Preparation and Application of Microporous TPX Membranes

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Summary: In the present work, poly(4-methyl-1-pentene) (TPX) was used to prepare hydrophobic microporous membranes, and the application of the prepared membranes to pervaporation and osmotic distillation was also investigated. The TPX/cyclohexane solution inclines to undergo solid-liquid demixing and form polymer particles at room temperature. The solid-liquid demixing is strongly related to the crystallization process. During membrane formation, the competition between solid-liquid demixing and polymer precipitation determines if particulate membranes can be prepared. By using suitable coagulant, such as propanol, the solid-liquid demixing process occurs before polymer precipitation, particulate TPX membranes with interconnected pores can thus be successfully fabricated. By adjusting the coagulation environment, the pore size of the porous TPX membrane can be tailored. Experiments were performed to evaluate the performance of the prepared membranes in pervaporation and osmotic distillation. The results indicate that the performance of the microporous TPX membranes prepared in the present work is comparable to the commercial PTFE membranes.

Introduction

The porous hydrophobic membrane with appropriate pore size is not wetted by water and can therefore serve as contactors for membrane distillation[1] and membrane extraction[2]. There are commercially available porous hydrophobic membranes made by polytetrafluroethylene (PTFE), polyvinylidenefluoride (PVDF), or polypropylene (PP). In the present work, we discuss how to prepare the porous hydrophobic membrane by using another hydrophobic polymer: poly(4-methyl-1- pentene), and evaluate its performance in pervaporation and osmotic distillation.

Poly(4-methyl-1-pentene) (commercial name: TPX) is known for its high gas permeability and good mechanical property. It has been applied in gas separation[3], and dehydration pervaporation[4]. In the present work, we are interested in its other properties: strong hydrophobicity and high degree of crystallinity (ranges from 55% to 85%)[5]. Due to its strong hydrophobicity, TPX is a potential material for preparing porous hydrophobic membrane. The high crystallinity allows the formation of porous

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TPX membranes with particulate structure. The idea of using high crystallinity to prepare particulate membranes is originated from the works presented in[6-10].

The porous hydrophobic membrane has been used as the ethanol-selective membrane in the pervaporation process[11]. When being applied to the pervaporation process (the downstream is vacuumed), the porous TPX membrane needs to resist a penetration pressure of 1 atm to prevent the occurrence of wetting. Hence, the pore diameter should be small enough to form a stable solution-gas interface. How to control the pore size of the TPX membrane in a reasonable range is also discussed in this work.

The application of the prepared TPX membranes in osmotic distillation to concentrate protein solution is also discussed in this work. In such a process, the porous TPX membrane is used to separate a protein solution (the feed solution) and a saturated salt solution (the strip solution). Because of its hydrophobicity, the porous TPX membrane can provide a stable vapor gap between the two solutions. The water vapor pressure in the strip solution is lower than that in the feed solution because of the high osmotic activity of salt. The difference in water vapor pressure drives the transport of water vapor from the feed solution to the strip solution, and the concentration of the feed solution can thus be accomplished. If the TPX membrane can form a stable vapor gap was examined, and the water flux through the membranes was also measured.

Experimental Part

Materials

Two types of poly(4-methyl-1-pentene) were used in this study: one was supplied by Aldrich (product number 190985) and the other by Mitsui (MX-002). The molecular weight of the Mitsui TPX is about 500,000, measured by GPC (Waters, M-45). And the molecular weight of the Aldrich TPX is about 200,000. The solvent (cyclohexane) and the coagulants (methanol, ethanol, 1-propanol, and 1-butanol) were of reagent grade. All the chemicals were used without further purification.

