solubility of polymer at low temperatures. Therefore, the remaining polymer solution enters into unstable region and starts to demix. The polymer concentration in the remaining liquid phase is much higher than that of the adjacent polymer solution at higher temperature, which makes polymer diffuse to the high temperature plate. The increase of concentration reduces the melting point of the solution, which results in the formation

of a constitutional supercooling zone and finally breaks down the planar interface, and the crystal cell grows for a far longer time. On the other hand, the diffusion of solute is negatively correlated with the viscosity of the solution. As the solution concentration increases from 20 wt% to 30 wt%, the solute concentration gradient decreases, and results in gradually open micro-channels structure at low concentrations and vertically oriented cylindrical pores at high concentrations. The detailed fish-bone morphology (inset in Fig. 2a) results from the formation of DPS crystal side branches. When PS freeze-concentrates around the primary DPS crystal cells, it causes secondary instability formation perpendicular to the freezing direction at low concentrations^[13]. A dense separation layer is formed at the bottom side because of the fast cooling of stainless steel plate, which leads to freeze of PS solute before the crystallization of DPS (Figs. 2d–2f). In fact, just a few pores can be observed on the bottom layer. The pore size decreases as the concentration increases (Figs. 2g–2i). Fig. 3(a) indicates that the pore size and porosity of PS membranes decrease with concentration. Moreover, pore size distribution becomes narrow when solution concentration increases, which is due to the growth hindrance of DPS cells (Fig. 3b).

We used 30 wt% PS/DPS as a model system to conduct a detailed analysis (Fig. 4). It can be seen from Fig. 4(a) that a layer with a thickness of about 15 μm shows cellular-like pores because the solution close to the stainless steel plate cools down too fast. Results from the cross-sectional analysis show that the structure is perfectly vertical to the membrane surfaces with a pore size of ~270 nm (Figs. 4b and 4c). Fig. 4(d) schematically illustrates the formation of vertically oriented pores. First, cellular-like pores form; then, the DPS

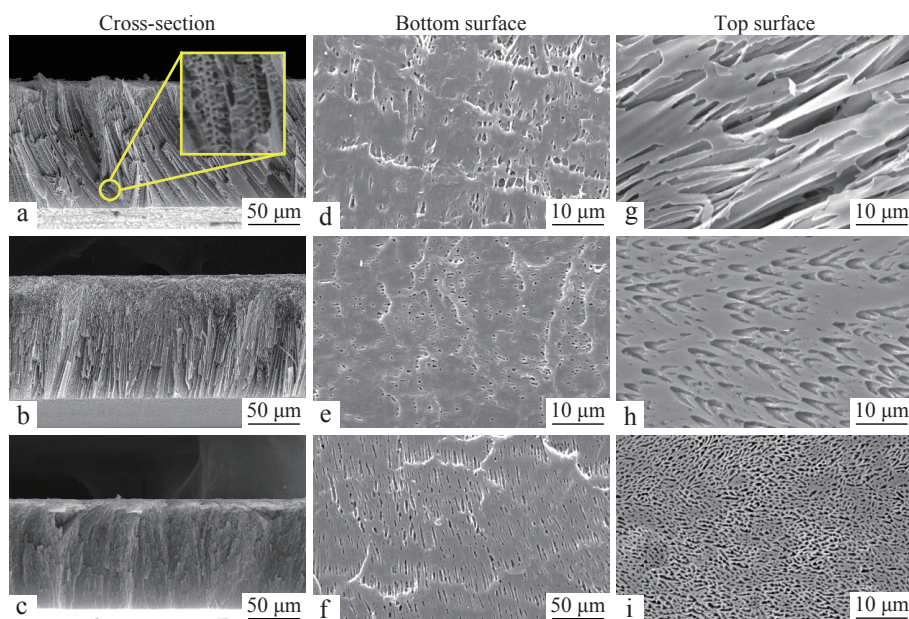


Fig. 2 SEM images of PS membranes with vertical pores prepared at different polymer concentrations: (a, d, g) 20 wt%; (b, e, h) 25 wt%; (c, f, i) 30 wt%. Water temperature is 30 °C and water flow rate is 2.75 L·min⁻¹.

