

# Preparation of Poly(phthalazinone ether sulfone ketone) Hollow Fiber Membrane for Gas Separation

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**ABSTRACT:** Poly(phthalazinone ether sulfone ketone) (PPESK) asymmetric hollow fiber membranes for gas separation were prepared by dry/wet phase inversion technique. The effects of various preparation conditions such as solvent, nonsolvent-additives (NSA), PPESK concentration, and air gap on the membrane performance were studied. The heat resistance of the PPESK hollow fiber membrane was also examined. The hollow fiber membrane prepared from solvent with stronger solubility showed low gas permeation and high O<sub>2</sub>/N<sub>2</sub> selectivity due to the denser skin layer. Hollow fiber membrane made from PPESK/DMAc/EtOH/THF system had thicker skin layer than that made from PPESK/DMAc/GBL system with the same ratio of near-to-cloud-point of NSA, which resulted in the higher O<sub>2</sub>/N<sub>2</sub> selectivity. Along with the increase of NSA content, the gas permeation increased and the O<sub>2</sub>/N<sub>2</sub> selectivity decreased. The O<sub>2</sub>/

N<sub>2</sub> selectivity of hollow fiber membranes made from PPESK/DMAc/GBL and PPESK/DMAc/EtOH/THF systems were 4.9 and 4.8 respectively, when the membrane forming systems contained appropriate content of NSA. The high polymer concentration resulted in low gas permeation and high O<sub>2</sub>/N<sub>2</sub> selectivity. When the air gap was excessively long, the membrane performance dropped because of the damage to the dense skin layer. There was no significant drop on the membrane performance when the operation temperature was elevated to 90°C. The average O<sub>2</sub>/N<sub>2</sub> selectivity was higher than 3.0 at 70°C during a long period of 55 days' test time. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 405–411, 2007

**Key words:** hollow fiber membrane; poly(phthalazinone ether sulfone ketone); gas separation

## INTRODUCTION

The polymeric membranes for gas separation has been attached much attention since 1970s.<sup>1–3</sup> This is based on the fact that the polymeric membrane is very effective to be used in the fields of air separation, recovery and separation of hydrogen, acid gas, and organic vapor. In addition, the membrane-based gas separation process is very energy-efficient and free from contamination, which is the most important advantages among the various merits of membrane gas separation process compared with the traditional separation process.

In the last two decades, great advances have been achieved in the field of gas separation membrane. First, the development of technology has perfected the membrane fabrication. The preparation of single layer membrane with ultrathin dense-selective layer has

been no longer too hard to actualize.<sup>4–11</sup> Even the dual-layer asymmetric hollow fiber membranes have been produced by Singaporean researchers in recent years.<sup>12–15</sup> The key of this technology is simultaneous coextrusion approach. Second, various newly synthesized polymers were applied in the fabrication of membrane.<sup>2,16–18</sup> Cellulose acetate, polysulfone, polyethersulfone, polyimide, polyetherimide have been widely used in the preparation of gas separation membrane since 1970s.<sup>19–24</sup> In this article, a new kind of polymer, PPESK, was used as the membrane material.

In most gas separation process, it is desirable to employ membranes having the maximized surface area over volume. Thus, numerous researches have been focused on the development of hollow fiber membranes.<sup>5,8,10–15,25</sup> The ideal polymeric gas separation membranes having high gas permeability and selectivity has become a subject with strong research interest because such membranes are very meaningful to the membrane-based gas separation process. One way of achieving such a membrane is to fabricate an asymmetric polymer membrane consisting of a defect-free skin layer, which has high gas permeability without a significant decrease in gas selectivity.<sup>26</sup> However, only a very few realized high gas transport performance of hollow fiber membrane without an

