

Hydrophilic Microporous PES Membranes Prepared by PES/PEG/DMAc Casting Solutions

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ABSTRACT: Microporous poly(ether sulfones) (PES) membranes were prepared via phase inversion using poly(ethylene glycol) (PEG) as additive and *N,N*-dimethylacetamide (DMAc) as solvent. Thermodynamic of the casting solutions was studied by coagulation value while precipitation rate was observed by light transmittance measurement. It was found that casting solution with PEG200 as additive was thermodynamically less stable than those with PEG400 and PEG600 as additive and easier to cause phase separation in exposure time. With the increase of PEG200 concentration, the casting solution became thermodynamically less stable and easier to cause phase separation in exposure time, but precipitation rate during immersion precipitation decreased because of the increased viscosities. ATR-FTIR spectra and TGA curves showed that the membranes prepared using PEG200 as additive had less PEG residual than

those of PEG400 and PEG600, but it showed better permeation performance than that prepared using PEG400 and PEG600 as additive. With the increase of PEG200 concentration from 30 to 70 wt %, the cross section structure changed from macrovoid to sponge-like, micropores with a mean pore size around 0.1 μm began to form on the top surface. When the PEG200 concentration is 60 wt %, the pure water flux was $1845 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, which is the highest value. As the PEG200 concentration increased from 30 to 60 wt %, the contact angles decreased from 82.1° to 58.2° . As the addition amount of PEG200 increased, the residual PEG made the prepared membranes more hydrophilic. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 4100–4108, 2008

Key words: poly(ether sulfones); membranes; phase separation; morphology

INTRODUCTION

Microporous membrane has been widely applied on the separation of liquid/liquid or liquid/solid mixtures. Poly(ether sulfones) (PES) is a kind of high-performance polymer and very suitable for the preparation of microfiltration (MF) and ultrafiltration (UF) membranes.^{1–9} Usually, phase inversion process is used for the preparation of most asymmetric polymeric membranes. In this process, a homogeneous polymer solution precipitates was formed at first and then immersed in a nonsolvent bath. In phase inversion process, both thermodynamic and kinetics factors affect the morphology and performance of the prepared the membrane greatly; thermodynamic determines whether the casting solution is stable and kinetics determines which degree the phase separation could reach, and how quick it reaches. To measure the thermodynamic stability of the casting solution, cloud point measurements¹⁰ or coagulation

value (CV) measurement^{11,12} were employed. Two experimental techniques have been used to investigate the kinetics of membrane formation including light transmittance measurement technique^{12,13} and optical microscopy technique.^{14,15} Light transmittance measurement can be used to investigate the precipitation type and rate. Kim and Lee¹² have successfully applied it on the investigation of the precipitation kinetics change of PSF/NMP/PEG system.

It has been reported the properties of polymer membrane can be improved by the addition of additive. PES membrane prepared without any additive has a very rough surface and the permeation flux is low; so, it is necessary to use some additive to get PES membrane with good performance. Several authors have reported that using low molecular weight alcohol^{1–3} and inorganic additive¹⁶ as nonsolvent additive can enhance the porosity and flux. High molecular weight additives such as poly(vinyl pyrrolidone) (PVP)^{7,17} and poly(ethylene glycol) (PEG) have also been reported as pore-forming agents.^{4–6,18}

Among all these additives, PEG ($\text{C}_{2n}\text{H}_{4n+2}\text{O}_{n+1}$) has wide range molecular weight from 200–20,000 and it has been reported that it plays the role of pore formation agent. Ani et al.⁵ used PEG200, PEG400, and PEG600 as additives to prepare PES UF flat sheet membranes. The MWCO of the membranes increased

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from 26 to 45 kDa when the molecular weight of PEG increased from 200 to 600. A significant change also occurred in pure water permeation when concentration of additives increased from 5 to 25 wt % in casting solution. Xu et al.¹⁸ used PEG600 as additive, and showed that the T_g of a PEI/PEG membrane decreased because PEG600 remained inside the polyetherimide matrix. Kim et al.¹² studied the precipitation kinetics of PSF/NMP/PEG casting solution and showed that precipitation rate decreased while the concentration of PEG600 and molecular weight of PEG increased. According to the report of Liu et al.,⁶ PEG400 could be added to PES casting solution in large amounts without causing phase separation (NMP/PEG ratio 1:9, PES concentration ~ 11 wt %).

In the previous works, PEG was major used as an additive to prepare UF membranes and usually its concentration was not larger than 30% in casting solution except the study of Liu et al.⁶ There were rare studies on the kinetics factor of PES/PEG/Solvent system as well as the miscibility of PEG and PES. In this work, PEG with a molecular weight range from 200 to 600 were used as additives and added to the casting solution in large amount (30–70 wt %). PEG was usually minor part in the casting solution in former reports but in this work could be the major part. By this way, hydrophilic microporous PES membranes could be obtained without any substantial treatment and modification. To have a fundamental understanding on the membrane formation process, thermodynamic factors and kinetics factors in phase inversion were studied by experimental methods. The different membrane morphologies could be well explained. Furthermore, this work showed how the PEG concentration and PEG molecular weight affect the membrane morphology and performance.

