# Performance control of asymmetric poly(phthalazinone ether sulfone ketone) ultrafiltration membrane using gelation

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**Abstract**−We studied the influence of the gelation conditions on the formation kinetics of the polyphthalazine ether sulfone ketone (PPESK) membrane via wet phase inversion process experimentally and theoretically. Membrane formation and its morphology were first observed with an online optical microscope - CCD camera system. The resulting membranes prepared under various gelation conditions were then characterized by the gelation parameter, optical microscope, and SEM. Lastly, the relationship between the final membrane structure/permeation properties and the gelation parameter was discussed extensively. The results showed that both the gelation rate and the membrane flux increased dramatically as the gelation temperature increased. Moreover, the membrane structures became loose, and the porosity of membrane increased. Different non-solvent could change the solubility parameter between the polymer and the non-solvent, and thus the gelation rate greatly. With the increasing number of carbons in non-solvent, the gelation rate became slow, and the membrane gradually changed from a finger structure into a sponge structure. Adding NMP into the non-solvent changed the difference in the chemical potential and the solubility parameter between the polymer solution and the non-solvent, which in turn changed the gelation rate of polymer solution greatly. With the increasing concentration of NMP in non-solvent, the gelation rate became very slow and sponge structures formed with the non-solvent system of 80% NMP. A novel conclusion could be made that we could control the flux and reject of membrane just by changing the mean diffusion coefficient of skin, D, and the diffusion coefficient of skin, $D_1$, in the process of membrane formation.

Key words: PPESK, Gelation Kinetics, Gelation Temperature, Non-solvent, Phase Inversion

## INTRODUCTION

Since the initial development by Loeb and Sourirajan [1], asymmetric membranes have been widely used in numerous applications, such as food and chemical processing, water waste handling, drug delivery medium, artificial human organs, etc. Now, more and more separation operations require high-temperature resistance and chemical stability. However, many membrane materials cannot be applied to high temperature and chemical processing. Therefore, it is necessary to develop high-temperature resistant and chemical stability membrane materials. Poly(phthalazine ether sulfone ketone) (PPESK) is a novel polymer, which was synthesized by Xigao Jian et al. [2]. And the polymer contains rigid aromatic rings and shows superior mechanical strength, chemical resistance and very high glass transition temperature (Tg) [3]. It could be concluded from the polymer's properties that the polymer has potential for longer life and lower capital cost membrane preparation. It was also demonstrated that PPESK is a potential membrane material for UF [4] and high temperature gas separation [2].

Asymmetric membranes were prepared by the so-called phase inversion process, which involves phase separation from an initially homogeneous polymer solution into two phases, a polymer poor liquid phase which forms the membrane pores and a polymer rich solid phase which forms the membrane structure.

Numerous researches were conducted to rationalize the asymmetric membrane preparation procedure. A ternary phase diagram for a polymer-solvent-nonsolvent (precipitant) system was usually used to describe the precipitation pathway of the casting polymer solution during membrane formation [5-9] Several researches measured the rate of precipitation of asymmetric systems [6,8]. According to Strathmann et al. [6] a plot of the square value of the movement of the precipitation front, $X^2$ against the time t, should give a straight line. This prediction was supported by several previous investigations [6,8]. However, a conclusion contrary to Strathmann's results was obtained in our previous paper [10]. Since an asymmetric membrane was not homogeneous in structure, it was not reasonable to use the same equation to describe the formation of different membrane structures. Usually the top layer was very thin, usually several microns or even less than one micron. The formation of the top layer was usually very fast, within several seconds or even less than 1 second. Therefore, observation of the evolution of a top layer was usually very difficult. For example, the first picture Kang et al. obtained during their research was over 20 s. This point may be already in the formation process of the sublayer.

Phase-inversion process is very complicated, which involves both thermodynamic and kinetic processes. Because of the strong dependence of the morphology and performance of membrane on these two factors, numerous works studied the mechanism of asymmetric membrane formation via the phase-inversion process [11-17].
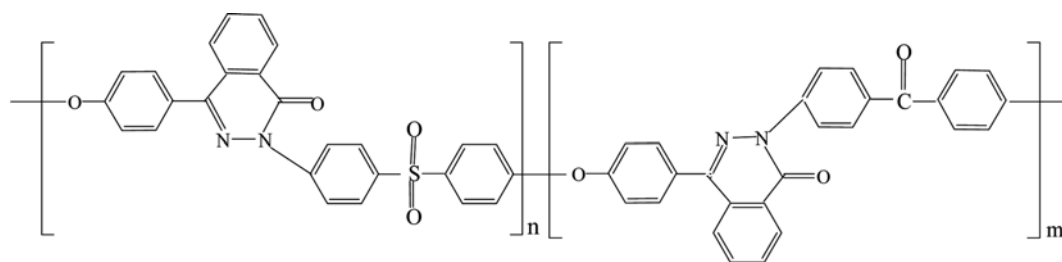
**Fig. 1. Chemical structure of PPESK.**

However, most of them focused mainly on the thermodynamic terms. Moreover, it was well known that pore-size distribution, in addition to skin and macrovoid formation, was mainly controlled by kinetic effects [18-20]. Many works [21-27] showed that gelation medium mass transfer played an important role in determining the structure of the membrane. Different exchange rate of solvent and non-solvent could result in various asymmetric structures. However, it was still difficult to describe accurately the role of gelation conditions in changing the membrane performance.

