



## Poly (phthalazinone ether sulfone ketone) properties and their effect on the membrane morphology and performance

Peiyong Qin<sup>a,b\*</sup>, Binbing Han<sup>c</sup>, Cuixian Chen<sup>b</sup>, Shintani Takuji<sup>d</sup>, Jiding Li<sup>b</sup>, Benhui Sun<sup>e</sup>

<sup>a</sup>College of Life Science and Technology, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

<sup>b</sup>Department of Chemical Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Tel. +86-10-64448962; Fax. +86-10-64448962; email: qpy@mem.tsinghua.edu.cn

<sup>c</sup>Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, USA

<sup>d</sup>Core Technology Center, Nitto Denko Corporation, Osaka 5678680, Japan

<sup>e</sup>College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Received 2 April 2008; Accepted 1 September 2009

### ABSTRACT

Poly (phthalazinone ether sulfone ketone) (PPESK) copolymer is a relatively newly developed material, which contains different component ratios of diphenyl ketone and diphenyl sulfone with respect to a certain amount of 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one. In this study, the physico-chemical characteristics of this copolymer, including the glass transition temperature, the intrinsic viscosity, the DSC (differential scanning calorimeter) and FT-IR spectra have been investigated. The chemical stability of this copolymer has been tested with several commonly used acids, bases and oxidants. The apparent viscosity of this copolymer dissolved in *N*-methyl pyrrolidone (NMP) solvent at different concentrations and temperatures has been measured. The effect of two additives, polyethylene glycol (1000 g mol<sup>-1</sup>) and Tween80, on the apparent viscosity of the PPESK/NMP solution, has been investigated. Further, the PPESK/NMP solution has been used to prepare asymmetric ultrafiltration membranes, and the influence of the solution viscosity on the gelation rate, the membrane structure and the ultrafiltration performance has been studied. The results present here provide fundamental data on this promising copolymer material, and will be beneficial for its future application, especially in the membrane formation area.

**Keywords:** Poly (phthalazinone ether sulfone ketone); Ultrafiltration; Chemical stability; Rheological property; Gelation

### 1. Introduction

Ultrafiltration has been widely used in numerous applications [1], such as in food and pharmaceutical processing, chemical separation, waste water treatment, and so on. In practice, ultrafiltration membranes are highly desired to possess an ability to tolerate different oxidants, acids, bases, free chlorine, etc. [2–5]. Various polymeric materials have been synthesized and used to prepare ultrafiltration membranes, including regenerated

cellulose (RC), cellulose acetate (CA), cellulose triacetate (CTA), polyacrylonitrile (PAN), polyvinyl alcohol (PVA), polysulfone (PSf), polyethersulfone (PES), aromatic polyamide (PA), polyimide (PI), etc. [6]. Each material has both advantages and limitations. For example, CA membranes are relatively easy to fabricate. However, their applicable temperature and pH range is limited. Further, they show a poor resistance to chlorine exposure. PSf membranes, on the other hand, possess a relatively wide temperature range, good pH resistance, satisfactory chlorine tolerance and chemical stability. However, the pressure limit for these membranes is relatively low [6]. Further, the

\*Corresponding author.

maximum temperature for PSf membranes is usually less than 100°C. Thus, there is still a great need to develop new materials, especially those materials with excellent high-temperature resistance and chemical stability.

Poly(phthalazinone ether sulfone ketone) copolymer (PPESK) is a very attractive material with high temperature stability, excellent mechanical properties, and superb radiation and hydrolytic resistance. Further, it is easy to process [7–9]. Fig. 1 shows the chemical structure of this copolymer. As can be seen, it contains different component ratios of diphenyl ketone and diphenyl sulfone with respect to a certain amount of 4-(4-hydroxyphenyl)-2,3-phthalazin-1-one. Its glass transition temperature ( $T_g$ ) varies from 263 to 305°C, depending on the ratio of the ketone component to the sulfone component [7]. The chemical stability of this copolymer has been briefly tested with several chemicals, and this copolymer is stable in these chemicals for at least two weeks. Further, when a prepared membrane from this copolymer was incubated in sea water, no changes were observed for up to six months in terms of the membrane's thickness and weight [9]. Recently, several functional groups, e.g. carboxyl, sulfoxyl, and quaternary ammonium, have been introduced onto the chains of the copolymer [10–12]. These charged groups may increase the glass transition temperature as well as increase the solubility of this copolymer in water and other organic solutions.

PPESK copolymer, its various derivatives as well as their blends with other organic or inorganic materials have been exploited in several areas, to prepare various membranes used in gas separation [7,13], ultrafiltration and nanofiltration [9,10,12–26], direct methanol fuel cell [27,28], and pervaporation [29], as well as to prepare micrometer and nanometer composite particles and PPESK/liquid crystalline blends [30–36]. These results are very promising. However, so far, no systematic studies have been reported to provide a complete understanding on the chemical stability, mechanical characteristics, rheological property, and solubility of this material. Further, for the membranes preparation study, no results have been reported to investigate the effect of the rheological property on the membrane morphology and performance. In this study, we have systematically investigated these properties. We also investigated the viscosity effect on the membrane structure and performance to find the relationship between these. The results may provide a

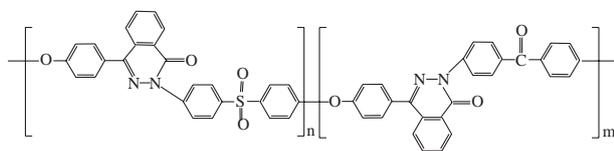


Fig. 1. Chemical structure of PPESK.

guide for the membrane preparation in the application of this promising copolymer and its various derivatives.

## 2. Experimental details

### 2.1. Materials

PPESK was obtained from Dalian Polymer New Material Co., People's Republic of China. *N*-Methyl pyrrolidone (NMP), HCl, H<sub>2</sub>SO<sub>4</sub>, NaOH, H<sub>2</sub>O<sub>2</sub>, NaClO and PEG1000 were obtained from Beijing Yili Fine Chemicals Co., People's Republic of China. Tween80 was obtained from Tianjin Tiantai Fine Chemicals Co., People's Republic of China. Bovine serum albumen (BSA, Molecular weight 67 KDa) was obtained from Sino-American Biotechnology Co. All reagents were used without further purification.