EXPERIMENTAL

Materials

The membrane-forming polymer, poly(ether sulfones) (PES) [Characteristic Viscosity: $\eta = 0.48 \text{ dL g}^{-1}$, density = 1.370 g cm^{-3}], was produced by Jilin Jida High Performance Materials (China). The polymer was dried at 90°C for 3–4 h prior to the used. *N,N*-dimethylacetamide (DMAc) was purchased from Shanghai Xiang-Yang Chemical Reagent Corporation (China). PEG200, PEG400, PEG600 were purchased from Shanghai Sinopharm Chemical Reagent Corporation (China). All the water used in this work was deionized water.

Determination of coagulation value

Coagulation value (CV) can be used as a measurement of the thermodynamic stability of the casting

solution system. Fifty grams of PES/PEG/DMAc casting solution was kept at a constant temperature and DMAc/H₂O (50/50 wt %) mixture was slowly added drop by drop. Every drop caused local coagulation and further addition was carried out only after the casting solution became homogeneous again. When the addition solution caused remarkable coagulation and the coagulation was not dissolved at 20°C in 24 h, CV can be calculated by the addition amount of DMAc/H₂O (50/50 wt %) mixture:

$$\text{CV} = \frac{m_a}{m_s} \times 100\% \quad (1)$$

where m_a is the mass of the addition DMAc/H₂O (50/50 wt %) mixture (g), m_s is the mass of the PES casting solution (g).

Light transmittance measurement

Light transmittance measurement experiments were carried by a self-made device as described by Lang et al.¹⁹ A collimated laser was directed on the glass plate immersed in a nonsolvent coagulation bath or exposure on air. The light intensity information was captured by the light detector and then recorded in the computer. The precipitation rate of the casting solution could be characterized by the curve of light transmittance to immersion time.

Preparation of microporous membrane

The microporous membranes were prepared as flat membranes employing a combined vapor induced phase separation (VIPS)/immersion precipitation process. DMAc and PEG were mixed equally at first and then the polymer (PES) was dissolved in the mixed solvent at 20°C . The composition of the casting solution was: 15 wt % (PES)/30–70 wt % (PEG)/15–55 wt % (DMAc). The viscosity of casting solutions was measured at 20°C on a NDJ-79 rotation viscometer produced by Shanghai Precision & Scientific Instrument (China). After being strongly stirred for 5 days, the casting solution was degassed at 20°C for at least 24 h to remove air bubbles, and then cast on a glass plate using a casting knife with a gap of $380 \mu\text{m}$ at 20°C . The casting solution was exposed in a humid air environment (RH = 90%) for 30 s and then immersed in a nonsolvent coagulation bath (water, 20°C). The humidity was measured by humidimeter controlled by air condition and ultrasonic humidifier. The prepared membranes were washed with deionized water every 4 h in the first 2 days and kept in deionized water until used.

Membrane characterization

ATR-FTIR and TGA analysis

The spectra of top surface on the prepared membranes were carried by ATR-FTIR method (Nicolet 380 FTIR Spectrometer, USA) in the wavenumber range of 400–4000 cm^{-1} . The thermal stability of the PES membranes was evaluated by TGA (TGA, TA SDT-Q600, USA). The TGA measurements were carried out under nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ from 20 to 800°C .

Scanning electron microscopy

The wet membranes were first immersed in ethanol for 4 h and then immersed in hexane for 4 h, finally dried in air. Samples of the membranes were frozen in liquid nitrogen and then fractured. Cross section and surface of the membranes were sputtered with gold and then transferred to the microscope. The morphology of the cross section and surface of the membranes were inspected by scanning electron microscopy (SEM) using a JEOL Model JSM-6360LV scanning electron microscope (Tokyo, Japan).

Permeation test

PES microporous membranes were characterized by determination of pure water permeation flux (PWP), porosity (ε), minimum bubble point pressure, and mean pore radius (r_m). A self-made dead-end stirred cell (effective area 19.63 cm^2) was used to measure the pure water flux of the PES membranes at 25°C . All the values reported are the average of five different measurements.

The pure water permeation flux is defined as:

$$\text{PWP} = \frac{Q}{A \times T} \quad (2)$$

where Q is the volume of the permeate pure water (L), A is the effective area of the membrane (m^2), and T is the permeation time (h).

Porosity and pore size characterization

The porosity can be determined by gravimetric method, it is defined as:

$$\varepsilon = \frac{m_1 - m_2}{\rho_w \times A \times l} \quad (3)$$

where m_1 is the weight of the wet membrane; m_2 is the weight of the dry membrane; ρ_w is the water density (0.998 g cm^{-3}); A is the effective area of the membrane (m^2); l is the membrane thickness (m).