In this study, the effect of gelation conditions on membrane structure and performance was investigated by using a recently developed optical microscope/CCD camera experimental system. A novel conclusion could be made that the mean diffusion coefficient of skin, D, was not the only factor to determine the membrane performance. The diffusion coefficient of skin, $D_1$, could be used to describe well the reject performance of membrane. The results presented here may provide better understanding on the formation mechanism of asymmetric membranes.

## EXPERIMENTAL

### 1. Materials

All reagents were used without further purification. Poly(phthalazine ether sulfone ketone) (PPESK) was bought from Dalian Polymer New Material Co., Ltd., Liaoning Province, P. R. China. N-methyl pyrrolidone (NMP) used as solvent was obtained from Beijing Yili Fine Chemicals Co., Ltd., Beijing, P. R. China. Tween (Tianjin Tiantai Fine Chemicals Co., Ltd., Taijin, P. R. China), PEG600 (Beijing Yili Fine Chemicals Co., Ltd., Beijing, P. R. China) were used as a non-solvent additive. PEG (MW=6,000, MW=20,000, MW= 35,000), PEO (MW=100,000, MW=200,000, MW=400,000, MW= 1,000,000), and γ-Globulins (MW 150,000), were bought from Beijing Xin Jing Ke Biotechnology Co., Ltd, Beijing, P. R. China.

### 2. Gelation Rate Determination

The gelation rate of casting solution was determined with an online optical microscope - CCD camera experimental system (OM-CC system). This system contains an Olympus IX71 optical microscope (Olympus, Japan), a Basler A101f CCD camera (Basler AG, Ahrensburg, Germany), a personal computer and a specially designed

**Table 1. Spinning parameters for PPESK hollow fiber membranes**

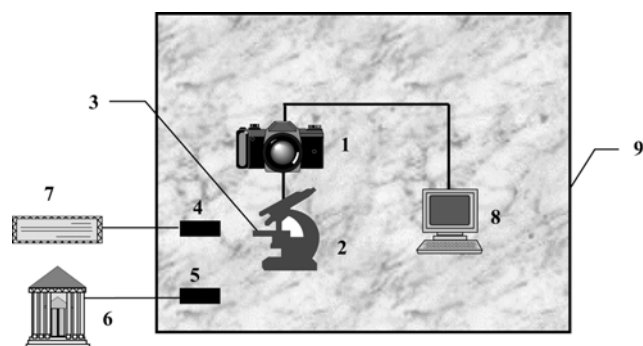| Dope composition | PPESK/NMP |
|---|---|
| External/internal coagulant | Water |
| Dope flow rate (cm³/min) | 2.0 |
| Internal coagulant flow rate (L/h) | 0.5 |
| Air gap distance (cm) | 0 |
| Spinneret and coagulant temperature (ºC) | 25 |
| Spinneret parameters (mm) | o.d.: 1.5, i.d.: 1.2 |
| Ratio of take up rate to dope extrusion rate | No extension |
| Room temperature (ºC) | 20 |
| Room humidity | 60-70% |

o.d., outer diameter; i.d., inner diameter.



**Fig. 2. Experimental setup for the observation of the gelation process.**
1. CCD camera
2. Optical microscope
3. Special microscope accessory
4. Temperature sensor
5. Humidity sensor
6. Dehumidifier
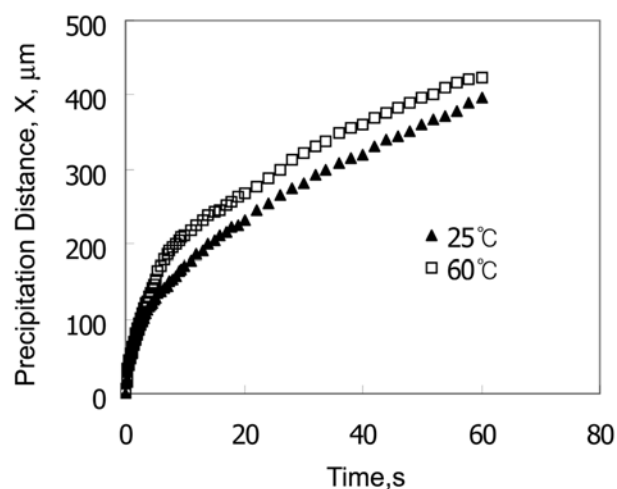7. Air-condition
8. Personal computer
9. Clean room