### 2.2. Characterization test

The molecular weight of the PPESK material was measured using a Viscotek TDA 302 GPC (Viscotek Corporation, USA). Standard polystyrene (Supelco Spe, USA, molecular weight 200,000) was used as the standard material, chloroform was used as the mobile phase, and a Styragel HR4 column (Waters Corporate, USA) was used as the separation column. The analysis was conducted at room temperature (25 ± 0.5°C) and a solvent flow rate of 0.4 mL min<sup>-1</sup>. The glass transition temperature was measured using a SII Model DSC6200 Thermal Analyst (Seiko Instruments Inc., Japan). Fourier transform infrared (FT-IR) spectra were obtained using a Nicolet NEXUS FT-IR spectrometer (Thermo Nicolet Corporation, USA) at room temperature.

### 2.3. Chemical stability test

PPESK copolymer was added in NMP at a concentration of 16.7 (wt.%) and the solution was stirred at 120 rpm for 72 h at 65°C. After filtered and vacuumed to remove bubbles, the solution was cast onto a glass plate. The membranes were first dried several days in air at room temperature, then in a vacuum drier for 24 h at 150°C. The membranes were stored in a desiccator for future use. The prepared membrane was homogeneous. To test the membrane property, the weight and thickness of several selected membranes were first measured using a BP210S electronic balance (Sartorius AG, Germany) and a Shan screw micrometer (Guilin Liangju Corporation, People's Republic of China), respectively. Then, the membranes were incubated into a chosen solution at 40°C. Seven sorts of solution were chosen for this test. The solutions were H<sub>2</sub>O, HCl (2%wt), H<sub>2</sub>SO<sub>4</sub> (2%wt),

$\text{HNO}_3$  (2%wt),  $\text{NaOH}$  (5%wt),  $\text{NaClO}$  (5%wt), and  $\text{H}_2\text{O}_2$  (5%wt), respectively. All of sample solutions without change during testing were sealed to prevent evaporation and resolve of solutions. After a certain time, one membrane was removed from the solution, washed using DI water (de-ionized water) thoroughly, and dried for 24 h in a vacuum drier at  $100^\circ\text{C}$  and vacuity  $<200\text{Pa}$ . Then, the weight and thickness of this membrane was measured again. The tensile strength of the membrane was also measured using a Gotech TS-2000-M instron tensile strength tester (Gotech Inc., Taiwan) at a speed of  $10.0\text{ mm min}^{-1}$  under room temperature. Each test was repeated at least three times and the average value was reported in this study.

#### 2.4. Rheological property test

PEG1000 and Tween80 were selected since they are frequently used as additives to prepare membranes. Various PPEsk/NMP, PPEsk/PEG1000/NMP and PPEsk/Tween80/NMP solutions at different compositions were prepared as described above. A Brookfield DV-II+CP viscometer (Brookfield, USA) was used to measure the viscosity of these solutions at various temperatures and compositions. The intrinsic viscosity of the PPEsk copolymer in a very diluted NMP solution ( $0.005\text{ g mL}^{-1}$ ) was measured using an Ubbelohde capillary viscometer (Shanghai Baoshan Qihang Glass Inc., People's Republic of China) at  $30 \pm 0.1^\circ\text{C}$ .

#### 2.5. Gelation process characterization

The gelation process was visually observed using an online Optical Microscope - CCD Camera experimental system (OM-CCD). This system contains an Olympus IX71 optical microscope (Olympus, Japan), a Basler A101f CCD camera (Basler AG, Germany), a personal computer and two specially designed microscope slides. This system allows to capture 12 frames of images per second. The magnification varies from 120 to 2000 times. During the test,  $10\ \mu\text{L}$  PPEsk/NMP solution was first placed in a compartment formed by the two microscope slides. Then,  $1\text{ mL}$  DI water (as the precipitant) was carefully injected into the compartment using a syringe. The images were automatically captured by the camera and stored in the computer using a high speed digital video recording software (Video Savant 4.0, Industries Inc., Canada). The thickness of the precipitated polymer layer was then determined using an image processing and analysis software (ImageJ, National Institute of Mental Health, USA). The room temperature was kept at  $25^\circ\text{C}$  while the relative humidity was 60–70% [37].

#### 2.6. Ultrafiltration membrane preparation and characterization

Flat sheet asymmetric ultrafiltration membranes were prepared by phase inversion method. Dope solution was made by first dissolving PPEsk copolymer and additive in NMP at around  $65^\circ\text{C}$  for 72 h with vigorous stirring at 120 rpm. Then, the homogeneous polymer solution was filtered and vacuumed to remove bubbles. Dope solution was cast on a non-woven fabric, and then was immersed into a DI water tank. The coagulant temperature was kept at  $25^\circ\text{C}$  while the room relative humidity was maintained at 60–70%. Under these conditions, the gelation time for the membrane formation was about several minutes. The flat sheet membranes were then washed and stored in an ultrapure water bath for at least 1 day to completely leach out the residual solvents and additives. The thickness of the prepared membrane was about  $150\ \mu\text{m}$ . A Cambridge S-250 Field Emission SEM (Cambridge INC, England) was used to observe the membrane morphology. The membrane flux was measured using DI water at room temperature and a trans-membrane pressure drop  $0.1\text{ MPa}$ . BSA was used to measure the rejection of the prepared membranes [37].

### 3. Results and discussions

#### 3.1. Intrinsic viscosity, thermal stability and characteristic groups

The measured weight-average molecular weight of PPEsk material is  $218,900\text{ g mol}^{-1}$ , and its number-average molecular weight is  $197,400\text{ g mol}^{-1}$ . The determined intrinsic viscosity, which is an extrapolated value when the concentration of PPEsk reaches to 0%, is  $0.580\text{ dL g}^{-1}$  at  $30 \pm 0.1^\circ\text{C}$ . Fig. 2 shows a DSC curve of this copolymer. The determined glass transition temperature is  $279^\circ\text{C}$ , which is higher than many commonly used materials to prepare ultrafiltration membranes. This high glass transition temperature is due to the presence

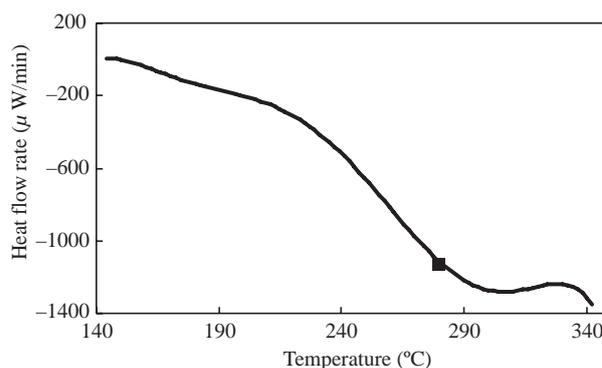


Fig. 2. DSC spectrum of PPEsk.