Mean pore radius was determined by filtration velocity method. It is a measure for the permeation and retention properties of membrane and related with filtration velocity and other important structure parameters of the membrane. According to Guerout-Elford-Ferry equation,²⁰ r_m could be calculated:

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q}{\varepsilon \times A \times \Delta P}} \quad (4)$$

where η is water viscosity ($8.9 \times 10^{-4} \text{ Pa s}$); l is the membrane thickness (m); ΔP is the operation pressure (1 bar).

Maximum pore radius can be characterized by bubble point procedure. Bubble point pressure is determined by a DJ-5 membrane bubble point testing instrument (maximum input pressure $\leq 0.6 \text{ MPa}$) produced by Shanghai Eling filter equipment (China). Membrane was immersed in ethanol for 3 h and fitted on the testing instrument. Then bubble point pressure can be obtained automatically. According to Laplace's equation, maximum pore size could be calculated:

$$R_{\max} = \frac{2\sigma \cos \theta}{P} \quad (5)$$

where σ is the surface tension of ethanol ($22.8 \times 10^{-3} \text{ N m}^{-1}$); θ is the contact angle of ethanol to membrane; P is the minimum bubble point pressure.

Water contact angles

Contact angles (θ) between water and membranes were measured at room temperature on a JC2000A Contact Angle Meter produced by Shanghai Zhongcheng Digital Equipment (China). Because water can gradually penetrate into the sublayer of the membrane through the micropores on the top surface, to measure the true hydrophilicity of the membranes, contact angles should be measured quickly after the water contact with the top surface. Twenty microliters of water was carefully dropped on the top surface and contact angles were determined in 10 s after the water was dropped and without apparent change in contact angle. The reported values are the average of at least five different measurements.

RESULTS AND DISCUSSION

Solubility parameters prediction

Hansen solubility parameter is a good measurement for the solubility of solvent to polymer or the miscibility between polymers. In this work, a group molar contribution method suggested by Hoftyzer and Krevelen²¹ was introduced and the Hansen solubility

TABLE I
Component Group Contributions to Hansen Solubility Parameters

Structure group	F_{di} ($J^{1/2} \text{ cm}^{3/2} \text{ mol}^{-1}$)	F_{pi} ($J^{1/2} \text{ cm}^{3/2} \text{ mol}^{-1}$)	E_{hi} ($J \text{ mol}^{-1}$)
—CH ₂ —	270	0	0
—O—	100	400	3000
—OH	210	500	20,000

parameters of PEG were calculated. The V_m of PEG with different molecular weight is divided by its density (1.12–1.13 g cm⁻³). The group molar attraction constants are listed in Table I and Hansen's parameters were calculated using the following equations:

$$\delta_d = \frac{\sum F_{di}}{V_m} \quad (6)$$

$$\delta_p = \frac{\sqrt{\sum F_{pi}^2}}{V_m} \quad (7)$$

$$\delta_h = \frac{\sqrt{\sum E_{hi}}}{V_m} \quad (8)$$

$$\delta_t = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2} \quad (9)$$

where δ_d is the dispersive component of the solubility parameter; δ_p is the polar component of the solubility parameter; δ_h is the hydrogen-bonding contribution to the solubility parameter; i is the numbers the structural groups; F_{di} and F_{pi} are the group molar attractions; and E_{hi} is the cohesive energy contributed from hydrogen-bonding.

The calculated solubility parameters are listed in Table II. According to the calculated solubility parameters, all the three kinds of PEG have similar δ_t to PES, which means low molecular weight PEG is weak nonsolvent to PES. It is the reason that PEG can be added to PES casting solution in large amount. Considering the solubility parameters and molecular weight, when the added content in casting solution equals, PEG400 and PEG600 are presumed to have better miscibility with PES than that of PEG200.

TABLE II
Calculated Hansen Solubility Parameters

Substance	n	V_m (mL)	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	δ_t (MPa ^{1/2})
PEG200	4.136	177.65	16.7	7.6	14.5	23.4
PEG400	8.682	354.45	16.6	6.3	12.3	21.6
PEG600	13.227	530.97	16.6	5.8	11.4	21.0
PES ²¹	—	—	17.6	10.4	7.8	21.9

Thermodynamic of the casting solutions

To understand the mechanism in phase inversion process, the thermodynamic stability of the casting solutions should be investigated. In this work, CV was used to measure the thermodynamic stability of different casting solutions. The results are listed in Table III. When the PEG200 concentration in casting solution increased from 30 to 70 wt %, CV decreased from 11.2% to 2.6%. It means that the casting solution with high PEG200 concentration is thermodynamically less stable. And Table III also shows that the CV of the casting solution with PEG400 or PEG600 as additive was much higher than that of PEG200. It is well agreed with the prediction by the solubility parameters.