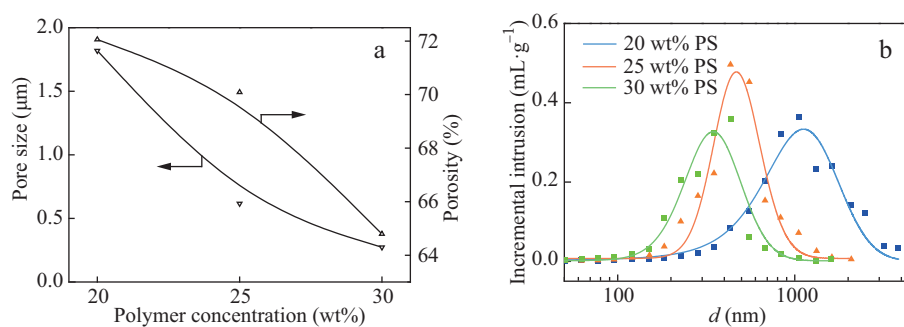


Fig. 3 (a) Porosity and pore size and (b) pore size distribution of PS membranes prepared at different polymer concentrations

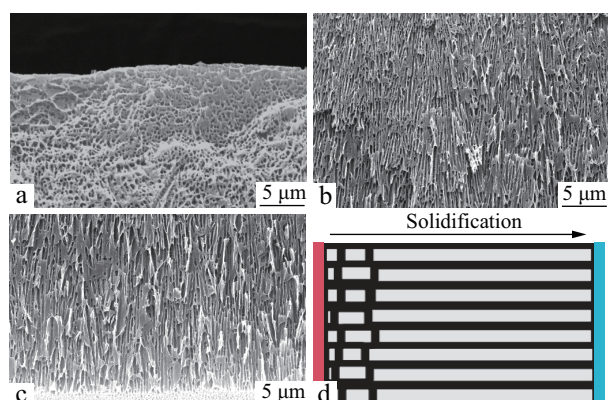


Fig. 4 (a–c) SEM images of PS membranes with vertical pores at different areas of the cross-section including (a) bottom, (b) middle, and (c) top areas; (d) Schematic representation of the cross-sectional structure of PS membranes. Polymer concentration is 30 wt% and water flow rate is 2.75 L·min⁻¹.

crystal grows vertically to the membrane surfaces to form vertically oriented pores because of the temperature gradient.

Compared with the vertically oriented pores formed *via*

bidirectional freezing, unidirectional freezing results in PS membranes with different pore structures (Fig. S2, in ESI). It can be seen that the cross-section is rather dense (Fig. S2a, in ESI). In addition, pores on the membrane surface are unconnected (Figs. S2b and S2c, in ESI). This may be induced by the too fast cooling rate, which leads to rapid nucleation and growth of crystal on the surface (Fig. S2d, in ESI).

To investigate the effect of polymer concentration on membrane structures, XRD was used to examine the DPS crystals under different conditions (Fig. 5). Compared with XRD patterns of pure DPS (Fig. S3, in ESI), the diffraction peak intensity of the powder is reduced by an order of magnitude (Figs. 5a and 5b). The feature peaks of DPS coincide with pure DPS although the diffraction peak intensity of PS/DPS powder prepared *via* unidirectional freezing decreases. It can be deduced that in this process PS hinders the growth of DPS while does not change the crystal form. However, in the case of bidirectional freezing, the feature peaks of DPS, including (−110) (100) (011) (−102) faces, change with PS concentration and even disappear at 30 wt% PS (Fig. 5b). As mentioned above, cooling *via*