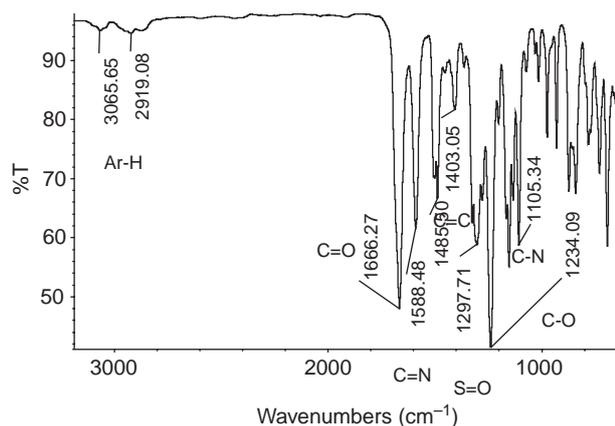


Fig. 3. Infrared spectrum of PPESK.

of those rigid aromatic rings in the copolymer chains. Fig. 3 shows the FT-IR spectrum. Clearly, all the important characteristic peaks, including Ar-H (3065 and 2919  $\text{cm}^{-1}$ ), C=C (1485 and 1403  $\text{cm}^{-1}$ ), C=N (1588  $\text{cm}^{-1}$ ), C=O (1666  $\text{cm}^{-1}$ ), S=O (1298  $\text{cm}^{-1}$ ), C=O (1234  $\text{cm}^{-1}$ ), and C=N (1105  $\text{cm}^{-1}$ ) have been detected.

### 3.2. Chemical stability

Ultrapure DI  $\text{H}_2\text{O}$ , 2 wt.% HCl, 2 wt.%  $\text{H}_2\text{SO}_4$ , 2 wt.%  $\text{HNO}_3$ , 5 wt.% NaOH, 5 wt.% NaClO, and 5 wt.%  $\text{H}_2\text{O}_2$  solution have been used to test the chemical stability of the prepared PPESK homogeneous membrane. These chemicals represent the most commonly used acids, base and oxidants [2–5,39–41]. Figs. 4–6 show the stability results. In Fig. 4, the  $x$ -axis gives the test time in days, while the  $y$ -axis gives the relative membrane weight, which is defined as the ratio of the membrane weight at time  $t$ ,  $W_t$ , to the initial membrane weight,  $W_0$ . Since the membrane is hydrophilic (the measured contact angle is  $74^\circ$ , and Contact angle measurements were performed

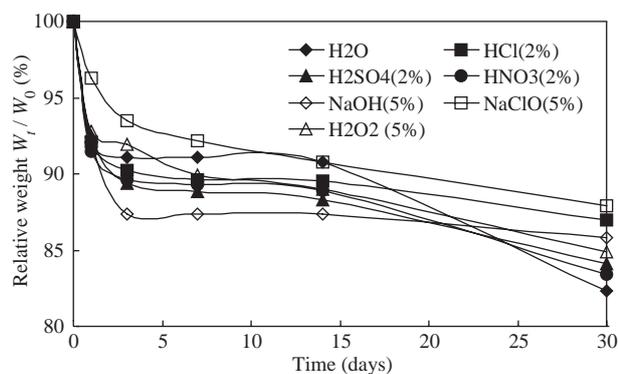


Fig. 4. Influence of chemical solutions on the relative weight of PPESK homogeneous membranes. Temperature of membranes treating by reagents was  $40^\circ\text{C}$ .

according to [42]), water molecules can adsorb into the membrane. In order to exclude this effect, the membrane was vacuum dried at  $100^\circ\text{C}$  and vacuum  $<200\text{Pa}$  for 24 h prior to the membrane weight measurement. Previous test showed that 24 h vacuum drying is enough to reach a steady mass. It can be seen that the dry membrane weight decreased after immersed into these chemicals. Further, after 3 days immersion, the relative membrane weight decreases, indicating that something has been extracted out of the membrane. It is less possible that these lost substances are PPESK copolymer. During the synthesis of the PPESK copolymer, two monomers, one catalyst, and one dehydrant were added into a solvent. Then, the product was filtered, precipitated and dried. Usually, the polymerization reaction is not 100% completed. Thus, there may be some monomers, catalyst, or dehydrant left in the copolymer matrix. These substances could be removed out once the prepared membrane was immersed into those chemicals. Nevertheless, the weight loss is not significant. Further, no apparent membrane degradation was observed up to 30 days. Therefore, it can be concluded that the PPESK copolymer can tolerate these commonly used acids, bases and oxidants for at least one month under the experimental condition tested here.

Fig. 5 shows the variation of the membrane thickness as a function of time. The  $y$ -axis gives the relative thickness, which is defined as the ratio of the membrane thickness at time  $t$ ,  $L_t$ , to the initial membrane thickness,  $L_0$ . Again the membrane was vacuum dried before each measurement. It can be seen that for all the chemicals tested, the relative membrane thickness was less than one within the first several days, indicating that the membrane was shrunk. This may be due to the loss of the entrapped impurities (monomers, catalyst, and dehydrant etc) in the polymer matrix, as discussed above. However, as the immersion time increases, different chemicals show different trends. After 30 days immersion, the thickness of the membranes

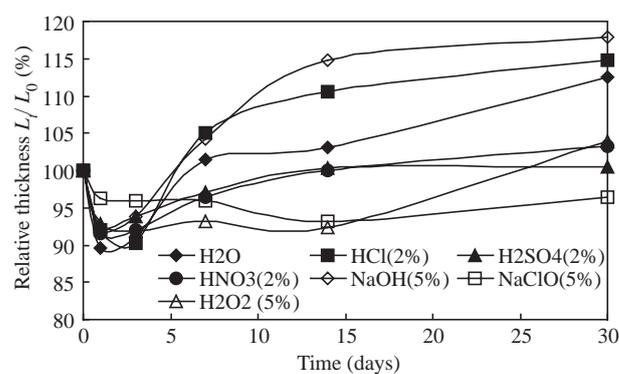


Fig. 5. Influence of chemical solutions on the relative thickness of PPESK homogeneous membranes. Temperature of membranes treating by reagents was  $40^\circ\text{C}$ .