**Fig. 3. Effect of temperature on gelation rate using 2.5% tween as additive (concentration of PPESK: 18%).**

**Table 2. Relationship between pure water flux of membrane, diffusion coefficient, D and temperature (concentration of PPESK and Tween is 18%, 2.5%, respectively)**

| Temperature | Flux (L/m²h) | Cut off molecular weight | Porosity | Diffusion coefficient, D (μm²/s) | | | |
|---|---|---|---|---|---|---|---|
| | | | | $D_1$ | $D_2$ | $D_3$ | D |
| 25 °C | 162 | 66,000 | 80.9% | 2815 | 3737 | 2693 | 1006 |
| 60 °C | 359 | 106,000 | 82.5% | 3150 | 5020 | 3004 | 1177 |
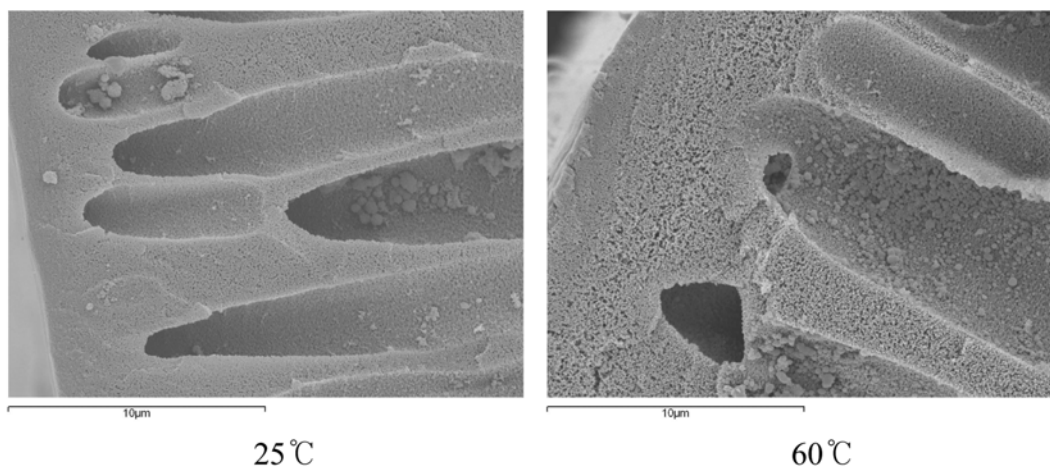


Fig. 4. SEM of membrane prepared by varying gelation temperature using 2.5% tween as additive.
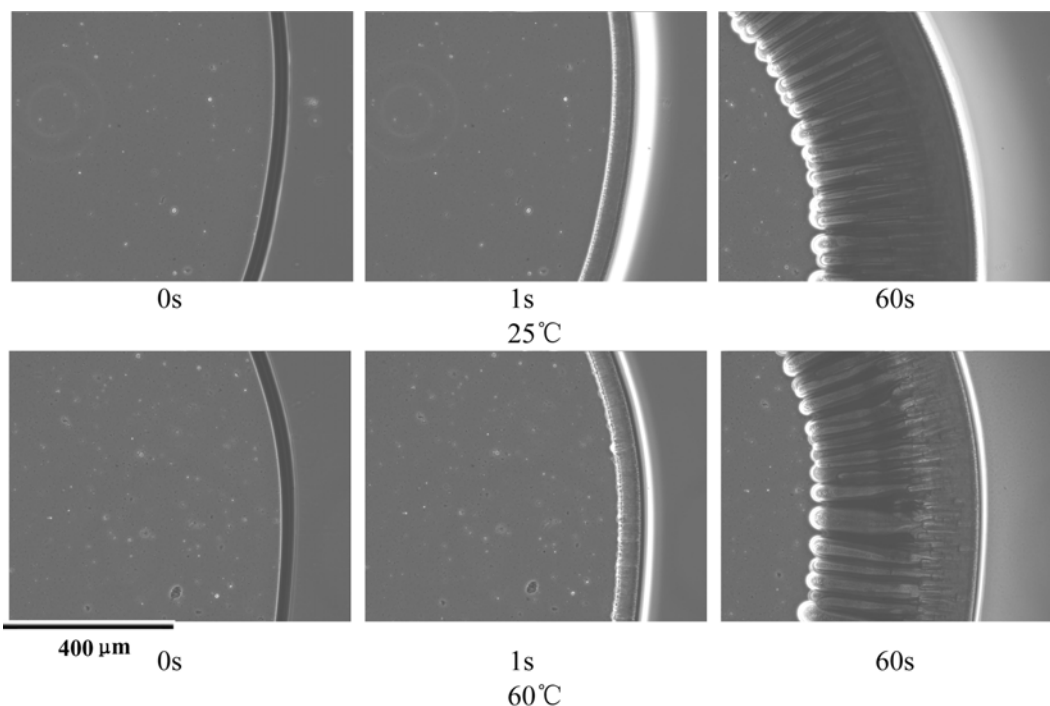


Fig. 5. Optical micrograph of membrane prepared by varying gelation temperature using 2.5% tween as additive.

microscope slide. Images of twelve frames per second can be obtained by using the OM-CC system. The magnification was from 120× to 2,000×. About a 10 microliter casting PPESK-NMP solution was placed between two special microscope accessories, and then another 1 ml drop of the precipitant (DI water) was immediately introduced on these accessories.