Membrane preparation

TPX was dissolved in cyclohexane at 50°C to prepare the casting solution. When the Aldrich TPX was used, the polymer concentration was 7 wt%. For the Mitsui TPX , the polymer concentration was lowered to 5 wt% to make the solution viscosity roughly the same as that of the Aldrich TPX solution. The solution was degassed at 50°C and then cast on a glass plate to a thickness of 300 μm. The casting solution was immersed in a

coagulation bath at 25 °C. After 10 minutes, the plate was removed from the first coagulation bath and immersed in a second coagulation bath for 12 hours to remove the residual solvent and the coagulant absorbed in the first bath, a step that can alleviate the membrane shrinkage in the drying stage[3]. The resulted membrane was peeled off and dried in air. The coagulants used in the first bath were methanol, ethanol, 1-propanol, or 1-butanol. The coagulant used in the second bath was methanol.

Pervaporation

One can refer to[4] for details of the pervaporation set-up. The feed solution, kept at 28 °C, was ethanol aqueous solution, containing 6.5 wt% of ethanol. The permeation flux was determined by measuring the weight of the permeate, and the composition of the permeate was analyzed by gas chromatography (G.C. China, 8700T).

Osmotic distillation

Experiments of osmotic distillation were performed by using side-by-side cells. One can refer to[12] for details of the side-by-side cells. The BSA (bovine serum albumin) solution was placed in the donor cell, the $CaCl_2$ solution in the receptor cell, and the porous TPX membrane was clamped in between. Due to the difference in water vapor pressure between the donor and receptor cells, water vaporized from the donor cell (BSA solution), transported through the membrane pores, and then condensed to the receptor cell ($CaCl_2$ solution). Hence, the BSA concentration in the donor cell increased. The BSA solution was sampled automatically every 20 minutes and the BSA concentration was assayed spectrophotometrically at 280 nm (ultraviolet). The time dependence of BSA concentration can then be determined. With the increasing rate of the BSA concentration, the decreasing rate of water volume in the donor cell can be calculated. The water flux through the membrane can then be determined.

Results and Discussion

Characteristic of the TPX/cyclohexane solution

Clear solution was obtained by dissolving 7 wt% of TPX (from Aldrich) in cyclohexane at 50°C. When the clear solution was lowered to 25°C, the solution was clear for about two hours. Then, the solution became turbid. After the onset of turbidity, the solution lost its fluidity and finally gelled. Obviously, because of the lowering of temperature, the TPX solubility in cyclohexane decreased. The decrease in solubility

resulted in phase separation so that the solution became turbid. Theoretically, the phase separation could either be liquid-liquid demixing or solid-liquid demixing. Since liquid-liquid demixing is a fast process[13], the phase separation discussed above should be solid-liquid demixing (it took 2 hours to bring about the phase separation).

The following results can give more evidence to support that the phase separation is solid-liquid demixing. Quenching the clear TPX solution in liquid nitrogen resulted in the structure shown in Fig.1a. It should be noted that the quenched solution was freeze-dried before performing the SEM analysis. The elongated pores could be originated from the expelling of solvent from polymer (liquid-liquid demixing) during the quenching process[14]. The structure of the turbid solution (Fig.1b) is different from that depicted in Fig.1a. It can be seen that the turbidity is caused by the occurrence of suspended polymer particles, supporting that the phase separation is solid-liquid demixing. It can also be seen that the TPX gel is in fact composed of TPX particles (Fig.1c). The above results suggest that the TPX/cyclohexane solution incline to undergo solid-liquid demixing and result in particulate structure.