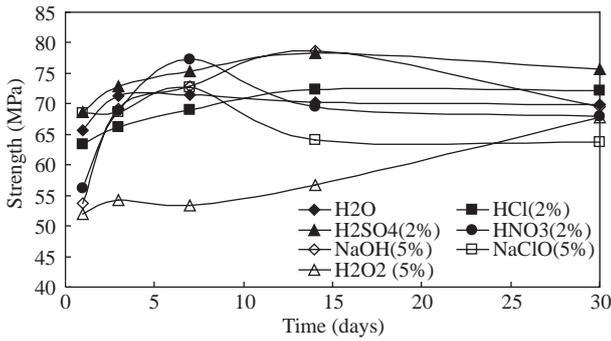


Fig. 6. Influence of chemical solutions on the strength of PPESK homogeneous membranes. Temperature of membranes treating by reagents was 40°C.

immersed in NaClO, H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> is similar to that of the fresh membranes. However, the thickness of those membranes immersed in H<sub>2</sub>O, HCl and NaOH is significant larger than that of the fresh membranes, indicating that the membranes were swollen in these chemicals. Interestingly, when the 30th day data in Fig. 4 is compared to that in Fig. 5, the order of these values from the top to the bottom in these two figures is in general reversed. For example, Fig. 4 shows the largest and smallest loss of the membrane weight in NaOH and NaClO, respectively, while Fig. 5 shows the largest increase and decrease of the membrane thickness in NaOH and NaClO, respectively. This is because the more swollen a membrane by a chemical, the larger distance between the polymer chains, and the larger free volume or passage path to allow the impurity molecules move out of the polymer matrix. From Figs. 4 and 5, it can be seen that the PPESK copolymer is more tolerant for oxidants than bases.

Fig. 6 shows the variation of the membrane strength as a function of time. Interestingly, for each chemical an initial increase in the membrane strength can be clearly seen. Presumably, the extraction of those impurities

(monomers, catalyst, and dehydrant etc) may contribute to this change. It seems that oxidants affect the membrane strength greater than acids and bases. However, except for H<sub>2</sub>O<sub>2</sub>, the membrane strength does not change significantly with time, for other chemicals. The average membrane strength was around 65 MPa.

Based on these results, it can be concluded that the PPESK copolymer has excellent resistance for acids, bases and oxidants.

### 3.3. Rheological property

The rheological behavior of a membrane casting solution is very important, since it determines the membrane morphology and performance. In this study, NMP was tested as the solvent, and two additives, PEG1000 and Tween80, have been used. Fig. 7 shows the variation of the apparent viscosity of the PPESK/NMP solution as a function of the PPESK concentration and temperature. The *y*-axis gives the natural logarithm of the apparent viscosity in cp,  $\ln(\eta)$ , while the *x*-axis gives the reciprocal value of the temperature in K,  $1/T$ . Six PPESK concentrations have been investigated. For each concentration, a straight line was obtained, indicating that the Arrhenius equation could be used to describe the temperature effect on the apparent viscosity of the polymer solution. The viscous flow activation energy, *E*, can be calculated from the slope of the straight line. Table 1 lists these equations and the calculated viscous flow activation energy. It can be seen that as the PPESK concentration increases, the viscous flow activation energy increases, i.e. the apparent viscosity of the PPESK/NMP solution increases with the increase of the PPESK concentration. The larger the viscous flow activation energy of a solution, the more energy is needed when the molecular conformation is transformed, and the more difficult for the membrane formation to happen. By correlating all the data, the following equation was obtained,

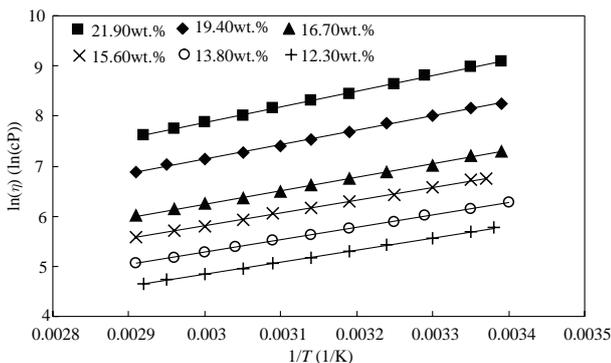


Fig. 7. Variation of the apparent viscosity of PPESK/NMP solutions with the PPESK concentration and temperature.

$$\ln(\eta) = \left( \frac{627.6}{RT} + 0.1202 \right) C + \left( \frac{11953}{RT} - 3.8044 \right) \quad (1)$$

where *C* is the PPESK concentration in wt. %. The relative error between the predicted values from Equation (1) and the experimental results is less than 2%.

Fig. 8 shows the effect of PEG1000 on the apparent viscosity of the PPESK/PEG1000/NMP solution. The PPESK concentration was kept at 16 wt.%. Five PEG1000 concentrations have been investigated. Similarly, the Arrhenius equation was used to correlate the data, as listed in Table 2. It can be seen that as the PEG1000 concentration increases, the apparent viscosity increases. Therefore, although the addition of PEG1000 may enhance the formation of the membrane structure,

Table 1

Correlated Arrhenius equations and calculated viscous flow activation energy for PPESK/NMP solutions at different PPESK concentrations.

Concentration of PPESK wt.%	Arrhenius equation	Viscous flow activation energy, $E\eta$ (kJ/mol)
12.3	$\ln(\eta) = 2399.5/T - 2.3549$	19.949
13.8	$\ln(\eta) = 2477.3/T - 2.1497$	20.596
15.6	$\ln(\eta) = 2576.4/T - 1.9221$	21.42
16.7	$\ln(\eta) = 2671.9/T - 1.7771$	22.214
19.4	$\ln(\eta) = 2880.2/T - 1.5019$	23.946
21.9	$\ln(\eta) = 3124.8/T - 1.5001$	25.980

it also increases the viscosity of the membrane preparation solution. Thus, the additive concentration should be optimized. A general correlation was obtained as

$$\ln(\eta) = \left( \frac{268.7}{RT} + 0.0605 \right) C + \left( \frac{21867}{RT} - 1.7964 \right). \quad (2)$$

The relative error is less than 1%.