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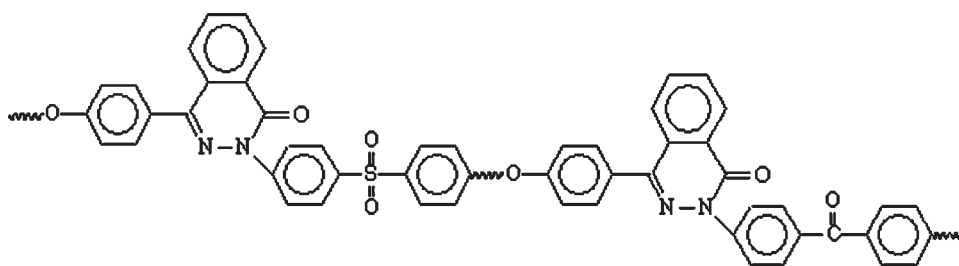


Figure 1 Structure of PPESK.

additional coating process.<sup>27,28</sup> This is because the formation of hollow fiber membranes with completely defect-free skin layer is complex and involves many factors such as dope composition, type of bore fluid, air gap, coagulation bath, and rates of fiber take-up and dope and bore extrusion. It is also known that the controlling factors for the hollow fiber morphology are quite different from that for the flat membrane morphology and that it is difficult to simulate the hollow fiber fabrication process by adopting the process conditions developed for the flat membranes.

PPESKs were previously synthesized.<sup>29–31</sup> These novel polymers with high glass transition temperatures (263–305°C) show excellent comprehensive properties and outstanding thermal stabilities. Dense films and asymmetric membranes made from PPESKs show good properties for gas and liquid separation.<sup>31–34</sup> The structure of PPESK(S : K = 1 : 1) is shown in Figure 1. In this study, PPESK asymmetric hollow fiber membranes for gas separation were prepared by dry/wet phase inversion technique. By coating the silicone rubber on the outer surface of the PPESK hollow fiber membrane, the defects on the skin layer of PPESK hollow fiber membranes were sealed. The effects of different preparation conditions such as solvent, NSA, PPESK concentration, and air gap on the membrane performance were studied. The heat-resistance examination showed the PPESK hollow fiber membrane had very good thermal stability.

## EXPERIMENTAL

### Materials

PPESK(S : K = 1 : 1) was provided by Dalian Polymer New Material Co., Ltd.(China). *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP),  $\gamma$ -butyrolactone (GBL), ethanol (EtOH), tetrahydrofuran (THF), were analytical grade. All chemicals were commercial without further purification. The coating solution was prepared by mixing silicone rubber and curing agent in petroleum ether.

### Preparation of hollow fiber membrane

Asymmetric PPESK hollow fibers were fabricated by a dry/wet spinning process. PPESK was dissolved in the mixture of solvent and NSA under stir. The spin-

ning solution was filtered and degassed before spinning. The nascent fiber passed through an air gap at room temperature and immersed in the external coagulant of water. Water was also used as internal coagulant. The fiber was finally gathered in water. The dimensions of the spinneret were 1000 and 600  $\mu\text{m}$  for outer diameter (OD) and inner diameter (ID), respectively. The fiber take-up velocity and spinning solution/bore fluid extrusion ratio were kept constant. The fibers were kept in water for at least 3 days so that the process of solvent exchange could be completed. Finally, these fibers were dried in the air at ambient temperature for further tests and study.

### Module fabrication and gas permeation tests

At least two test modules were made for each sample. Each module contains 35–40 pieces of fibers with the length of 25–30 cm. The shell side of the bundle was glued onto an aluminum holder using an epoxy resin, while the other end was sealed with epoxy resin. The silicone-coated membranes were prepared by a dilute solution immersion coating method under the vacuum. The coating solution was prepared with 2 wt % silicone rubber in petroleum ether. The permeation fluxes of silicone-coated asymmetric membranes for pure gases were measured at pressure difference of 0.8 MPa.