**3. Hollow Fiber Membrane Preparation**

PPESK hollow fiber membranes were prepared by phase inversion method. Details of the spinning parameters are listed in Table 1. Dope solution was prepared by dissolving PPESK copolymer and additive in NMP first at around 65 °C for 72 hrs with vigorous stirring until a homogeneous polymer solution was obtained, then the poly-

mer solution was filtrated and bubbling was removed with a vacuum drier. Based on our previous study, a PPESK concentration of 16.7 (wt) % was chosen for the membrane preparation. Ultrapure DI water was used as both the external and inner coagulants for the membrane preparation. A tube-in orifice type spinneret with a outer diameter (OD) of 900 mm and inner diameter (ID) of 500 mm was used. The extrusion rate of the dope solution was controlled at 2 mL/min while the injection rate of the inner coagulant was kept at 8.3 mL/min. The spinneret and coagulant temperature was kept at 25 °C while the room relative humidity was 60-70%. The tip of the spinneret was directly contacted with the external coagulation water bath. Thus, the emerged nascent hollow fibers from the tip of the spinneret entered directly into the external coagulant without exposure to the air. The take-up velocity was kept the same as the free falling velocity of the nascent hollow fibers. The hollow fiber membranes were then washed and stored in ultrapure water bath for at least 1 day to completely leach out the residual solvent and additives. They were then immersed in a 60 (wt) % glycerol solution for at least 1 day, then sealed.

Membrane modules, consisting of 5-6 fibers with a length of 23 cm, were prepared to test the hollow fiber separation performance in terms of permeation flux and rejection. Before a test, each module was immersed in water for 1 day to eliminate the effect of the residual glycerol on membrane module performance.

## 4. Pure Water Permeation Flux and Rejection

Water permeation and rejection tests were performed with cross-flow manner in a hollow fiber membrane module. All experiments were performed at room temperature with a transmembrane pressure of 1 bar, and all results were the average of three parallel modules.

De-ionized water was used to measure the pure permeation water flux of the hollow fiber membrane. 0.05 (wt) % PEG (MW=6,000, MW=20,000, MW=35,000) and PEO (MW=100,000, MW=200,000, MW=400,000, MW=1,000,000) aqueous solution were used for the rejection measurement, then its cut off molecular weight was calculated.

## 5. Measurement of Membrane Porosity

Hollow fiber membrane was immersed in isopropanol for 24 hour to make the membrane pore full of isopropanol. Then eliminating the isopropanol on the hollow fiber membrane surface, the membrane full of isopropanol was weighed, $w_1$. The membrane was dried and weighed, $w_2$. Porosity was calculated according to the following equation:

$$\text{Porosity} = \frac{(w_1 - w_2)/\rho_{isopropanol}}{w_2/\rho_{polymer} + (w_1 - w_2)/\rho_{isopropanol}}$$

## 6. Scanning Electron Micrograph (SEM) Study

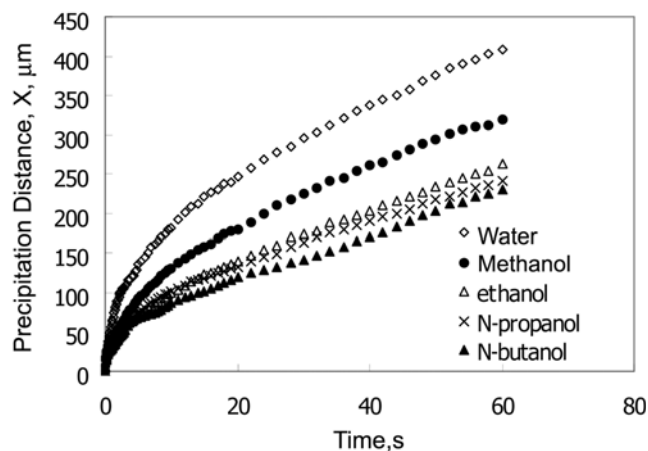To avoid destroying the structure of cross-sections of hollow fibers,



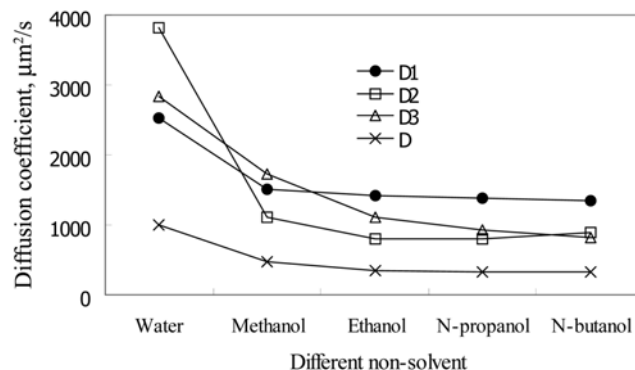**Fig. 6. Effect of different alcohols on gelation rate (concentration of PPESK: 16.7%).**