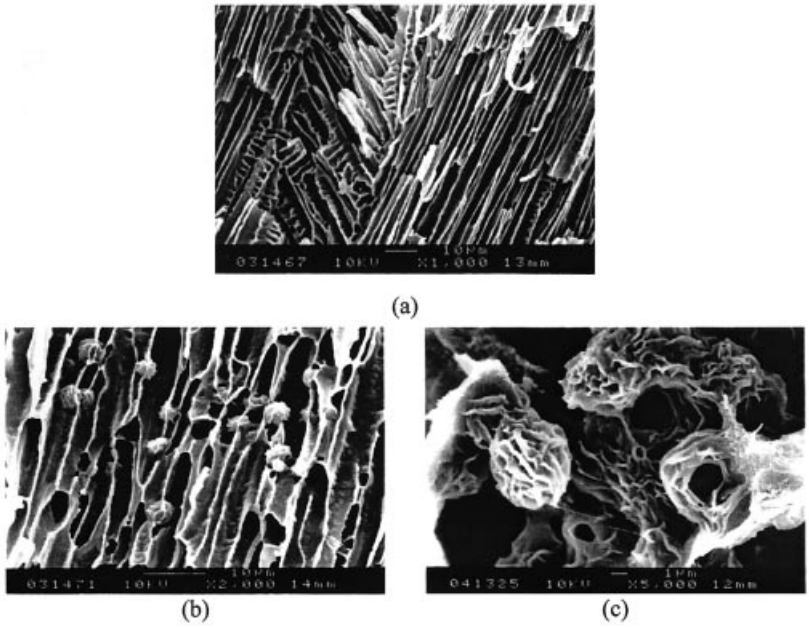

Fig. 1: Structure of TPX/Cyclohexane solution after quenching in liquid nitrogen
(a) clear solution, (b) cloudy solution, (c) gel

Competition between solid-liquid demixing and polymer precipitation

The characteristic of TPX/cyclohexane solution, inclining to undergo solid-liquid demixing, was used to prepare particulate TPX membranes. First, the dry method was used. The clear TPX/cyclohexane solution was cast and then dried in air. A homogeneously dense membrane was obtained and the particulate structure was not observed. The reason for the disappearance of particulate structure is discussed in the following. During the drying stage, the evaporation of cyclohexane (polymer solvent) would concentrate the TPX solution and result in the entanglement of polymer chains, which led to the precipitation of polymer and the formation of dense membrane. As discussed above, it required about two 2 hours to initiate the solid-liquid demixing process. On the other hand, the boiling point of cyclohexane is low (81°C) and the evaporation process was quite fast. Therefore, there was not enough time for the solid-liquid demixing process to occur before the precipitation of polymer. After polymer precipitation, the entanglement of polymer chains would impede the solid-liquid demixing process; hence, the particulate structure did not appear.

On the basis of the above discussion, it is known that during membrane formation the solid-liquid demixing process competes with the polymer precipitation process. To obtain membranes with particulate structure, the solid-liquid demixing process should occur before polymer precipitation. Therefore, trying to speed up the solid-liquid demixing process and slow down the polymer precipitation process is our strategy to fabricate particulate TPX membranes.

Effect of nonsolvent on the solid-liquid demixing process

The data presented below indicate that alcohol can speed up the solid-liquid demixing process of the TPX/cyclohexane solution. As mentioned above, the TPX solution was clear for a certain amount of time and then turned turbid. The time required for the solution to turn turbid is defined as the clouding time in this work. The clouding time of the TPX/cyclohexane solution was about 2 hours. It was observed that the clouding time decreased when alcohol (nonsolvent for TPX) was added in the TPX/cyclohexane solution (as shown in Fig.2), indicating that the addition of alcohol in the TPX solution can speed up the solid-liquid demixing process.

Because alcohol is nonsolvent for TPX, it is reasonable to suspect that the addition of alcohol might introduce liquid-liquid demixing. However, we believe that the dominant phase separation mechanism after the addition of alcohol is still solid-liquid

demixing for two reasons. First, although the clouding time decreases with the addition of alcohols, it still requires time to initiate the phase separation. If the phase separation were liquid-liquid demixing, the solution would have demixed almost immediately. Second, after the addition of alcohols, we quenched the clear solution, the cloudy solution, and the gel to investigate their structures. The results are similar to those presented in Fig.1, indicating that the phase separation is still solid-liquid demixing.