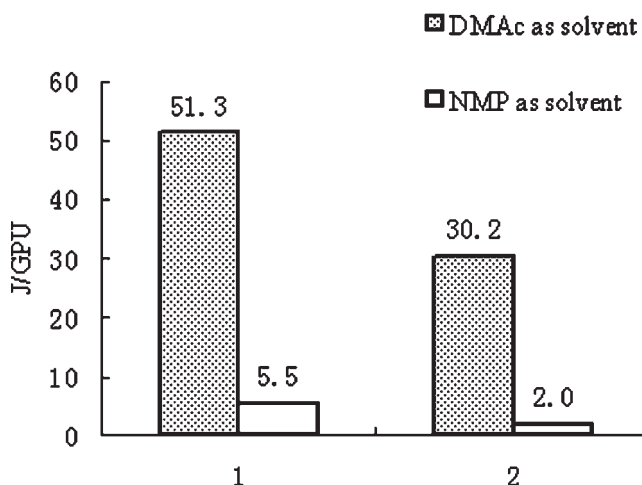
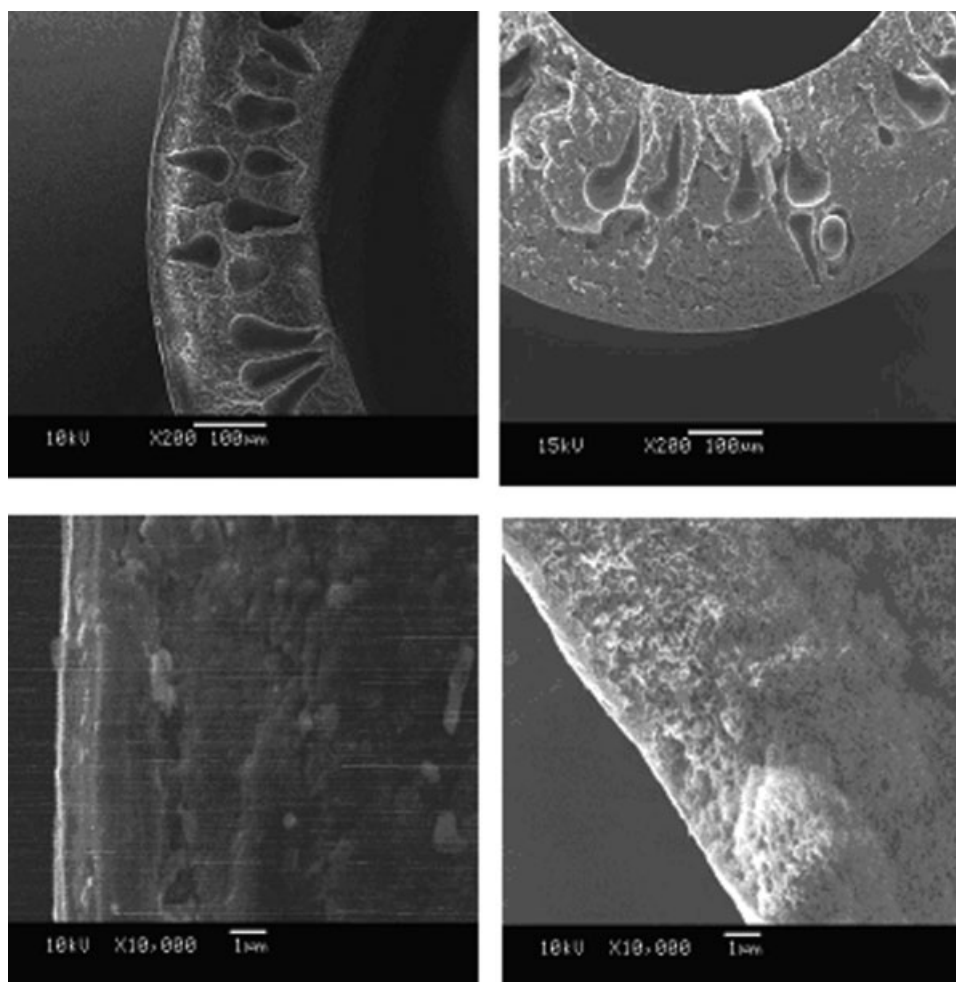


Figure 2 Effect of solvent on membrane performance (1 and 2 represent oxygen and nitrogen respectively).