Fig. 9 shows the effect of Tween80 on the apparent viscosity of the PPESK/Tween80/NMP solution. Again, the PPESK concentration was 16 wt.%. Five Tween80 concentrations have been investigated. Similarly, the Arrhenius equation was used to correlate the experimental data, as listed in Table 3. Similar to PEG1000, as the Tween80 concentration increases, the apparent viscosity increases. Thus, when Tween80 is used as an additive, its concentration should also be optimized. The following correlation can be used to calculate the viscosity for a PPESK/Tween80/NMP solution:

$$\ln(\eta) = \left( \frac{403}{RT} + 0.1008 \right) C + \left( \frac{21838}{RT} - 1.7533 \right). \quad (3)$$

The relative error is less than 1%.

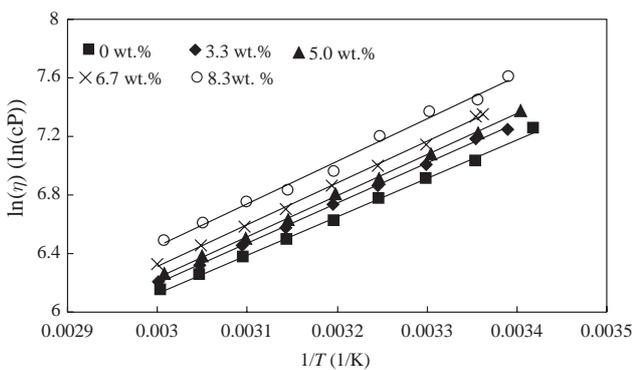


Fig. 8. Variation of the apparent viscosity of PPESK/PEG1000/NMP solutions with the PEG1000 concentration and temperature.

Comparing Equations (2) and (3), it can be seen that the effect of Tween80 on the apparent viscosity is greater than that of PEG1000, indicating that Tween80 depresses the solvation effect of the PPESK/NMP solution more significant than PEG1000. Tween80 has two effects. On the one hand, it is a surfactant which decreases the interfacial surface energy of the PPESK solution. On the other hand, it also combines strongly to NMP by hydrogen bond, to decrease the solubility of NMP. This results in an increased viscosity of the polymer solution.

#### 3.4. Viscosity effect on the membrane structure and performance

The precipitation rate (or gelation rate) of a PPESK/NMP solution immersed in DI water was investigated using the OM-CCD system [37]. Fig. 10 shows the variation of the thickness of the precipitated polymer layer as a function of time. Four different PPESK concentrations have been tested, i.e., 13.8, 15.6, 16.7 and 19.4 wt.%. As can be seen, a typical concave downward curve was obtained for each polymer solution. At the beginning, the precipitation rate was fast. It then gradually decreased. As the PPESK concentration increases, the precipitated polymer layer decreases, indicating a decreased precipitation rate. This phenomenon can be more clearly seen from the data obtained after the first 6 s. From the inserted picture in Fig. 10, it can be seen that the same phenomenon is also observed in the very beginning of the gelation process. The calculated average gelation rate within the first 0.1 s was 224.6, 177.1, 96.2, and 72.7  $\mu\text{m s}^{-1}$ , for polymer concentration of 13.8, 15.6, 16.7 and 19.4 wt.%, respectively.

According to Equation (1), for solutions with the PPESK concentration of 13.8, 15.6, 16.7 and 19.4 wt.%, the calculated viscosity (the room temperature is 25°C) is 477.7, 935.4, 1410.5, and 3864.9 cp, respectively. Based on the Stokes–Einstein equation shown in Equation (4), the diffusivity of a molecule within a polymer solution is inversely proportional to the viscosity of the solution. In Equation (4),  $D$  is the diffusion coefficient,  $k$  is the

Table 2

Correlated Arrhenius equations and calculated viscous flow activation energy for PPESK/PEG1000/NMP solutions at different PEG1000 concentrations.

Concentration of PEG1000 wt. %	Arrhenius equation	Viscous flow activation energy, $E_\eta$ (KJ/mol)
0	$\ln(\eta) = 2633.0/T - 1.7737$	21.891
3.3	$\ln(\eta) = 2739.6/T - 2.0241$	22.777
5	$\ln(\eta) = 2783.2/T - 2.1100$	23.140
6.7	$\ln(\eta) = 2840.4/T - 2.2079$	23.615
8.3	$\ln(\eta) = 2907.4/T - 2.2752$	24.172

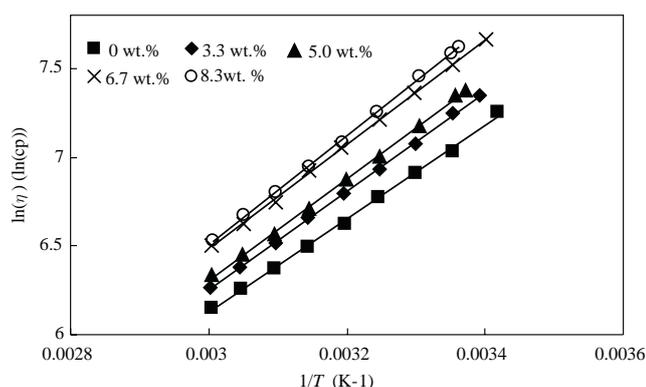


Fig. 9. Variation of the apparent viscosity of PPESK/Tween80/NMP solutions with the Tween80 concentration and temperature.

Boltzman constant,  $T$  is the temperature,  $\eta$  is the viscosity, and  $r$  is the particle radius. As the viscosity increases, the diffusivity of both the nonsolvent molecules (water in this study) into the polymer solution, and the solvent (NMP in this study) out of the polymer solution decreases, leading to a decreased gelation rate:

$$D = \frac{kT}{6\pi\eta r} \quad (4)$$

Fig. 11 shows the SEM images (magnification: 2500 $\times$ ) of the prepared ultrafiltration flat sheet membranes using the four PPESK solutions, while Fig. 12 shows the water permeation and BSA rejection results. From Fig. 11, obvi-