**Fig. 7. Effect of different alcohols on diffusion coefficient, D (concentration of PPESK: 16.7%).**
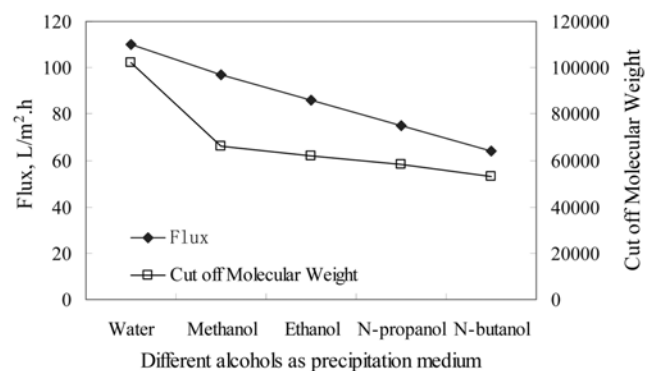


**Fig. 8. Effect of different alcohols on pure water flux, cut off molecular weight of membrane (concentration of PPESK: 16.7%).**

**Table 3. Relationship between solubility parameter difference and Precipitation value of PPESK with different non-solvent**

|  | Water | Methanol | Ethanol | n-Propanol | n-Butanol | PPESK |
|---|---|---|---|---|---|---|
| Solubility, (Mpa)$^{1/2}$ | 48 | 29.1 | 26.4 | 24.4 | 23.2 | 23.4 |
| Solubility parameter difference, (Mpa)$^{1/2}$ | 24.6 | 5.7 | 3.0 | 1.0 | 0.2 |  |
| Precipitation value* | 1.9 | 5.4 | 5.9 | 6.4 | 6.6 |  |