**Figure 3** SEM images of membrane cross section (left two: NMP as Solvent; right two: DMAc as solvent; first line:  $\times 200$ ; second line: vicinity of outside surface  $\times 10,000$ ).

The permeance  $J$  was calculated using the following equation:

$$J = \frac{Q}{\Delta P \cdot A} = \frac{Q}{n\pi D l \Delta P}$$

where  $Q$  is the flow rate of pure gas ( $\text{cm}^3/\text{s}$ ),  $\Delta P$  the gas pressure difference cross the membrane (Pa),  $A$  the surface area of testing fibers ( $\text{cm}^2$ ),  $n$  the number of fibers in one testing module,  $D$  the o.d. of the testing fibers (cm),  $l$  the effective length of the modules (cm). Permeance unit is GPU ( $1 \text{ GPU} = 7.5 \times 10^{-10} \text{ cm}^3 (\text{STM}) \cdot \text{cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ).

The ideal selectivity is defined as follows:

$$\alpha_{A/B} = \frac{J_A}{J_B}$$

where  $A$  and  $B$  represent pure oxygen and nitrogen respectively.

#### Characterization of hollow fiber membrane morphology

The morphology of hollow fiber membranes was characterized by scanning electron microscopy (SEM)

using a JEOL JSM-5600LV. Membrane samples were prepared with the procedure depicted in literature.<sup>35</sup>

## RESULTS AND DISCUSSION

### Effect of solvent

Hollow fiber membranes were prepared using NMP and DMAc as solvent respectively, with the same

**TABLE I**  
Effect of GBL Content on Membrane Performance

	$\alpha$			
	0.50	0.65	0.85	0.95
Before coating				
$J_{\text{oxygen}}/\text{GPU}$	51.3	127.8	688.7	1740.3
$J_{\text{nitrogen}}/\text{GPU}$	30.2	91.3	694.6	1933.6
$\alpha_{\text{oxygen/nitrogen}}$	1.7	1.4	1.0	0.9
After coating <sup>a</sup>				
$J_{\text{oxygen}}/\text{GPU}$	1.9	2.6	5.4	59.7
$J_{\text{nitrogen}}/\text{GPU}$	0.4	0.7	1.5	53.1
$\alpha_{\text{oxygen/nitrogen}}$	4.9	4.0	3.6	1.1

<sup>a</sup> Test temperature: 70°C.

**TABLE II**  
Effect of EtOH/THF Content on Membrane Performance

	$\alpha$			
	0.50	0.65	0.85	0.92
Before coating				
$J_{\text{oxygen}}/\text{GPU}$	2.0	7.4	30.1	772.0
$J_{\text{nitrogen}}/\text{GPU}$	1.0	4.4	18.8	825.3
$\alpha_{\text{oxygen/nitrogen}}$	2.0	1.7	1.6	0.94
After coating <sup>a</sup>				
$J_{\text{oxygen}}/\text{GPU}$	Permeation	Permeation	3.3	37.6
$J_{\text{nitrogen}}/\text{GPU}$	too low	too low	0.7	22.1
$\alpha_{\text{oxygen/nitrogen}}$			4.8	1.7

<sup>a</sup> Test temperature: 70°C.

PPESK concentrations as 25 wt % and the same GBL concentrations. NMP had stronger solubility for PPESK. The thermodynamic stability of NMP system was much higher than that of DMAc system containing the same amount of NSA. Thus, as can be seen in Figure 2, gas permeation of uncoated membrane made from spinning solution using NMP as solvent was much lower and the O<sub>2</sub>/N<sub>2</sub> selectivity was higher than that using DMAc as solvent. As shown in Figure 3, membrane made from NMP solvent system had a thicker outer surface skin layer than that from DMAc solvent system.