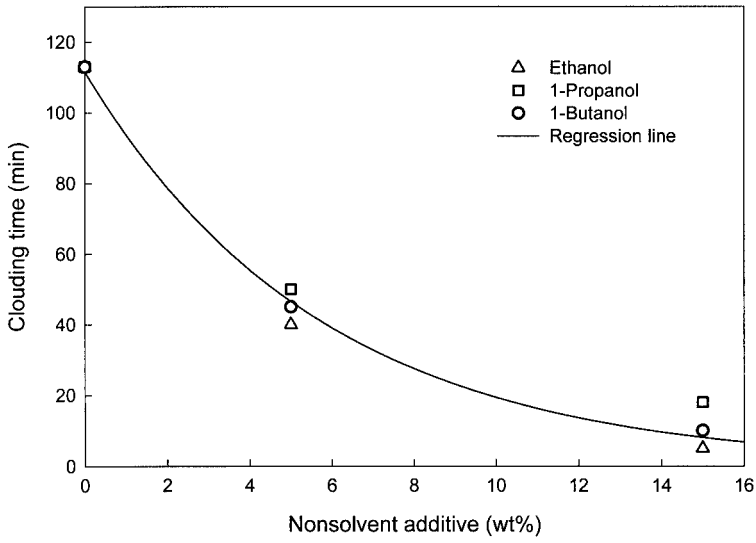

Fig. 2: Effect of nonsolvent on clouding time

Preparation of particulate TPX membranes by the wet inversion method

On the basis of the above discussion, it was proposed that TPX membranes with particulate structure should be able to be obtained by immersing the TPX/cyclohexane solution into the coagulation bath containing alcohol. The penetration of coagulant (alcohol) into the TPX/cyclohexane solution during membrane formation should be able to speed up the solid-liquid demixing process and result in particulate TPX membranes. Four alcohols, methanol, ethanol, 1-propanol, and 1-butanol, were used as coagulant to fabricate the TPX membrane. The results are shown in Fig.3. It can be seen that not all alcohols can fabricate particulate membranes, only propanol and butanol worked as expected. The reason why methanol and ethanol cannot function as expected is discussed in the following.