ously an asymmetric membrane structure was obtained for all four solutions, which consists of a dense layer and a finger pore type support layer. From Fig. 12, as the PPESK concentration increases, the BSA rejection increases. However, the water flux result is very interesting. It firstly decreases as the PPESK concentration was increased to 15.6 wt.% from 13.8 wt.%. However, it maintains almost a constant as the concentration is further increased. The BSA rejection is mainly affected by the top dense layer. The denser the top layer, the higher the BSA rejection. It is well known that a slow precipitation usually results in a denser, and more isotropic dense layer, while a rapid precipitation often produces a more porous and anisotropic dense layer [38]. The increase of the polymer concentration not only decreases the diffusivity of the nonsolvent and solvent molecules, but also decreases the mobility of the polymer molecules, leading to a longer time to separate the polymer solution into two phases, i.e., the polymer rich and poor phases. This slowed phase separation process provides enough time for the rich phase to coalesce, thus to form denser top layers [43,44]. Therefore, the BSA rejection results are reasonable. The water flux, on the other hand, is affected by both the dense layer and the support layer. Compared to the support layer, the dense layer may have much high resistance per unit thickness. However the total thickness of the support layer is much larger than the dense layer. For example, in this study, the thickness of the prepared dense layer is only several micrometers, while the support layer is around 150  $\mu\text{m}$ . Therefore, the resistance for the water passing through the support layer may not be ignored.

Table 3

Correlated Arrhenius equations and calculated viscous flow activation energy for PPESK/Tween80/NMP solutions at different Tween80 concentrations.

Concentration of Tween80 wt. %	Arrhenius equation	Viscous flow activation energy, $E_\eta$ (kJ/mol)
0	$\ln(\eta) = 2633.0/T - 1.7737$	21.891
3.3	$\ln(\eta) = 2773.8/T - 2.0664$	22.878
5	$\ln(\eta) = 2867.4/T - 2.2964$	23.839
6.7	$\ln(\eta) = 2930.0/T - 2.3033$	24.36
8.3	$\ln(\eta) = 3061.1/T - 2.6753$	25.45

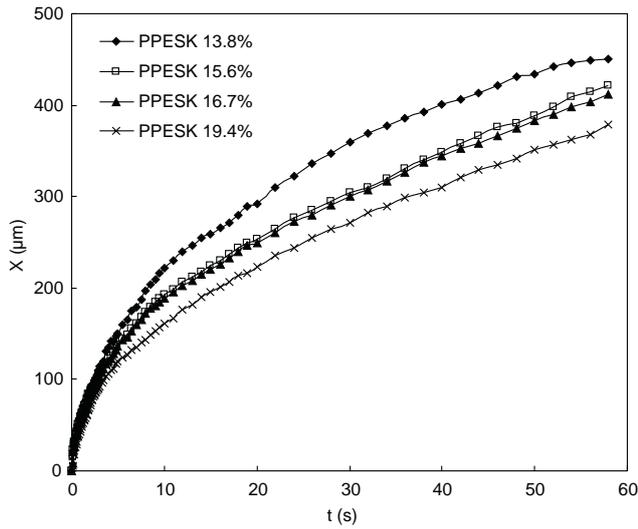


Fig. 10. Influence of the PPESK concentration on the gelation rate of the polymer solution.

From Fig. 11, one can see that as the PPESK concentration increases, the thickness of the dense layer increases. For the support layer, it is generally known that increased polymer concentrations suppress the macrovoid formation and the macrovoid size. However, on the other hand, the total membrane thickness might decrease when

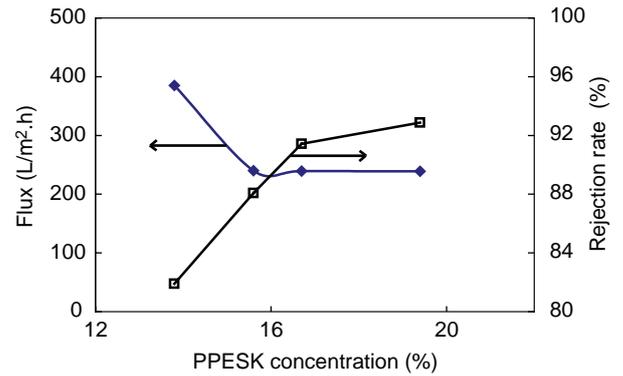


Fig. 12. Variation of the pure water flux and BSA rejection of PPESK membranes at various PPESK concentrations. Testing temperature was 25°C, and the trans-membrane pressure was 0.1 MPa.

using higher polymer concentrations. This may result in a decreased resistance for the water to pass through the support layer. However, this is just an assumption and further study is needed to better understand this issue.

These results presented here confirm that the viscosity of the membrane preparation solution has a significant effect on the performance of the prepared membranes. Therefore, it should be carefully optimized and controlled. The effect of the additives on the membrane morphol-

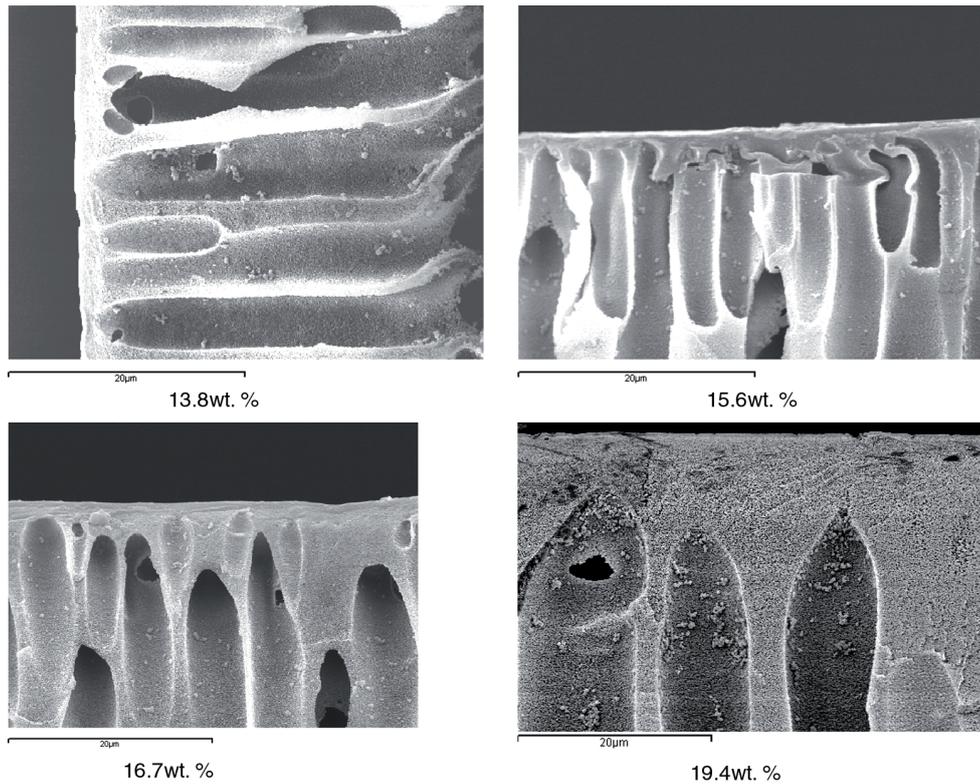


Fig. 11. SEM images of ultrafiltration membranes at various PPESK concentrations.

ogy and performance have been investigated and will be reported later.