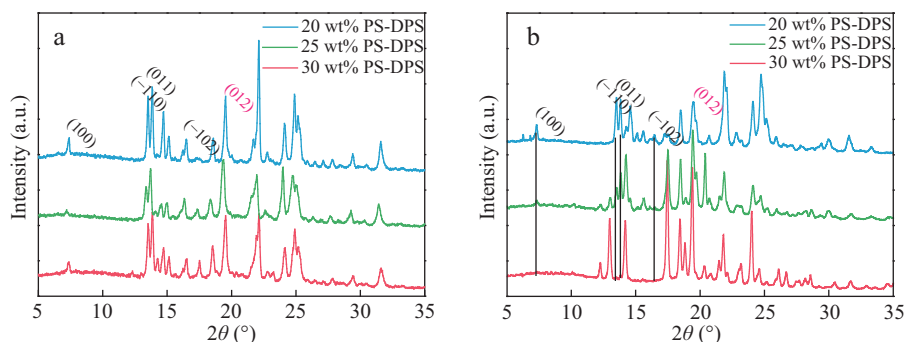


Fig. 5 XRD patterns of PS/DPS powder prepared *via* (a) unidirectional and (b) bidirectional freezing

unidirectional freezing is faster than bidirectional freezing. At high cooling rate, the nucleation and growth of DPS crystal are completed in a very short time, which reduces the impact of PS. In contrast, crystal deformation occurs with the increase of PS concentration at low cooling rate. Table 1 shows the simulation results of interactions between DPS crystal faces and PS trimer. Schematic diagrams of interactions between crystal faces and PS trimer are shown in Fig. S4 (in ESI). The interaction of PS with the crystal faces, including (-110) (100) (011) (-102) , is stronger than that

with (012) face which is retained. It means that DPS crystals undergo preferential growth. Therefore, crystal faces interacting with PS disappear when the membranes are prepared *via* bidirectional freezing. Higher concentration leads to better pore orientation, which is advantageous for the preparation of vertical oriented pores.

Influence of Temperature Gradient

In this work, temperature gradient is caused by two factors, *i.e.*, water temperature and thermal conductivities of the mold plates. Three different water temperatures were adopted to fabricate membranes with vertically oriented pores, including 20, 30, and 40 °C. As shown in Figs. 6(a) and 6(b), membranes with vertically oriented pores are successfully fabricated at different temperatures. Fig. 6(c) reveals that water bath at low temperature (20 °C) causes a large temperature difference (~ 19 °C) and a fast cooling rate (Fig. 7a). Under this condition, the pore size can be quickly

Crystal face	Interaction HF energy (kJ·mol ⁻¹)
(-110)	-105.02
(011)	-100.46
(-102)	-89.87
(100)	-81.41
(012)	-81.37

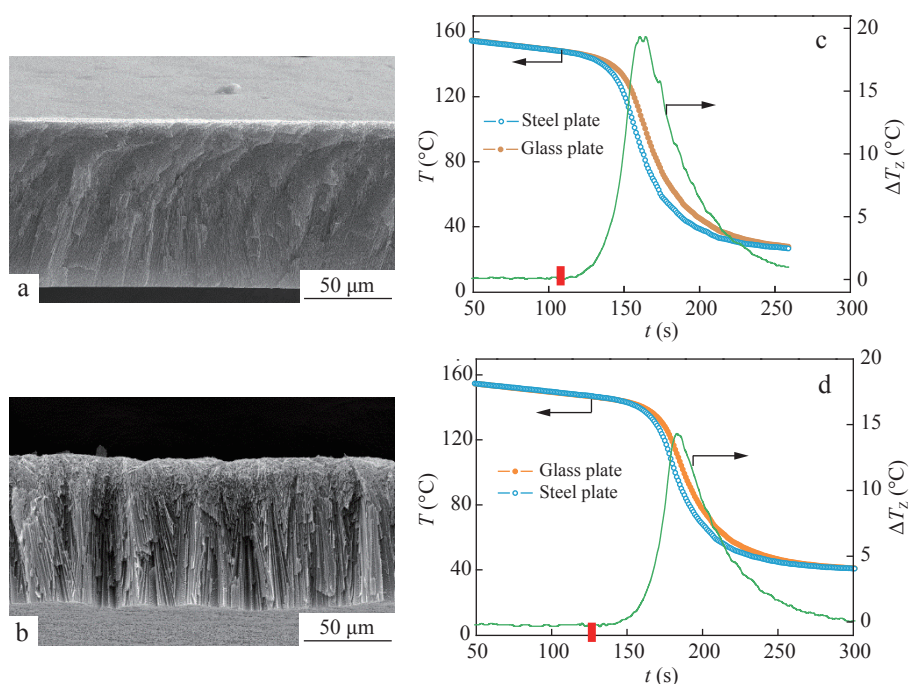


Fig. 6 (a, b) Cross-sectional SEM images of PS membranes prepared at different water temperatures; (c, d) Temperature profiles of stainless steel plate and glass plate at different water temperatures. (a, c) 20 °C and (b, d) 40 °C. The polymer concentration is 30 wt% and the water flow rate is 2.75 L·min⁻¹.