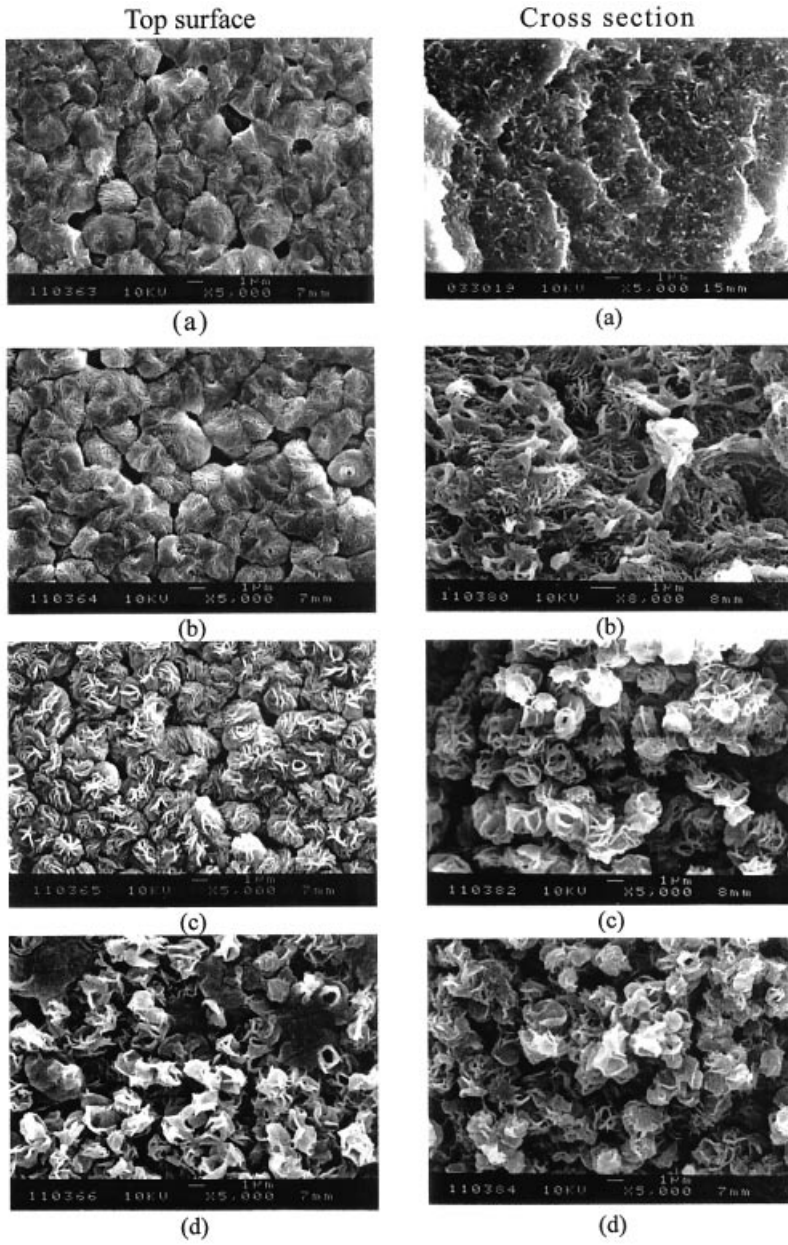

Fig. 3: SEM's of the membranes prepared by using different alcohols as coagulant (a) methanol, (b) ethanol, (c) 1-propanol, (d) 1-butanol

As discussed above, if TPX particles can occur depends on the competition between solid-liquid demixing and polymer precipitation. In the wet inversion process, although the penetration of coagulant could speed up the solid-liquid demixing process, the exchange of solvent and coagulant would also result in polymer precipitation. The polymer precipitation rate depends on the property of the coagulant used. The soft coagulant generally has lower polymer precipitation rate than the harsh one. By examining the solubility parameters of TPX and alcohols, it can be found that the alcohol with more carbon atoms is the softer coagulant for TPX. Hence, propanol and butanol have lower polymer precipitation rate than methanol and ethanol. When propanol or butanol was used as the coagulant, there was enough time for the solid-liquid demixing process to occur and membranes with particulate structure were thus be prepared. However, methanol and ethanol did not allow enough time for the solid-liquid demixing to occur before polymer precipitation.

[Crystallization and membrane formation]

The data presented in the following provide evidence to support that the slow solid-liquid demixing is related to the crystallization process. X-ray diffraction analysis was performed and the results are presented in Fig.4.

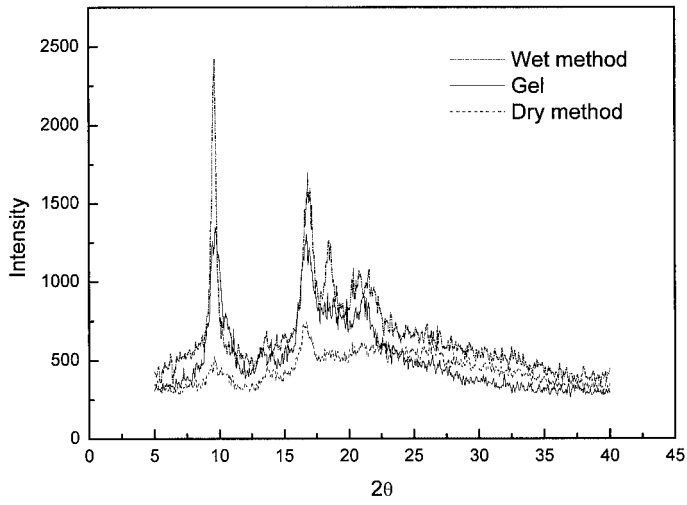

Fig. 4: XRD analysis of the TPX membrane

Three samples were analyzed: the TPX gel, the dense membrane, and the particulate membrane prepared by using propanol as coagulant. It can be seen that when the polymer particles can be clearly observed, such as the TPX gel and the particulate membrane, the diffraction peaks can also be clearly identified. On the other hand, when the polymer particles cannot be found, such as the dense membrane, the diffraction peaks are not clear and the diffraction intensities are much lower. Obviously, the occurrence of the particulate structure is strongly related to the crystallization process.