#### Membranes made from PPESK/DMAc/EtOH/THF and PPESK/DMAc/GBL system

Hollow fiber membranes were prepared from PPESK/DMAc/EtOH/THF and PPESK/DMAc/GBL systems in the presence of different content of GBL and EtOH/THF complex. Here the ratio of near-to-cloud-point,  $\alpha$ , was introduced to represent the NSA content. It described the degree of closeness between

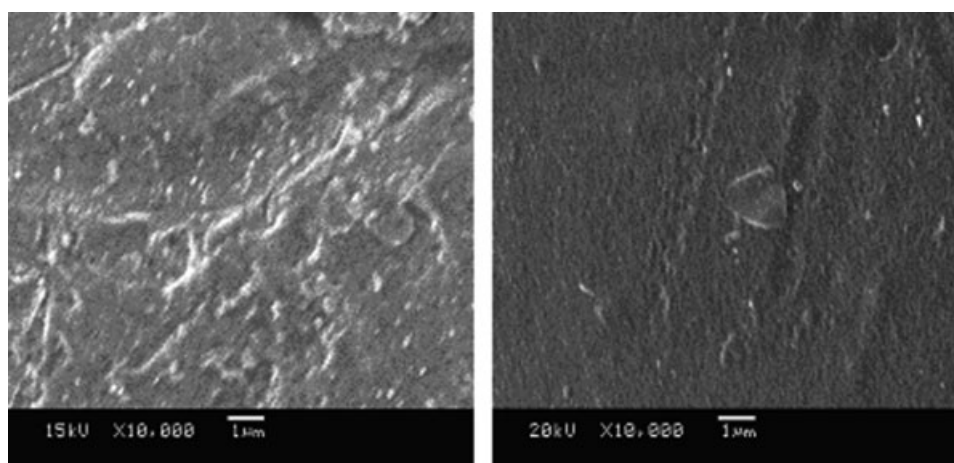
NSA content to the critical NSA content at phase separation. The definition of  $\alpha$  is as follows<sup>36</sup>:

$$\alpha = \frac{W_{\text{NSA}}/W_{\text{solv}}}{W_{\text{NSA, cp}}/W_{\text{solv, cp}}}$$

where  $W_{\text{NSA}}$  and  $W_{\text{solv}}$  represent the contents of NSA and solvent in the spinning dope;  $W_{\text{NSA, cp}}$  and  $W_{\text{solv, cp}}$  represent at phase separation, the contents of NSA and solvent of the system containing the same polymer concentration as the spinning dope.

As shown in Table I and Table II, the gas permeation of membrane made from GBL system was higher than that made from EtOH/THF complex system, and the gas selectivity was on the contrary. In the PPESK/DMAc/NSA system, GBL had very weak ability of precipitation. The thermodynamic stability of membrane forming system containing GBL as NSA was higher than that containing EtOH/THF complex as NSA. But the membrane forming process is very complex. It is controlled by not only the thermodynamic property of membrane forming system but also by the kinetic property of membrane forming process. EtOH/THF complex was very volatile. The evaporation process of the complex occurred during the formation of nascent hollow fiber membrane. This helped the polymer enrichment on the outer surface skin layer, which resulted in the dense skin layer. As shown in Figure 4, the outer surface of hollow fiber membrane made from EtOH/THF complex system was denser and smoother than that from GBL system.

As can be seen from Table I and Table II, along with the increase in  $\alpha$ , the gas permeation increased and the gas selectivity decreased. This is because along with the increase of  $\alpha$ , the solvation function of solvent decreased. Under this condition, more PPESK molecules were in the self-association conformation. This



**Figure 4** SEM images of membrane morphology ( $\times 10,000$ ; on the left: surface of membrane made from PPESK/DMAc/GBL system,  $\alpha = 0.85$ ; on the right: surface of membrane made from PPESK/DMAc/EtOH/THF system,  $\alpha = 0.85$ ).