Precipitation kinetics

Light transmittance measurement was used to investigate the precipitation kinetics both in immersion precipitation process and VIPS stage. The light transmittance curves shown in Figure 1 reveal the precipitation rate decreased as the increase of PEG200 content. Basically, the addition of PEG200 should influence the formation of membrane in two ways: firstly in thermodynamic the solution with higher amount of PEG200 becomes unstable, that means it is easier to cause phase separation; secondly the viscosity change caused by the addition of PEG200 (listed in Table III) will influence the multiexchange rate between solvent and water, or the precipitation kinetics. The light transmittance change during the immersion precipitation is mainly related to the kinetics of system, so the viscosity increase caused by the addition of PEG200 greatly decreased the precipitation rate. Light transmittance curves presented in Figure 2 show that the three casting solutions with different molecular weight PEG as additive had similar precipitation rate. It is because the viscosities of these casting solutions showed little differences, as seen in Table III.

In VIPS stage, a casting solution is exposed to a nonsolvent vapor (here humid air) for a fixed time interval prior to be immersed in coagulation bath, the diffusion of water vapor into casting solution and the evaporation of solvent could cause phase separation and the polymer solution would become

TABLE III
The Composition, Viscosity, and Coagulation Value of Different Casting Solutions

Composition (wt %) (PES/PEG/DMAc)	Molecular weight of PEG (g mol ⁻¹)	Viscosity of the casting solution (mPa s)	Coagulation value (%)
15/30/55	200	720	11.2
15/40/45	200	1080	9.2
15/50/35	200	2580	7.4
15/60/25	200	4220	5.6
15/70/15	200	9780	2.6
15/60/25	400	4560	13.6
15/60/25	600	4870	15.2

turbid. Phase separation in this stage is mainly affected by the thermodynamic of the casting solution as well as the relative humidity (RH).²²⁻²⁴ But few works have attempted to investigate the precipitation rate in VIPS stage by experimental methods. In this work, light transmittance measurement was also used to follow the precipitation rate in VIPS stage. Figure 3 shows the light transmittance curves obtained by exposing casting solutions with different PEG200 concentration on air (RH = 90%) in VIPS stage. It is obvious that the casting solution with higher concentration of PEG200 is easier to cause phase separation in the VIPS stage. Figure 4 presents the light transmittance curves obtained by exposing casting solutions with different molecular weight PEG on air (RH = 90%) in VIPS stage. Precipitation rate decreased with the increase of PEG molecular weight. The result is well agreed with the CV measurement and it can be concluded that thermodynamically less stable casting solution shows higher precipitation rate in VIPS stage.

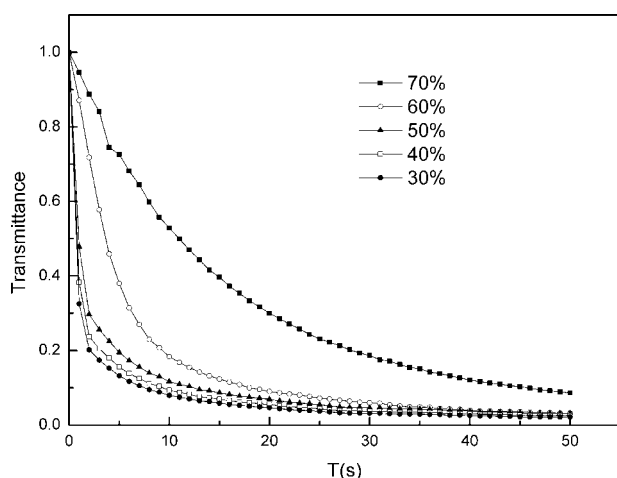


Figure 1 Light transmittance curves obtained by immersing PES casting solutions with different PEG200 concentration into water.

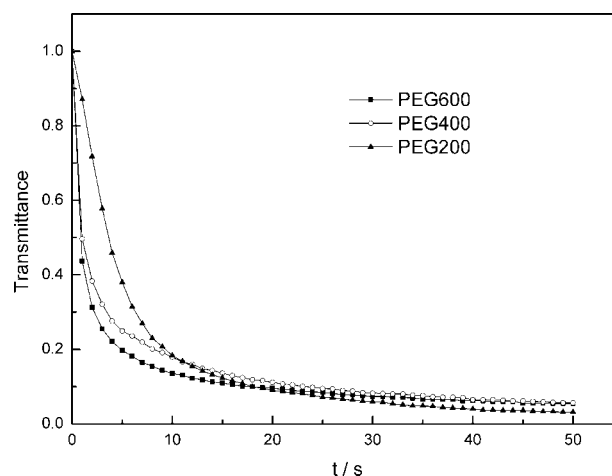


Figure 2 Light transmittance curves obtained by immersing PES casting solutions with different molecular weight PEG into water.

ATR-FTIR and TGA analysis

To investigate the composition of top surface on the prepared membranes, ATR-FTIR spectra of the top surface on membranes are measured and showed in Figure 5. It was found that all the IR spectrums showed no apparent difference in the range of 400–2000 cm⁻¹, and membrane using PEG400 and PEG600 represented a CH₂–CH₂ absorption peak arising from the saturated alkyl of PEG at 2900 cm⁻¹.