Control of the pore size of the porous TPX membrane

Besides using different coagulant, we also used additives to adjust the coagulation environment. We added methanol in propanol to make the mixture a harsher coagulant than pure propanol, and added cyclohexane to make the coagulation environment softer. By adding different amount of methanol or cyclohexane in propanol, we can easily adjust the coagulation environment. The effect of the coagulation environment on the membrane surface morphology is illustrated in Fig.5.

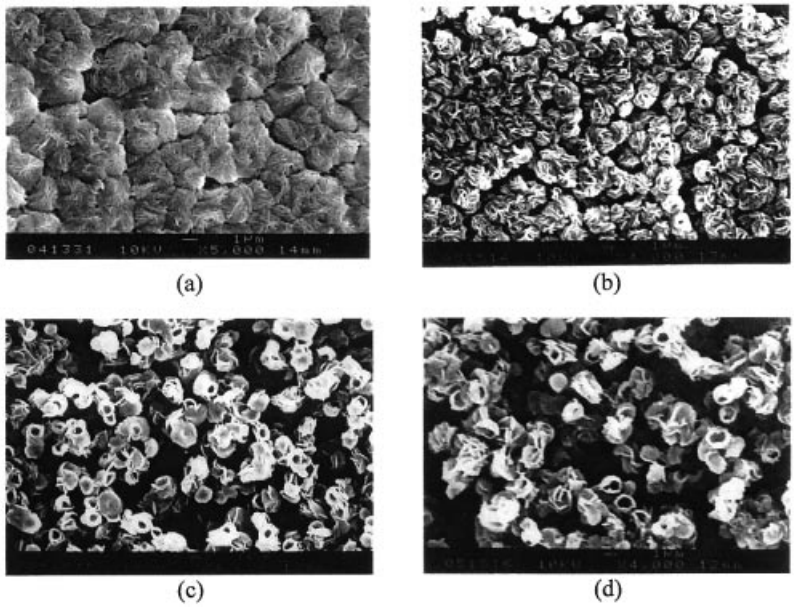

Fig. 5: Effect of coagulation environment on the morphology of membrane surface
Coagulant: 1-propanol; additive: (a) 20wt% methanol, (b) 10wt% methanol, (c) none, (d) 20wt% cyclohexane

The results indicate that the size of the surface pore is adjustable by varying the coagulation environment. In a softer environment, the polymer particles at the surface pack more loosely, resulting in larger surface pores.

By using the procedures discussed above, we can successfully prepare porous TPX membranes with different pore size. However, the prepared membranes are brittle so that the application is limited. For example, the membrane prepared by using butanol as coagulant is too fragile to be used in the pervaporation process. It was found that, by using the TPX with higher molecular weight, the mechanical property could be improved. But, the TPX with higher molecular weight required more time to proceed solid-liquid demixing than the TPX with lower molecular weight. Therefore, cyclohexane was added in propanol to slow down the polymer precipitation rate, allowing more time for TPX to proceed solid-liquid demixing. Then the particulate membrane can be prepared by using the TPX with higher molecular weight. The resulted membranes are not so brittle as the membranes prepared by the TPX with lower molecular weight.

Application of the porous TPX membranes

By adjusting the coagulation environment, particulate TPX membranes with different pore size and different porosity can be prepared. The effect of preparation condition on membrane porosity and pore diameter is illustrated in Table 1. The pore diameter was measured by a porosity meter (PMI Co., CFP-1500) on the basis of the permeability method and the bubble-point method[15]. It can be seen clearly that the softer coagulant can result in membranes with larger pore diameter and larger porosity.