**TABLE III**  
Effect of PPESK Content on Membrane Performance

	PPESK content (wt %)			
	22	25	27	30
Before coating				
$J_{\text{oxygen}}/\text{GPU}$	987.3	688.7	212.3	29.8
$J_{\text{nitrogen}}/\text{GPU}$	1097.1	694.6	163.3	15.7
$\alpha_{\text{oxygen/nitrogen}}$	0.9	1.0	1.3	1.9
After coating <sup>a</sup>				
$J_{\text{oxygen}}/\text{GPU}$	25.4	5.4	4.4	Permeation too low
$J_{\text{nitrogen}}/\text{GPU}$	9.8	1.5	1.2	
$\alpha_{\text{oxygen/nitrogen}}$	2.6	3.6	3.8	

<sup>a</sup> Test temperature: 70°C.

resulted in the defects and big voids on the outer surface skin layer of the hollow fiber membranes.

### Effect of PPESK content

Table III illustrates the effect of PPESK content on the membrane performance. The membrane forming system was PPESK/DMAc/GBL in which the  $\alpha$  of NSA was the same as 0.85. With increase in the PPESK content, the gas permeation decreased and the gas selectivity increased. As the concentration of the polymer increased, the thickness of the outer surface skin layer also increased, leading to lower gas permeation and higher gas selectivity. In Figure 5, SEM images of membrane morphology indicate that along with the increase of PPESK content, the quantity and the size of membrane voids decreased.

### Effect of air gap

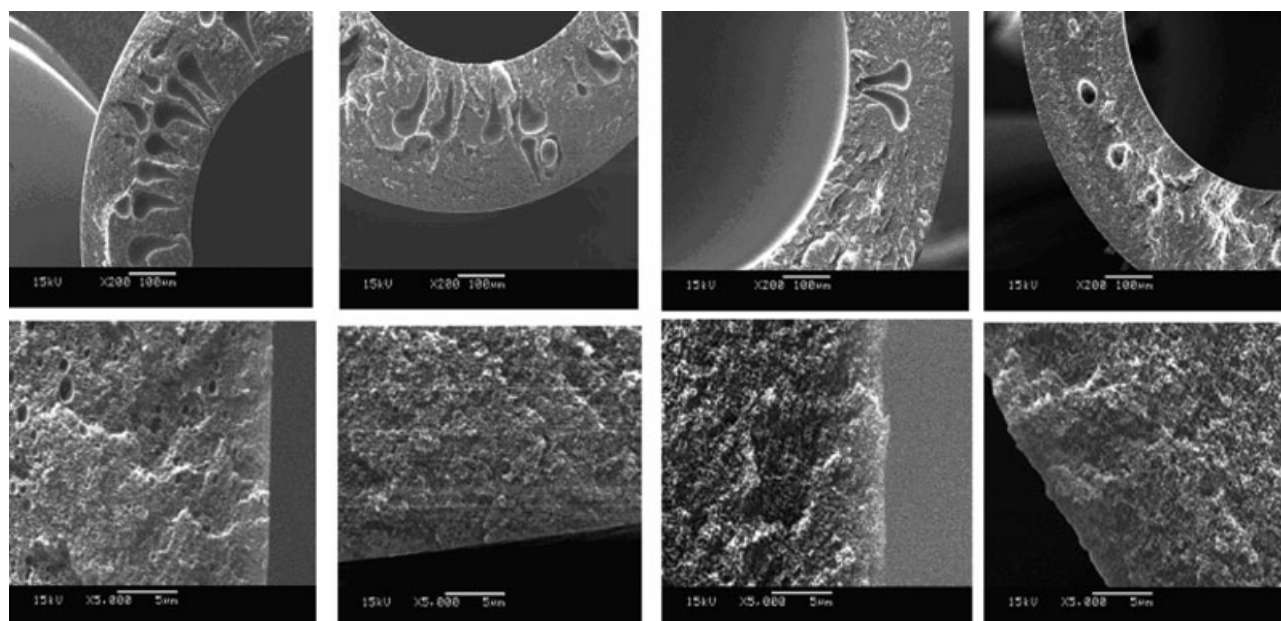
Table IV indicates the effect of air gap on the membrane performance. The membrane forming system was PPESK/DMAc/EtOH/THF in which the  $\alpha$  of NSA complex was the same as 0.85. As illustrated in Table IV, the gas permeation decreased and the gas selectivity increased with the increase of the air gap. But when the air gap was excessively long, the gas selectivity decreased. This result was the same as Wang's.<sup>10</sup> When the air gap was immoderately long, the front of internal coagulation might have moved to the outer surface skin layer. Water was used as internal coagulant in this research. A very strong interaction between PPESK and water existed. Thus, the diffusion of water to the outer surface might initial the occurrence of the liquid-liquid phase separation, resulting in the damage to the nascent dense skin layer formed due to the coalescence and deformation of polymer aggregates during the dry inversion process.<sup>10</sup> So defects and big voids appeared on the outer surface skin layer when the air gap was too long.