TGA curves reveal that as the increase of PEG200 content and the increase of PEG molecular weight, the prepared membrane had a higher decomposition rate, as shown in Figure 6. The boiling point of PEG is around 250°C, which is much lower than the decomposition temperature of PES (450°C), so the membrane has more residual PEG would lose more weight before PES began to decompose.

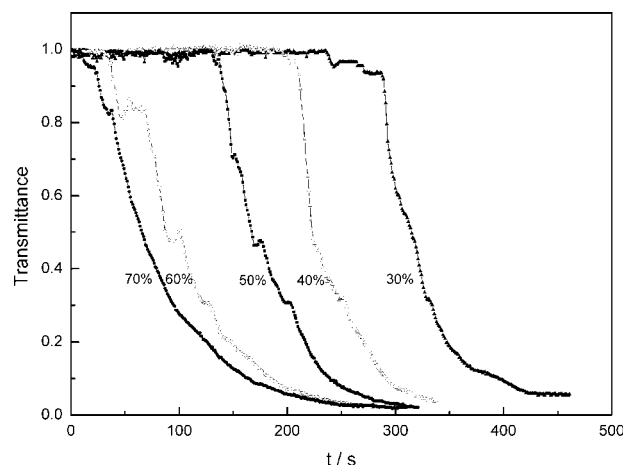


Figure 3 Light transmittance curves obtained by exposing PES casting solutions with different PEG200 concentration on air (RH = 90%).

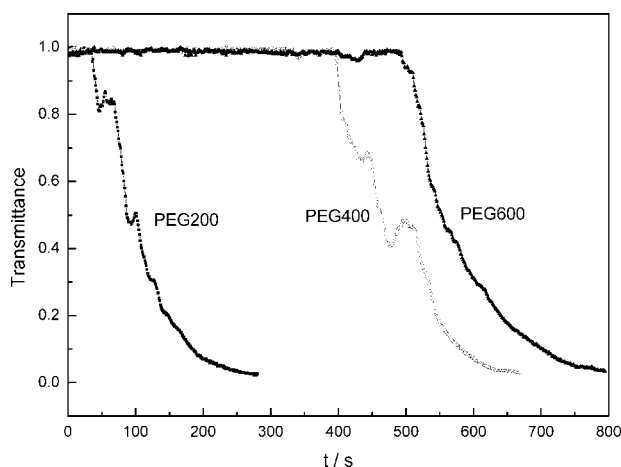


Figure 4 Light transmittance curves obtained by exposing PES casting solutions with different molecular weight PEG on air (RH = 90%).

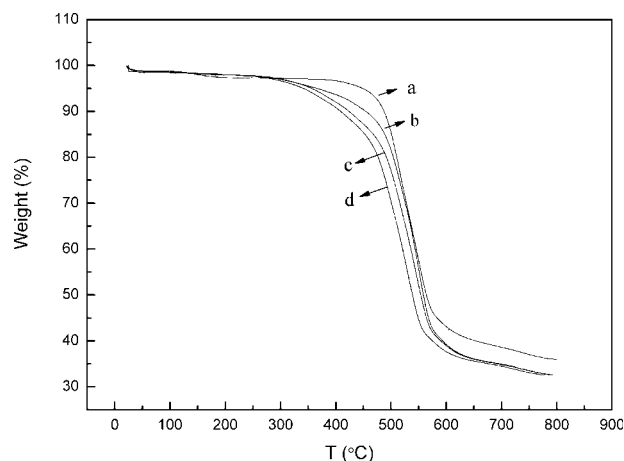


Figure 6 TGA curves of the PES membranes [a, PEG200 (30%); b, PEG200 (60%); c, PEG400 (60%); d, PEG600 (60%)].

In this work, a large part of PEG existed in the closed pore in the membrane matrix, the trace PEG on surface mainly absorbed on PES chain with hydrogen bonding so the amount on surface was less than some other cases, such as surface grafting or coating. In contrast to ATR-FTIR analysis, TGA measurement showed better evidence for the residual PEG in the membrane matrix. According to the ATR-FTIR and TGA analysis, it can be concluded that compared with PEG200, PEG400, and PEG600 has more residual on the membrane and the residual amount of PEG200 in membrane increases as the PEG200 content in casting solution.

Membrane morphology

Figure 7 shows the effect of the PEG200 concentration on membrane morphologies. From SEM photograph A1, B1, C1 in Figure 7, it can be observed that

the cross section structure changed from finger-like to sponge-like as the PEG200 concentration increased. It has been generally accepted that instantaneous demixing leads to macrovoid structure and delayed demixing leads to sponge-like structure. But techniques that used to delay the onset of demixing can usually result in the disappearance of macrovoid.²⁵ It can be concluded that although the large quantity addition of PEG200 caused the instability in thermodynamic, the low multiexchange speed of solvent and water led a slow precipitation rate; though the demixing types remained instantaneous demixing, a slower demixing process in sublayer caused by high viscosities led to a sponge-like structure.