The pervaporation performance of the prepared membranes was examined. To be able to act as a pervaporation membrane, the porous membrane must not be wetted by the feed solution to prevent the liquid flow through the membrane pores. Because there is a nearly 1 atm pressure difference across the membrane in pervaporation, the membrane pore should be small enough to resist this penetration pressure. It was observed that the membranes having pore diameter larger than 0.6 μm were wetted by the feed solution and cannot serve as pervaporation membranes. For the two membranes having pore diameter of 0.3 and 0.4 μm, pervaporation separation can be performed. The flux and the separation factor are reported in Table 1. The separation factor of ethanol to water is about 5 and the flux can be as high as 9.5 kg/m^2h. Compared with the commercial PTFE membrane, the separation factor is about the same but the permeation flux is higher.

Table 1. Performance of TPX membrane in pervaporation and osmotic distillation.

Coagulant[a] additive	average pore diameter (μm)	porosity (%)	pervaporation[b]		vapor[b] permeation		osmotic[c] distillation
			J (kg/m^{2}h)	α	J (kg/m^{2}h)	α	water flux (kg/m^{2}hr)
[L]10wt% methanol	0.40	69	7.5	4.6	8.9	6.0	2.9
[L]no additive	0.61	75	flow	0	15.5	5.8	2.6
[L]20wt% cyclohexane	1.06	80	flow	0	20.7	5.6	3.0
[H]20wt% cyclohexane	0.26	71	9.5	5.0	10.6	6.7	3.0
[H]50wt% cyclohexane	1.09	82	flow	0	21.6	6.1	3.7

[a]coagulant: propanol [b]downstream pressure: 0.1 cm-Hg [c]salt:$CaCl_2$
[H]high molecular weight TPX [L]low molecular weight TPX

Besides pervaporation, the application of the porous TPX membrane to vapor permeation was also examined. Vapor permeation is a similar process to pervaporation but the feed vaporizes before permeating through the membrane. Hence, the problem of wetting can be resolved. The separation performance is presented in Table 1. All the prepared membranes can be used in the vapor permeation process. The separation factor of ethanol to water is about 6 and the permeation flux can be as high as 20 kg/m^{2}h.

The porous TPX membrane can also be applied to the membrane distillation process. In the present work, the application of the prepared TPX membranes in osmotic distillation to concentrate protein solution was evaluated. The feed solution was a solution of bovine serum albumin (BSA) and the strip solution was a aqueous solution of calcium chloride ($CaCl_2$). Due to the hydrophobicity of TPX, the membrane was not wetted by the feed and strip solutions. Hence, the membrane pores functioned as a stable vapor gap between the two solutions. The difference in water vapor pressure between the two solutions drove the transport of water vapor from the feed solution to the strip solution, and the concentration of the BSA solution can thus be accomplished. The water permeation flux was measured and the results are presented in Table 1. When the BSA concentration was kept around 2000ppm, the water flux was about 3.7 kg/m^{2}h. The performance is comparable to the commercial PTFE membrane.

Conclusion

The results presented in the present work indicated that the TPX/cyclohexane solution inclined to undergo solid-liquid demixing and form polymer particles at room temperature. The solid-liquid demixing was strongly related to the crystallization process. By using suitable coagulant, the solid-liquid demixing process occurred before polymer precipitation, particulate TPX membranes with inter-connected pores can thus be fabricated. By using propanol/methanol and propanol/cyclohexane mixtures as coagulant, TPX membranes with pore diameter ranging from 0.2 μm to 1 μm were successfully prepared. The softer coagulant can result in membranes with larger pore diameter and larger porosity. When the prepared membranes were used in pervaporation to separate aqueous solution containing 7 wt% of ethanol, the permeation flux was about 9.5 kg/m^2h and the selectivity of ethanol to water was 5. When the membranes were used in osmotic distillation to concentrate protein solution, the permeation flux was about 3.7 kg/m^2h.

Acknowledgements

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