reduced to about 200 nm (Fig. S5). However, compared with membranes prepared at 30 °C, the channels are vertical but a bit tilted. At a slow cooling rate (40 °C), the membranes have an asymmetric structure with gradually open micro-channels. Apparently faster cooling rates induce smaller initial DPS crystallites, and the temperature gradients are also much steeper than the latter case (Figs. 6c and 6d), resulting in faster polymer diffusions. Fig. 7(b) shows that the solid-liquid interfaces advance at different water temperatures. At low temperature (20 °C) or high temperature (40 °C), solid-liquid interface fluctuates unsteadily above or under air-water interface, which leads to bended channels. At a moderate temperature (30 °C), solid-liquid interface moves smoothly and the membranes show vertically oriented pores.

On the other hand, the difference in thermal conductivities of mold plates also causes temperature gradient. We replaced stainless steel plate with aluminum plate and copper plate. It is known that the thermal conductivity of copper and aluminum is greater than that of stainless steel, which may cause a larger temperature gradient (Table S1, in ESI). It can be seen from Fig. 8 that ΔT_y is about 30 °C which is smaller than ΔT_y obtained between a stainless and glass plate. This result indicates that larger thermal conductivity of cold plates than stainless steel can generate instability of solid-liquid planar interface and lead to inhomogeneous pore structures (Figs. S6 and S7, in ESI). Also, there are different temperature profiles along z -axis when using aluminum or

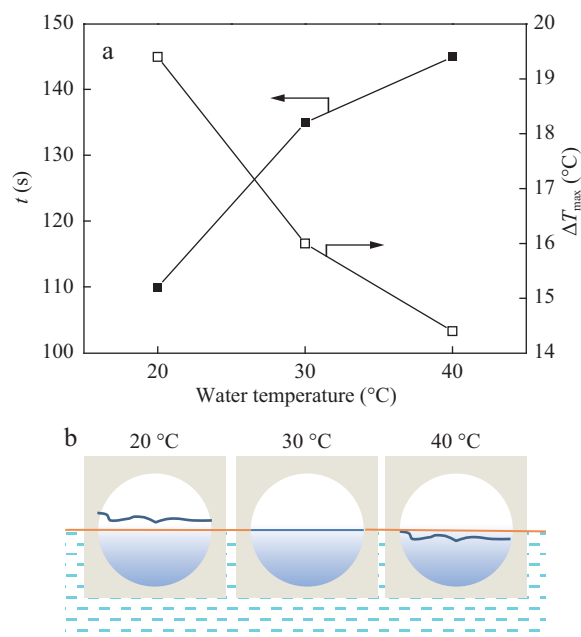


Fig. 7 (a) Dependence of beginning time and the maximum temperature difference on the temperature between stainless steel plate and glass plate; (b) Schematic representation of the solidification forward line of PS/DPS solution at different water temperatures. The polymer concentration is 30 wt% and the water flow rate is 2.75 L·min⁻¹.