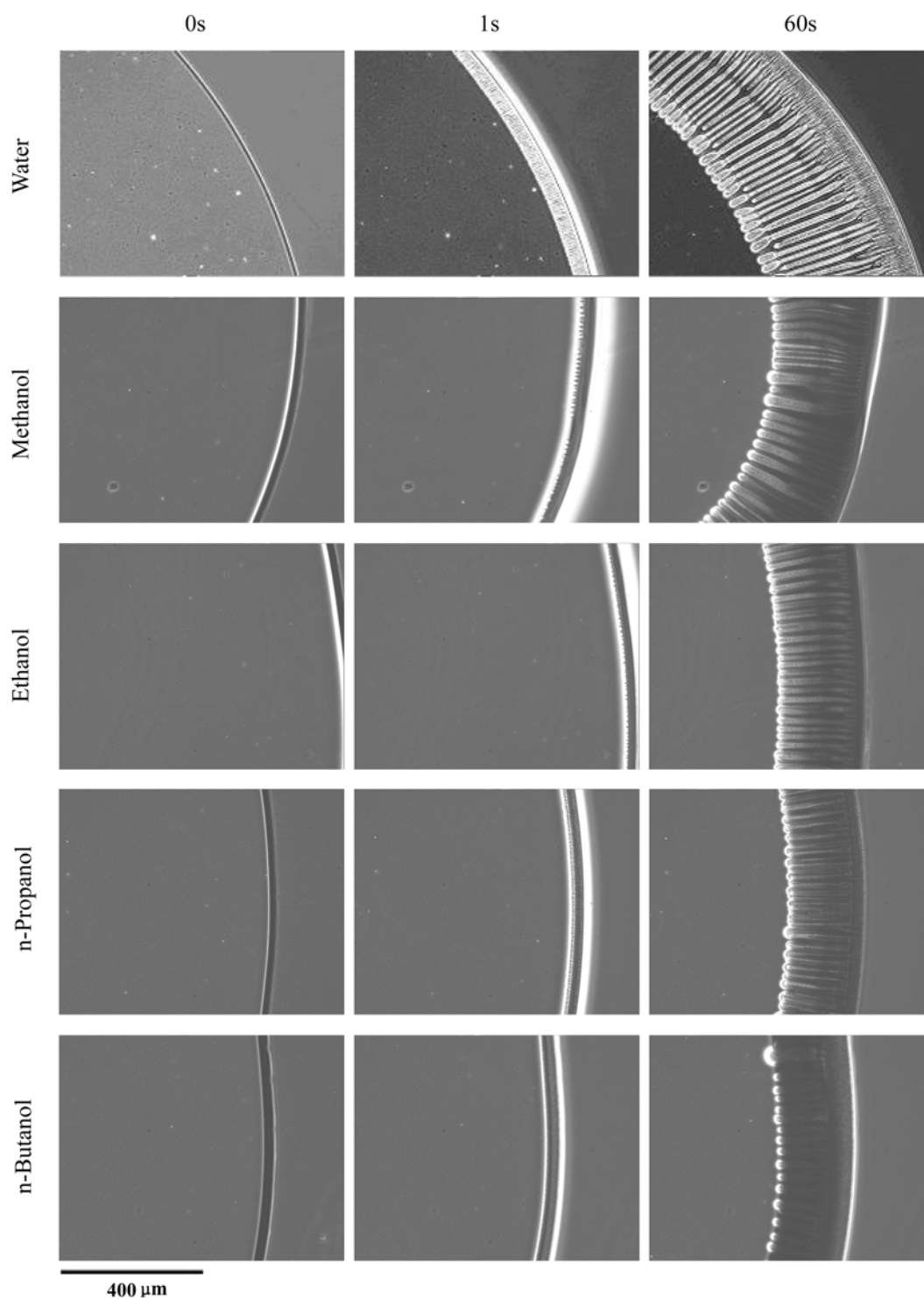*Unit: g/25 g 1 (wt) % polymer solution

**Fig. 9. Optical microscope of membrane prepared by varying non-solvent.**

membrane samples for scanning electron microscopy (SEM) were first immersed in liquid nitrogen, fractured and then sputtered with metallic gold to obtain an adequate contrast of the membrane fracture. CAMBRIDGE S-250 field emission SEM (Cambridge INC, England) was used to investigate the morphology of hollow fiber membranes.

**7. Precipitation Value Determination**

Non-solvent was added continually into 25 g polymer solution with 1 (wt) % with a buret at room temperature, until the polymer was precipitated. Then the solution was kept for one day to eliminate part precipitation. Finally, the volume of non-solvent was determined as the precipitation value.

**RESULTS AND DISCUSSION**

## 1. The Influence of Temperature of Precipitation Medium on Gelation Rate of PPESK Casting Solution

18 (wt) % PPESK casting solution was precipitated in distilled water with 2.5% Tween80 as additives. Effect of gelation temperature on the gelation rate of the system was showed in Fig. 3 In Table 2, as our previous paper [28] showed, $D_1$ stand for the value of diffusion coefficient of skin layer, $D_2$, transition layer, $D_3$, finger layer, and D, mean value of $D_1$, $D_2$, and $D_3$. It can be seen that the gelation rate of PPESK casting solution increased considerably with gelation temperature. High gelation temperature could sharply enhance mass exchange rate between solvent and non-solvent. Therefore, with increase of gelation temperature, membrane structure became much loose, and porosity of membrane increased substantially. Pure water flux of membrane also increased substantially with gelation temperature. Cut off molecular weight of the membrane with Tween 80 as additives decreased with the gelation temperature. Table 2 shows that the cut off molecular weight increases with increase of diffusion coefficient of skin, $D_1$. It was the little pore size of skin that brought about the low cut-off molecular weight, and that enhanced mass transfer resistance of the skin of membrane, and caused the diffusion coefficient of skin, $D_1$, drop. Further reasons need to be investigated.

The SEM and optical microscope observations are in Figs. 4-5. The observations illustrated that high gelation temperature could prevent the formation of macrovoid formation. When gelation temperature increased, the number of macropore decreased, and the distance from the top surface to the starting point of macrovoid formation became larger. Moreover, membrane structure became loosened, which gave a good correspondence with the value of porosity.

## 2. The Influence of Non-solvent on Gelation Rate of PPESK Casting Solution

Figs. 6 and 7 show the effect of different alcohols on the gelation rate of 16.7% PPESK casting solution. It can be seen that the gelation rate of PPESK casting solution ranks in the following order: water>methanol>ethanol>n-propanol>n-butanol. From Table 3, it can be seen that alcohol with the solubility parameter of large numbers of carbon atom was larger than those of small numbers of carbon, and that the solubility parameter difference between polymer and non-solvent decreased with the numbers of carbon atoms of non-solvent. The less solubility parameter difference, the higher affinity between polymer and non-solvent. That is, the affinity between polymer and non-solvent increased with the decrease of solubility parameter difference. Therefore, more non-solvent was needed to precipitate the same polymer solution, with long chain alcohol as non-solvent increased. In the ternary phase diagram, the homogeneous phase area became bigger, while the two phase area became smaller. Phase separation changed from instantaneous phase to delay phase separation. The results gave a good correspondence with the precipitate value data in Table 3. On the other hand, long chain alcohol showed larger mole volume, which enhanced diffusion resistance. Therefore, it became more difficult for non-solvent to diffuse into polymer solution. The diffusivity of coagulation medium into the PPESK polymer solution ranked in the following order: water>methanol>ethanol>n-propanol>n-butanol.

Figs. 7 and 8 show that pure water flux of membrane also increased slowly with the mean diffusion coefficient, D. The cut off molecular weight and diffusion coefficient of skin, $D_1$ decreased sharply

when using methanol instead of water as non-solvent. The cut off molecular weight and diffusion coefficient of skin, $D_1$ decreased slowly when using methanol, ethanol, n-propanol, and n-butanol, respectively. This law gave a good correspondence with the results in Table 2.