### Heat-resistance of PPESK hollow fiber membrane

The heat-resistance property was tested using the hollow fiber membrane made from PPESK/DMAc/GBL system in which the ratio of near-to-cloud-point,  $\alpha$ , was 0.85.

### Effect of temperature on membrane performance

Membrane was tested under different temperatures. As shown in Figure 6, though there is a fluctuation,



**Figure 5** SEM images of membrane morphology (from left to right: membrane made from system containing 22 wt %, 25 wt %, 27 wt %, 30 wt % PPESK respectively; first line:  $\times 200$ , second line: vicinity of outside surface  $\times 5000$ ).

**TABLE IV**  
Effect of Air Gap on Membrane Performance

	Air gap (mm)			
	10	60	110	160
Before coating				
$J_{\text{oxygen}}/\text{GPU}$	246.5	72.3	30.1	512.0
$J_{\text{nitrogen}}/\text{GPU}$	224.1	51.6	18.8	568.9
$\alpha_{\text{oxygen/nitrogen}}$	1.1	1.4	1.6	0.9
After coating <sup>a</sup>				
$J_{\text{oxygen}}/\text{GPU}$	14.6	8.4	3.3	44.2
$J_{\text{nitrogen}}/\text{GPU}$	5.8	2.0	0.7	21.0
$\alpha_{\text{oxygen/nitrogen}}$	2.5	4.2	4.8	2.1

<sup>a</sup> Test temperature: 70°C.

the  $\text{O}_2/\text{N}_2$  selectivity remains 3.0–4.0 in the test temperature range of 50–90°C. Even at 90°C, the  $\text{O}_2/\text{N}_2$  selectivity was till higher than 3.0, indicating that the PPESK hollow fiber membrane has good heat resistance.

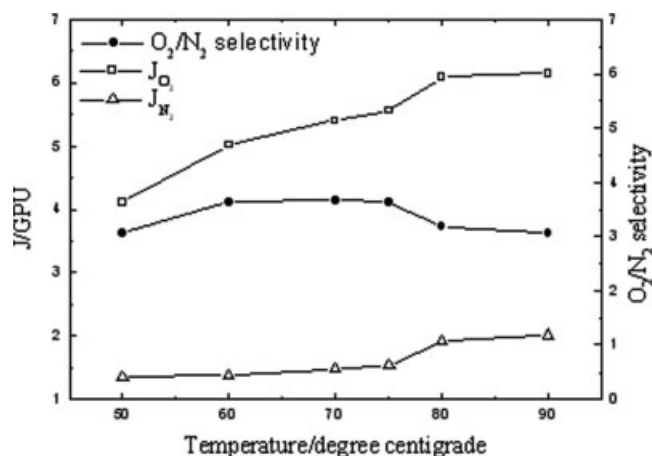
#### High temperature stability of PPESK hollow fiber membrane