#### 4. Conclusion

PPESK material shows a very high glass transition temperature of around 280°C, which makes it a very good material to be used in high temperature applications. This copolymer also possesses a superior mechanical strength, excellent acidic resistance, alkali resistance and oxidative tolerance. PPESK can be easily dissolved in NMP. The addition of additives, either PEG1000 or Tween80, all increases the viscosity of the membrane preparation solution. Ultrafiltration membrane results show that, the viscosity of the membrane casting solution has a significant effect on the membrane performance. Therefore, the membrane casting solution should be carefully optimized. The results presented here show that PPESK is a very promising material to prepare membranes, which may find potential application in high temperature or other hostile environment.

#### Acknowledgements

Financial support was provided by the Major State Basic Research Development Program of China (973 Program, No. 2003CB61570, No. 2007CB714304), the National Natural Science Foundation of China (No. 20806006).

#### References

- [1] W.S.W. Ho and K.K. Sirkar, *Membrane Handbook*, van Nostrand Reinhold, New York, 1992.
- [2] J. Schaefer, Reliable water supply by reusing wastewater after membrane treatment, *Desalination*, 138 (2001) 91.
- [3] R.W. Baker, E.L. Cussler, W. Eykamp, W.J. Koros, R.L. Riley and H. Strathmann, *Membrane Separation System*, Noyes Data Corporation, 1991.
- [4] M.J.H. Snow, D. de Winter, R. Buckingham, J. Campbell and J. Wagner, New techniques for extreme conditions: High temperature reverse osmosis and nanofiltration, *Desalination*, 105 (1996) 57.
- [5] A. Erswell, C.J. Brouckaert and C.A. Buckley, The reuse of reactive dye liquors using charged ultrafiltration membrane technology, *Desalination*, 70 (1988) 157.
- [6] M. Cheryan, *Ultrafiltration and Microfiltration Handbook*; Pa. Technomic Publishing, Lancaster, 1998.
- [7] Y. Meng, A.S. Hay, X. Jian and S.C. Tjong, Synthesis of novel poly (phthalazinone ether sulfone ketone)s and improvement of their melt flow properties, *J. Appl. Polym. Sci.*, 66 (1997) 1425.
- [8] X. Jian, Y. Dai, L. Zeng and R. Xu, Application of poly (phthalazinone ether sulfone ketone)s to gas membrane separation, *J. Appl. Polym. Sci.*, 71 (1998) 2385.
- [9] X. Jian, Y. Dai, G. He and G. Chen, Preparation of UF and NF poly (phthalazine ether sulfone ketone) membranes for high temperature application, *J. Membr. Sci.*, 161 (1999) 185.
- [10] Y. Xuan, Y. Gao, Y. Huang and X. Jian, Synthesis and characterization of a novel phthalazinone poly(aryl ether sulfone ketone) with carboxyl group, *J. Appl. Polym. Sci.*, 88 (2003) 1111.
- [11] Y. Dai, X. Jian, X. Liu and M.D. Guiver, Synthesis and characterization of sulfonated poly (phthalazinone ether sulfone ketone) for ultrafiltration and nanofiltration membranes, *J. Appl. Polym. Sci.*, 79 (2001) 1685.
- [12] Y. Su, X. Jian, S. Zhang and G. Wang, Preparation and characterization of quaternized poly (phthalazinone ether sulfone ketone) NF membranes, *J. Membr. Sci.*, 241 (2004) 225.
- [13] B. Zhang, T.H. Wang, S.H. Zhang, J.S. Qiu and X.G. Jian, Preparation and characterization of carbon membranes made from poly (phthalazinone ether sulfone ketone), *Carbon*, 2006, 44(13) 2764.
- [14] Y. Dai, X. Jian, S. Zhang and M.D. Guiver, Thermostable ultrafiltration and nanofiltration membranes from sulfonated poly (phthalazinone ether sulfone ketone), *J. Membr. Sci.*, 188 (2001) 195.
- [15] Y. Dai, X. Jian, S. Zhang and M.D. Guiver, Thin film composite (TFC) membranes with improved thermal stability from sulfonated poly (phthalazinone ether sulfone ketone) (SPPEK), *J. Membr. Sci.*, 207 (2002) 189.
- [16] S. Zhang, X. Jian and Y. Dai, Preparation of sulfonated poly (phthalazinone ether sulfone ketone) composite nanofiltration membrane, *J. Membr. Sci.*, 246 (2005) 121.
- [17] J.B. Li, J.W. Zhu and M.S. Zheng, Morphologies and properties of poly (phthalazinone ether sulfone ketone) matrix ultrafiltration membranes with entrapped TiO<sub>2</sub> nanoparticles, *J. Appl. Polym. Sci.*, 103(6) (2007) 3623.
- [18] B. Zhang, T.H. Wang, S.L. Liu, S.H. Zhang, J.S. Qiu, Z.G. Chen and H.M. Cheng, Structure and morphology of microporous carbon membrane materials derived from poly (phthalazinone ether sulfone ketone), *Micropor. Mesopor. Mater.*, 96(1–3) (2006) 79.
- [19] Y.Q. Yang, D.L. Yang, S.H. Zhang, J. Wang and X.G. Jian, Preparation and characterization of poly (phthalazinone ether sulfone ketone) hollow fiber ultrafiltration membranes with excellent thermal stability, *J. Membr. Sci.*, 280(1–2) (2006) 957.
- [20] C.R. Wu, S.H. Zhang, D.L. Yang, J. Wei, C. Yan and X.G. Jian, Preparation, characterization and application in wastewater treatment of a novel thermal stable composite membrane, *J. Membr. Sci.*, 279(1–2) (2006) 238.
- [21] L.P. Zhu, B.K. Zhu and Y.Y. Xu, Preparation and performances of poly (phthalazinone ether sulfone ketone) hollow fiber membranes with excellent thermotolerance, *J. Appl. Polym. Sci.*, 101(2) (2006) 878.
- [22] J. Wei, S.H. Zhang, C.N. Wu and X.G. Jian, Relationship between interfacial polymerization monomer structure and separation properties of PPESK based composite membranes, *Acta Polymerica Sinica*, 2 (2006) 298–302.
- [23] P.Y. Qin, C.X. Chen, Y.B. Yun, Z. Chen, T. Shintani, X. Li, J.D. Li and B.H. Sun, Formation kinetics of a poly (phthalazine ether sulfone ketone) membrane via phase inversion, *Desalination*, 188(1–3) (2006) 229.
- [24] Y.Q. Yang, X.G. Jian, D.L. Yang, S.H. Zhang and L.J. Zou, Poly (phthalazinone ether sulfone ketone) (PPESK) hollow fiber asymmetric nanofiltration membranes: Preparation, morphologies and properties, *J. Membr. Sci.*, 270(1–2) (2006) 1.