The optical micrograph observations are presented in Fig. 9. The observations illustrated that long chain alcohol as non-solvent could prevent the formation of macrovoid formation. With long chain alcohol as non-solvent, the number of macrovoids became less, the
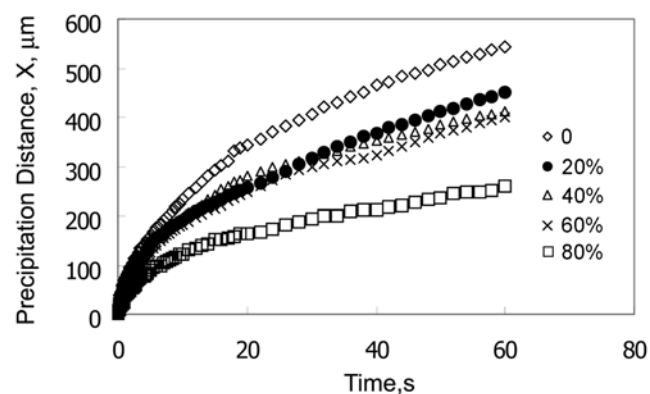


**Fig. 10. Effect of non-solvent component on gelation rate using 6.7% tween as additive (concentration of PPESK: 16.7%).**
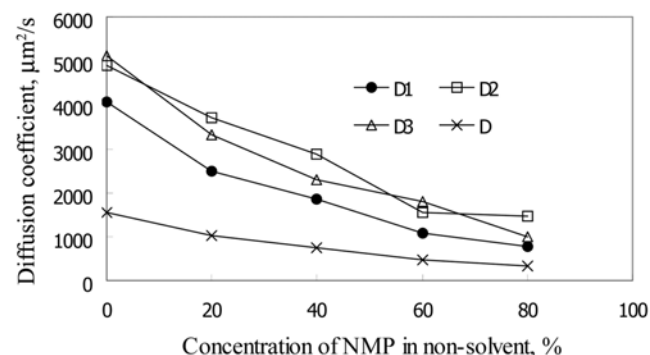


**Fig. 11. Effect of non-solvent component on diffusion coefficient, D using 6.7% tween as additive (concentration of PPESK: 16.7%).**
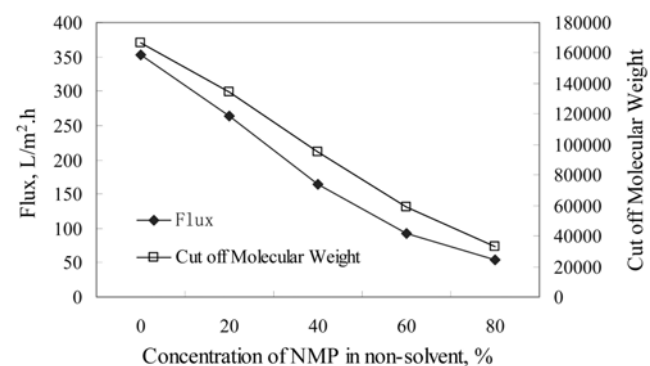


**Fig. 12. Effect of non-solvent component on pure water flux, cut off molecular weight of membrane (concentration of PPESK: 16.7%).**
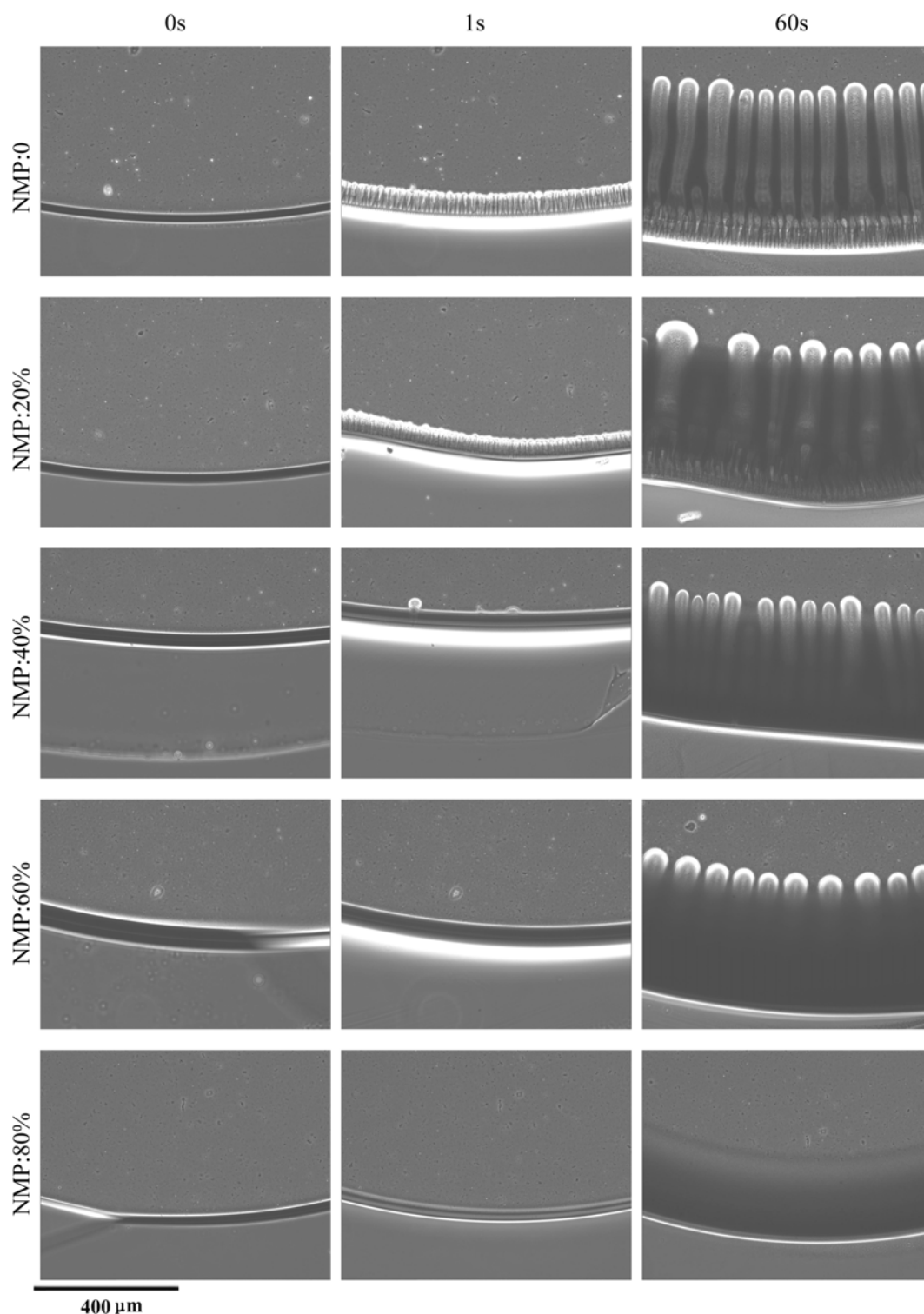
**Fig. 13. Optical microscope of membrane prepared by adding NMP into non-solvent.**