SEM photograph A2, B2, C2 in Figure 7 show that different surface morphologies formed with the increasing PEG200 concentration. When PEG200 concentration was 30 wt %, no micropore formed on the top surface; when PEG200 concentration was 50 wt %,

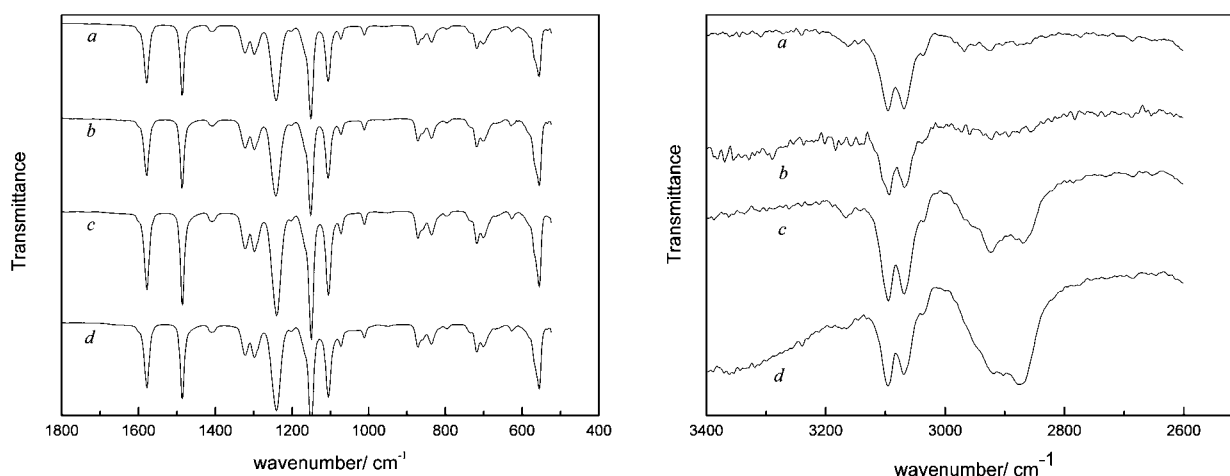


Figure 5 ATR-FTIR spectra of the PES membranes [a, PEG200 (30%); b, PEG200 (60%); c, PEG400 (60%); d, PEG600 (60%)].

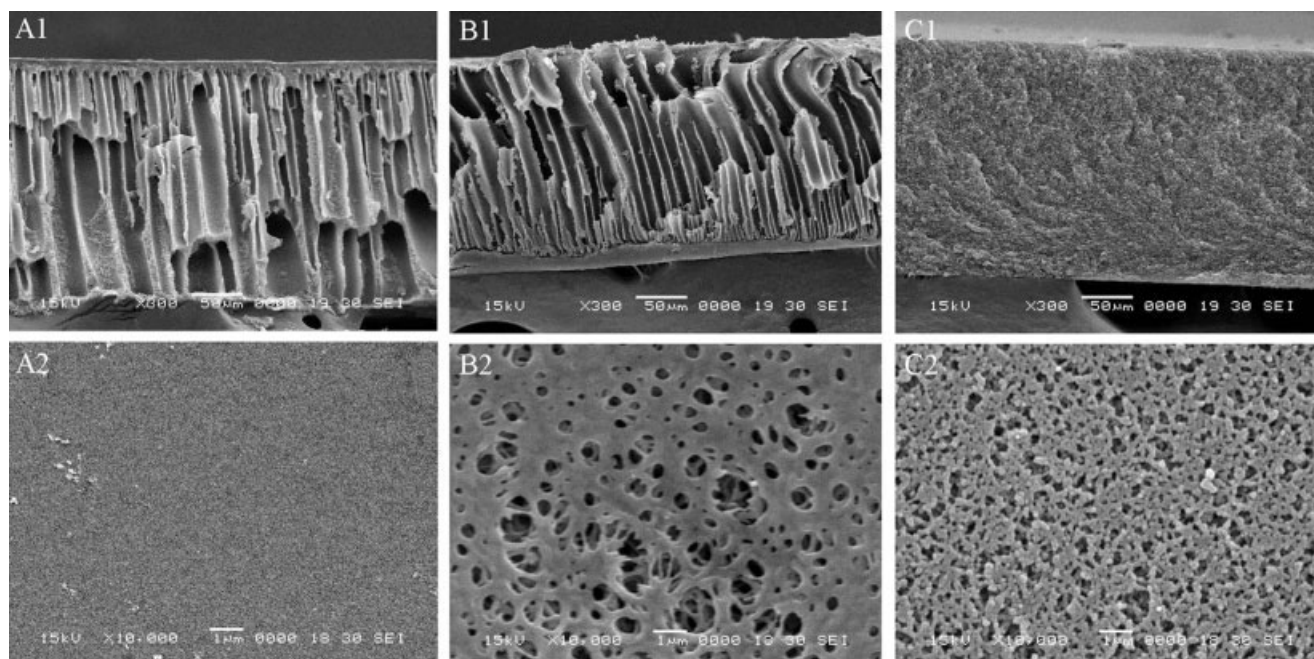


Figure 7 SEM photographs of PES membranes prepared by casting solutions with different PEG200 concentration: A (30%), B (50%), C (70%); 1 (cross section), original magnification $\times 300$; 2 (top surface) original magnification $\times 10000$.