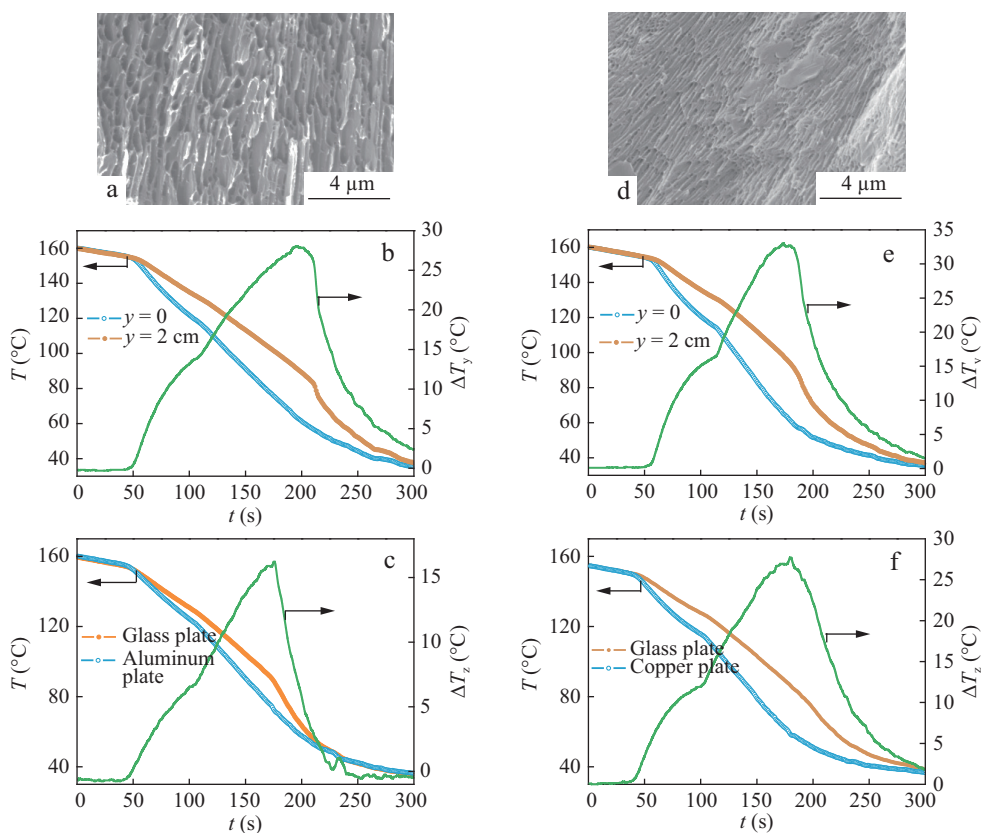


Fig. 8 (a, d) SEM images of membrane cross-section; Temperature profiles with time of two spots at the plates along the y -direction, $y = 0$ or 2 cm, between (b) aluminum plate and glass plate and (e) copper plate and glass plate; Temperature profiles with time of the surfaces of glass plate and (c) aluminum plate or (f) copper plate. The water temperature is 30 °C and the water flow rate is 2.75 L·min⁻¹.

copper plates. As the thermal conductivity increases, the peaks of temperature difference are broadened, meaning that the temperature difference between both sides becomes larger (stainless steel: 16.0 °C, aluminum: 16.3 °C, copper: 27.0 °C). Larger temperature difference along *z*-axis results in faster polymer diffusions and hence leads to smaller pore size (Figs. 8a and 8d).

Oil-Water Separation

Oil pollution is an urgent problem to be solved in many areas. The traditional separation techniques include gravity separation, skimming and flotation^[25]. Due to the low cost and ready availability, porous membranes are frequently used in practical operation^[26], but they still face limitations of pore clogging and surface fouling by oil or grease. Vertically oriented microporous membranes prepared in this work may have extremely high flux because of the straight through pore structure.

The flux of unmodified PS membranes is as high as $\sim 20000 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$. It decreases to some extent after the third cycle use (Fig. S8, in ESI). In recent years, Janus membrane has been applied to oil-water separation for its anti-fouling property^[27]. In our case, vertical pores endow the membranes with very low tortuosity that provides direct paths for water or oil permeation compared to traditional membranes. This may help to reduce the effect of reduction in flux caused by membrane fouling. Furthermore, membranes modified by surface deposition of PDA/PEI were