macrovoid size became much bigger, and the distance from top surface to the starting point of macrovoid formation became larger. The membrane structure changed dramatically from finger structure into sponge structure with n-butanol as non-solvent.

**3. The Influence of Non-solvent Component on Gelation Rate of PPESK Casting Solution**

It is well known that the solvent content of precipitate medium could acutely change the relative rate of phase separation during precipitation. By using a soft non-solvent bath containing a substantial amount of solvent, the mass transfer rate of solvent and non-solvent across the membrane-bath interface would dramatically slow down, and would cause the formation of a dense skin. Figs. 10 and

11 show the effect of different non-solvent components on the gelation rate for 16.7% PPESK casting solution with 6.7% tween as additive. It can be seen that the gelation rate of PPESK casting solution decreased considerably with the concentration of NMP in non-solvent. The chemical potential difference between polymer solution and non-solvent dropped with the concentration of NMP in non-solvent. Therefore, it was difficult for non-solvent to diffuse from non-solvent into polymer solution, and it was also difficult for NMP to diffuse out of polymer solution. On the other hand, the solubility parameter of non-solvent decreased with the concentration of NMP in non-solvent, and the solubility parameter difference between polymer and non-solvent decreased at the same time. That is, the affinity between polymer and non-solvent increased with the decrease of solubility parameter difference. Therefore, more non-solvent was needed to precipitate the same polymer solution, with increasing of concentration of NMP in non-solvent. The diffusivity of coagulation medium also decreased considerably with the increase of concentration of NMP in non-solvent.

Figs. 11 and 12 also show that pure water flux of membrane and the mean diffusion coefficient, D, also increased significantly with concentration of NMP in non-solvent, and that the cut off molecular weight decreased substantially with the increase of diffusion coefficient of skin, $D_1$. The main reason was that the concentration gradient across the membrane-bath interface, which governed the nonsolvent-solvent exchange rate, became small in the soft nonsolvent bath. Therefore, the casting dope enters the phase separation boundaries sluggishly, leading to the so-called delayed-type phase separation [29]. That means that a dense skin would form in such bath during membrane formation. As a result, the pure water flux of membrane drop down and rejection capability was greatly improved.

The optical micrograph observations are presented in Fig. 13. The observations illustrated that a soft non-solvent bath can prevent the formation of macrovoid formation. With higher concentration of NMP in non-solvent, the number of macrovoids becomes less, the macrovoid size becomes big, and the distance from top surface to the starting point of macrovoid formation becomes larger. Finally, sponge structure formed when concentration of NMP was 80% in non-solvent.

## CONCLUSIONS

The relationship between gelation parameter and membrane performance was investigated in the phase inversion process. PPESK was dissolved in NMP, and different non-solvents were used as a coagulant. In order to understand the effects of gelation conditions on membrane formation, precipitated kinetics of membrane-forming system were carefully investigated by measuring gelation rate, optical microscope, and SEM.

The membrane structure showed a relationship with the gelation rate. With increasing of the mean diffusion coefficient of skin, D, pure water flux of membrane grew greatly. Moreover, membrane structure became very loose, and porosity of membrane increased. When the gelation rate became very slow, the sponge structure came into being, while the cut off molecular weight of membrane showed a close relationship with the diffusion coefficient of skin, $D_1$.

Therefore, we could control the structure and performance of

the membrane just by changing the mean diffusion coefficient of skin, D, and the diffusion coefficient of skin, $D_1$ in the process of membrane formation.

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