micro cellular pores formed on the top surface and when the PEG200 concentration reached 70 wt %, micro lacy pores formed on the top surface. There are several different paths for the phase separation in the ternary phase diagram of the membrane formation and they will lead to completely different surface

morphologies.²⁶ Gelation always leads to a dense skin-layer; nucleation growth with polymer-poor phase always leads to the cellular pore structure; while the lacy (bicontinuous) structure was induced by spinodal decomposition. So it can be concluded that as the PEG200 concentration ranged from 30–70 wt %,

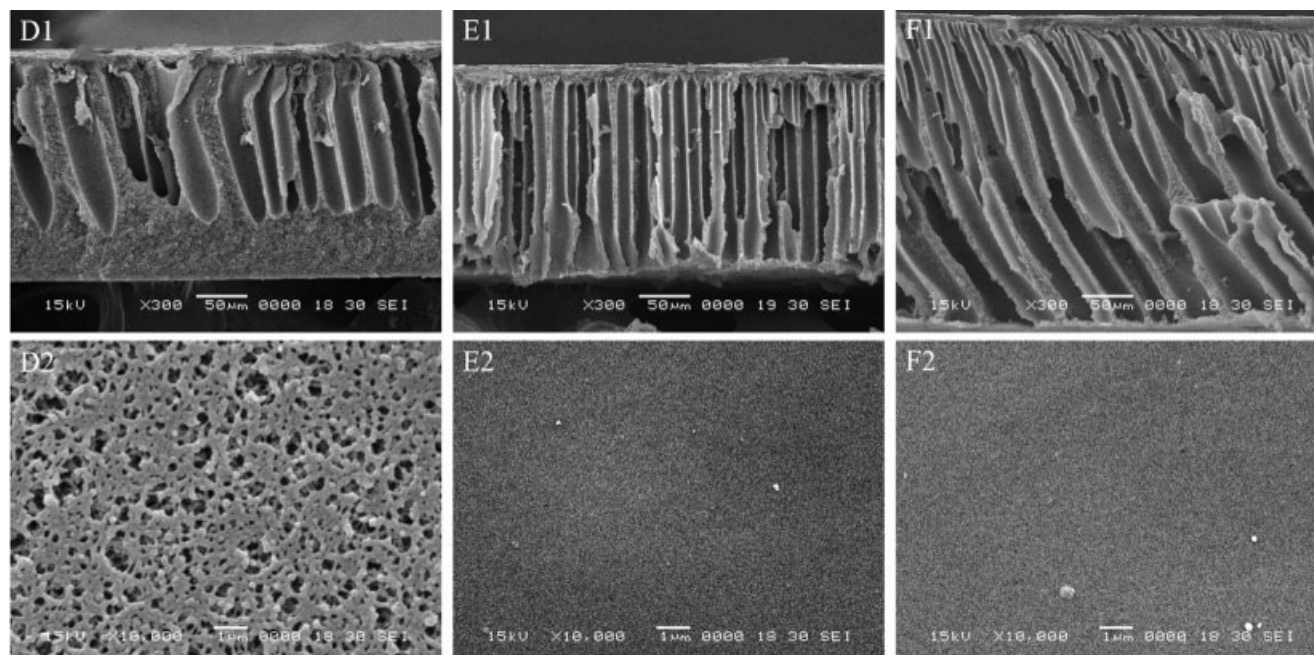


Figure 8 SEM photographs of PES membranes prepared by casting solutions with different molecular weight PEG as additive: D (PEG200), E (PEG400), F (PEG600); 1 (cross section), original magnification $\times 300$; 2 (top surface) original magnification $\times 10000$.

TABLE IV
Permeation Properties and Pore Size of PES Membranes Prepared by Different Casting Solutions

Composition (wt %) (PES/PEG/DMAc)	Molecular weight of PEG (g mol ⁻¹)	PWP (L m ⁻² h ⁻¹)	ϵ	r_m (μm)	R_{max} (μm)
15/30/55	200	1276 \pm 84	0.836	0.079	–
15/40/45	200	1802 \pm 109	0.831	0.104	0.251
15/50/35	200	1834 \pm 91	0.827	0.107	0.352
15/60/25	200	1845 \pm 118	0.822	0.110	0.391
15/70/15	200	1759 \pm 125	0.814	0.106	0.598
15/60/25	400	1073 \pm 77	0.842	0.084	–
15/60/25	600	856 \pm 58	0.847	0.079	–

different phase inversion mechanisms corresponded to the different surface morphologies.