- [25] Y.B. Yun, Y.H. Tian, G.L. Shi, J.D. Li and C.X. Chen, Preparation, morphologies and properties for flat sheet PPESK ultrafiltration membranes, *J. Membr. Sci.*, 270(1–2) (2006) 146.
- [26] J. Wei, X.G. Jian, C.R. Wu, S.H. Zhang and C. Yan, Influence of polymer structure on thermal stability of composite membranes, *J. Membr. Sci.*, 256(1–2) (2005) 116.
- [27] D.S. Kim, K.H. Shin, H.B. Park and Y.M. Lee, Preparation and characterization of sulfonated poly (phthalazinone ether sulfone ketone) (SPPEK)/silica hybrid membranes for direct methanol fuel cell applications, *Macromol. Res.*, 12 (2004) 413.
- [28] S. Go, G.H. He, X.M. Wu, C.N. Li, H.J. Liu, C. Lin and X.C. Li, Synthesis and characteristics of sulfonated poly (phthalazinone ether sulfone ketone) (SPPEK) for direct methanol fuel cell (DMFC), *J. Membr. Sci.*, 281(1–2) (2006) 121–129.
- [29] C.Y. Zeng, J.D. Li, P. Li, T.Q. Chen, Y.Z. Lin, D. Wang and C.X. Chen, A novel transport model for sorption and desorption of penetrants in dense polymeric membranes, *Chem. Eng. Sci.*, 61(6) (2006) 1892.
- [30] X. Shao, W. Liu and Q. Xue, The tribological behavior of micrometer and nanometer  $\text{TiO}_2$  particle-filled poly (phthalazine ether sulfone ketone) composites, *J. Appl. Polym. Sci.*, 92 (2004) 906.
- [31] X. Shao, J. Tian, W. Liu, Q. Xue and C. Ma, Tribological properties of  $\text{SiO}_2$  nanoparticle filled-phthalazine ether sulfone/phthalazine ether ketone (50/50 mol %) copolymer composites, *J. Appl. Polym. Sci.*, 85 (2002) 2136.
- [32] Y. Meng, S.C. Tjong and A.S. Hay, Morphology, rheological and thermal properties of the melt blends of poly (phthalazinone ether ketone sulfone) with liquid crystalline copolyester, *Polymer*, 39 (1998) 1845.
- [33] W. He, G.X. Liao, X.G. Jian and X.B. Feng, Dynamic mechanical thermal behaviour of novel poly (phthalazinone ether sulfone ketone) and poly (tetrafluoroethylene) blends, *J. Polym. Eng.*, 26(6) (2006) 617.
- [34] P. Chen, C. Lu, Q. Yu, Y. Gao, J.F. Li and X.L. Li, Influence of fiber wettability on the interfacial adhesion of continuous fiber-reinforced PPESK composite, *J. Appl. Polym. Sci.*, 102(3) (2006) 2544.
- [35] W. He, G.X. Liao, X.G. Jian, L.M. Dong and P. Wang, A study on thermal and dynamic mechanical properties of PPESK/PES blends, *Acta Polymerica Sinica*, 1 (2006) 108.
- [36] X. Shao, Q.J. Xue, W.M. Liu, M.Y. Teng, H.H. Liu and X.Q. Tao, Tribological behavior of micrometer- and nanometer- $\text{Al}_2\text{O}_3$ -particle-filled poly (phthalazine ether sulfone ketone) copolymer composites used as frictional materials, *J. Appl. Polym. Sci.*, 95(5) (2005) 993.
- [37] P. Qin, C. Chen, B. Han, S. Takuji, J. Li and B. Sun, Preparation of poly (phthalazinone ether sulfone ketone) asymmetric ultrafiltration membrane: II. The gelation process, *J. Membr. Sci.*, 268 (2006) 181.
- [38] R.W. Baker, *Membrane Technology and Applications*; McGraw-Hill, New York, 2000.
- [39] S. Zhang, Y. Qu, Y. Liu, F. Yang, X. Zhang, K. Furukawa and Y. Yamada, Experimental study of domestic sewage treatment with a metal membrane bioreactor, *Desalination*, 177 (2005) 83.
- [40] M. Amara and H. Kerdjoudj, A modified anion-exchange membrane applied to purification of effluent containing different anions. Pre-treatment before desalination, *Desalination*, 206 (2007) 205.
- [41] J. Zhang, L. Chen and H. Zeng, Pilot testing of outside-in MF and UF modules used for cooling tower blowdown pretreatment of power plants, *Desalination*, 214 (2007) 287.
- [42] K. Boussua, B. Van der Bruggena, A. Volodinb, C. Van Haesendonck, J.A. Delcour, P. Van der Meeren and C. Vandecasteele Characterization of commercial nanofiltration membranes and comparison with self-made polyethersulfone membranes, *Desalination*, 191 (2006) 245.
- [43] T.H. Youn and L.W. Chen, Pore formation mechanism of membranes from phase inversion process, *Desalination*, 103 (2005) 233.
- [44] Y.D. Kim, J.Y. Kim, H.K. Lee and S.C. Kim, Formation of polyurethane membranes by immersion precipitation. II. Morphology formation, *J. Appl. Polymer Sci.*, 74 (1999) 2124.