applied for oil-water separation. Nonwovens were used to enhance the strength of the membranes (Figs. S9 and S10, in ESI). Fig. 9(a) shows the fabrication process by single-surface deposition of PDA/PEI^[28]. PS membrane was pretreated by ethanol before deposition. In this case, PDA and PEI form a hydrophilic cross-linked coating on the contacted membrane surface. After deposition of PDA/PEI, the two sides of the membrane are different, *i.e.*, the modified side is hydrophilic while the other side is still relatively hydrophobic. The asymmetric surface property can be identified by water contact angles (WCAs) on each surface of the membranes (Fig. 9b). The hydrophilic surface of modified PS membrane shows an initial WCA of about 48°, which rapidly and continuously decreases to about 0° within 30 s. On the other hand, the initial WCA of hydrophobic surface is nearly 95° and slowly decreases to 0° within 120 s. The decrease is due to the porous structure. We used the modified membrane for the separation of *n*-hexane and water. The hydrophilic membrane surface is toward to the mixture of oil and water. As shown in Fig. 9(c), the modified PS membranes exert a very high oil flux up to $36000 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$, and maintain a very stable flux in five cycles. However, the oil flux of traditional PS membranes is much lower and declines rapidly from $19000 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$ to $5200 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}\cdot\text{bar}^{-1}$. It may be attributed to the straight pores and slight resistance of membranes with vertically oriented pores.

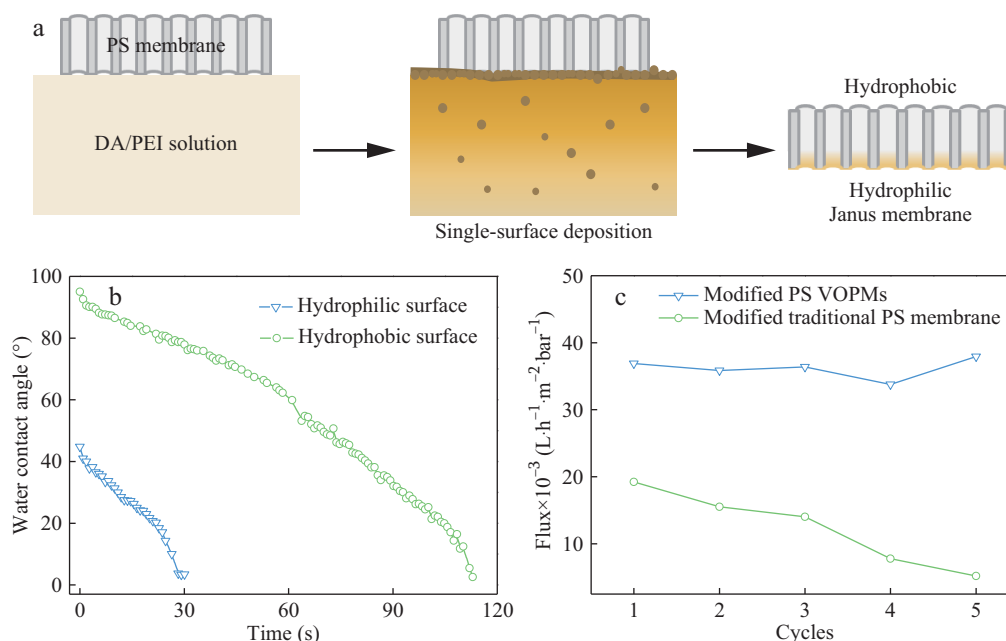


Fig. 9 (a) Illustration of the fabrication process for PS membrane by single-surface deposition of PDA/PEI; (b) Dynamic water contact angles on each surface of the modified membrane; (c) Recyclability for oil-water separation by modified PS vertically oriented porous membranes (VOPMs) and modified traditional PS membranes. The membranes were prepared with 30 wt% polymer concentration in water bath at 30 °C. The water flow rate is $2.75 \text{ L}\cdot\text{min}^{-1}$.

CONCLUSIONS

In summary, the bidirectional freezing process has been

successfully applied to the preparation of PS membranes with well controlled vertically oriented pores by using crystallizable solvents with high melting point. The influence

in the growth of DPS crystal has been evidenced by XRD and simulations. Moreover, effects of temperature gradient generated by water temperatures and thermal conductivities of mold plates are elucidated. Moderate water temperature and thermal conductivity of mold plates are necessary for the fabrication of membranes with vertically oriented pores. Modified PS membranes with vertically oriented pores show a very large and stable oil flux ($36000 \text{ L} \cdot \text{h}^{-1} \cdot \text{m}^{-2} \cdot \text{bar}^{-1}$) which is crucial in applications.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2113-z>.

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