Figure 8 shows the effect of PEG molecular weight on membrane morphologies. It can be seen that the membrane prepared using PEG200 as additive had many micropores on top surface and sponge-like structure began to develop on the cross section. The membranes prepared using PEG400 and PEG600 as additive had no micropore on top surface and the finger-like structure occupied the whole cross-section. Though the three different casting solutions showed the similar precipitation rate, different type of cross section structure was obtained. It may be caused by the micropores on the top surface; a porous toplayer can suppress macrovoid formation of the sublayer and result in a porous, sponge-like structure.

Permeation properties

The relationship between PEG200 content and pure water flux was listed in Table IV. When PEG200 content in casting solution was 30%, pure water flux was only 1276 L m⁻² h⁻¹ because no micropore formed on top surface in this case. When PEG200 content was between 40 and 60%, the pure water flux exceeded 1800 L m⁻² h⁻¹ because a porous top surface could decrease the resistance to water permeation. When PEG200 content was 70%, the pure water flux decreased slightly because the sponge-like structure led to higher resistance compared with macrovoid structure. Table IV also shows how the PEG molecular weight affected the permeation properties. Under the same precipitation conditions, when the addition PEG concentration was 60%, the membrane prepared using PEG200 as additive had much higher flux than those of PEG400 and PEG600. It can be concluded that the micropores on top surface are vital for high flux, while the types of the surface pores and cross section structure seems have less effect on the permeation properties.

The porosity and pore size information of the prepared membranes are listed in Table IV. It can be noticed that the membranes with lower porosity

leads to higher flux, which is similar to the results of Shin et al.¹ This result can be explained by the membrane morphology: membranes with higher flux usually have more sponge-like structure on cross section and this structure leads to lower porosity compared with macrovoid. When the PEG200 content ranged from 40 to 70 wt %, membranes with a mean pore radius over 0.1 μm were prepared and the calculated pore radius were very similar though the morphologies exhibited difference. The bubble point pressure data shows that the maximum pore radius increased with the PEG200 concentration. So, it should be pointed out that thermodynamically less stable casting solution would induce several large pores more easily in VIPS stage.

Hydrophilicity of the membranes

Hydrophilicity is one of the important properties of membranes, which affects the flux and antifouling ability of membrane greatly. As shown in Table V, with the increase of PEG200 concentration from 30 to 60 wt %, the contact angles decreased from 82.1° to 58.2° and when the PEG200 concentration increased to 70 wt %, the contact angle was 63.5°. The contact angles of the membrane which placed at room temperature for 30 days after 3 h permeation were also measured. From Table V, it can be seen that the contact angle of these membranes increased slightly. In this work, the casting solution contained large amount of PEG, some PEG would be resident

TABLE V
Contact Angles of the Microporous PES Membrane

PEG200 content (%)	Contact angle ^a (°)	Contact angle ^b (°)
30	82.1 \pm 2.7	82.3 \pm 3.0
40	70.2 \pm 2.0	72.5 \pm 1.6
50	67.8 \pm 1.5	70.3 \pm 2.1
60	58.2 \pm 2.3	62.2 \pm 1.3
70	63.5 \pm 2.6	68.5 \pm 2.7

^a Newly prepared PES membrane.

^b Placed at room temperature for 30 days after permeation test for 3 h.

in the closed pore in membrane matrix and some PEG would also adsorb on PES firmly by hydrogen bonding. With the permeation time extended, some PEG would leach out but the membrane could still maintain its hydrophilic properties due to the immobile PEG. So, it can be concluded that generally the introducing of PEG200 would enhance the hydrophilicity of the membranes for long time.

CONCLUSIONS

PEG as an additive in the casting solution can play a role of pore formation agent. According to the calculated Hansen solubility parameters, PEG200, PEG400, and PEG600 are weak nonsolvent to PES and could be added in large amount in PES casting solution without causing phase separation; PEG400 and PEG600 may have better miscibility with PES than PEG200. The results of CV also support this prediction. It is found that with the increase of PEG200 concentration and the decrease of PEG molecular weight, the casting solution become thermodynamically unstable. The thermodynamically less stable casting solutions are easier to cause phase separation in the VIPS stage, and this process is vital for the formation of micropores on top surface. At the same time, viscosity of the casting solution affects the precipitation rate in immersion precipitation largely. With the increase of PEG200 concentration, the precipitation rate decrease and hence could lead to different morphologies.

ATR-FTIR spectra and TGA curves show that PEG400 and PEG600 have more residual in the matrix of membranes; but PEG200 induces higher flux and can be considered as a better pore forming agent in the preparation of microporous membranes. With the increase of PEG200 concentration from 30 to 70 wt %, different surface morphologies are obtained and the cross section change from macrovoid to sponge-like. Flux reaches the highest when the PEG200 concentration is 60%. Membranes with a mean pore size of over 0.1 μm are prepared when the PEG200 concentration ranges from 40 to 70 wt %. The contact angles show that with the increase of

PEG200 concentration, the prepared membranes become more hydrophilic as the residual of PEG200 in the matrix.

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