The hollow fiber membrane was tested under 70°C during a long period of 55 days to examine the thermal stability. As can be seen in Figure 7, though there is a decline in the initial several days, the  $\text{O}_2/\text{N}_2$  selectivity waved in a small range and the average  $\text{O}_2/\text{N}_2$  selectivity remained 3.0–4.0 at 70°C during the period of test time showing that the high thermal stability of PPESK hollow fiber membrane.

#### CONCLUSIONS

PPESK hollow fiber membranes for gas separation were prepared using NMP and DMAc as solvent respectively. The gas permeation of hollow fiber membrane made from PPESK/NMP/GBL system was much lower than that from PPESK/DMAc/GBL system. The gas selectivity of hollow fiber membrane made from PPESK/NMP/GBL system was higher than that made from PPESK/DMAc/GBL system.

Compared with the hollow fiber membrane made from PPESK/DMAc/GBL system, hollow fiber membrane made from PPESK/DMAc/EtOH/THF system had denser and smoother outer surface. Thus, the gas permeation of membrane made from PPESK/DMAc/EtOH/THF system was lower and the gas selectivity was higher than that made from PPESK/DMAc/GBL system. When the ratio of near-to-cloud-point,  $\alpha$ , was the same as 0.85, the gas selectivity of membrane made from PPESK/DMAc/EtOH/THF system was 4.8 but that made from PPESK/DMAc/GBL system was 3.6. Along with the increase of NSA content, the gas permeation increased and the gas selectivity decreased.

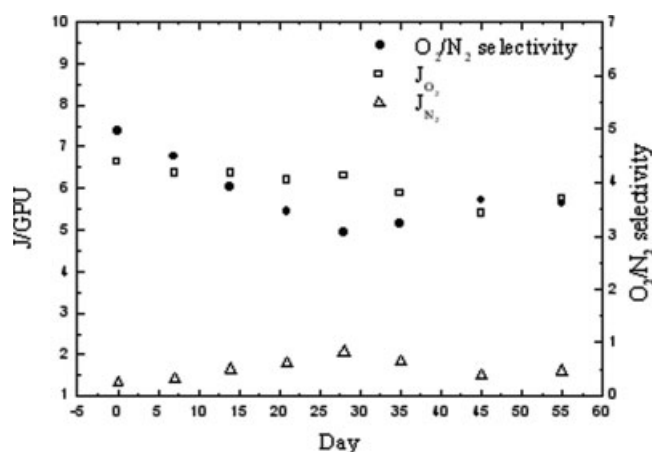


**Figure 6** Effect of operation temperature on PPESK hollow fiber membrane performance.

The high polymer concentration resulted in the smaller and fewer voids in the membrane and denser skin layer leading to the low gas permeation and high gas selectivity.

Along with the increase in air gap, the gas permeation decreased and the gas selectivity increased. When the air gap was excessively long, the membrane performance dropped. For PPESK/DMAc/EtOH/THF system, when the air gap was control as 110 mm, the gas selectivity of PPESK hollow fiber membrane reached the maximum value of 4.8.

Though there was a fluctuation, the performance of PPESK hollow fiber membrane remained good under elevating temperature and during a long period of time under high temperature. When the operation temperature was elevated to 90°C, the  $\text{O}_2/\text{N}_2$  selectivity of PPESK hollow fiber membrane could remain higher than 3.0. The average  $\text{O}_2/\text{N}_2$  selectivity was higher than 3.0 at 70°C during a long period of test time of 55 days.



**Figure 7** PPESK hollow fiber membrane performance under 70°C within 55 days.

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