

Preparation and Properties of Poly(aryl ether sulfone ketone) Ultrafiltration Membrane Containing Fluorene Group for High Temperature Condensed Water Treatment

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Abstract Novel poly(aryl ether sulfone ketone)s (PAESK) were synthesized from bisphenol A (BPA), 9,9'-bis(4-hydroxyphenyl) fluorene (BHPF), 4,4'-dichlorodiphenylsulfone (DCS) and 4,4'-difluorobenzophenone (DFB) via nucleophilic substitution polymerization, which were subsequently used to fabricate ultrafiltration membrane by phase-inversion method for high temperature condensed water treatment. The obtained high molecular weight co-polymers with fluorene group with good solubility and good thermal stability, can be easily cast into flexible, white and non-transparent flat films. The influence of molar ratio of BPA and BHPF on the properties of the prepared co-polymers and membranes was investigated in detail. SEM study of the morphology of the membranes indicated that the prepared membranes possessed homogeneous pores on the top surface and were sponge-like or finger-like in cross-section. Pure water flux of the membranes increased from $71.87 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ to $247.65 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$, while the retention of BSA decreased slightly, and the water contact angle decreased from 82.1° to 55.6° with the PVP concentration from 0 wt% to 10 wt%. With increasing concentration of PVP, the mechanical properties of membranes decreased, while the thermal stability increased. The permeate flux measurement showed that the PAESK membrane had the potential for high temperature condensed water treatment.

Keywords Poly(aryl ether sulfone ketone); Fluorene group; Thermal stability; Ultrafiltration membrane

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INTRODUCTION

High temperature condensed water (80–120 °C) is generated from condensation of high pressure steam during the heat exchange process^[1], which usually contains excessive content of oil and iron ion due to leakage and corrosion of equipments^[2]. If it is discharged directly to the aquatic environment, it can cause energy lost and thermal emission pollution^[3–5].

Several technologies have been used for condensed water treatment, including activated carbon adsorption, mixed-bed ion exchange, powder resin filtration, functional fiber filtration and electrodeionization^[6–8]. However, these conventional methods suffer from several problems, including operational instability, high cost and secondary waste pollution. On the other hand, membrane separation process, with the advantages of high separation efficiency, less energy consumption, simple operation, has been an attractive technique for water treatment^[9, 10].

Poly(phthalazine ether sulfone ketone) (PPESK), containing rigid phthalazine structure and aromatic rings, is known to be an excellent membrane material with

extraordinary mechanical strength, thermal stability, and good chemical resistance^[11–14]. However PPESK membrane is hydrophobic and often causes severe proteins or microorganisms fouling^[15].

Shimura *et al.*^[16] prepared a series of sulfonated poly(aryl ether sulfone)s from different sulfonated monomers and 9,9'-bis(4-hydroxyphenyl)fluorene (BHPF), and the obtained membranes showed high thermal stability and low dimensional change due to the incorporation of rigid fluorene moieties. Harrison *et al.*^[17] prepared sulfonated poly(aryl ether sulfone)s membranes with hexafluoro bisphenol A (6F-BPA) that demonstrated low glass transition temperatures and good mechanical property due to the flexible moieties. Hence, it is necessary to modify the chemical structure of polymer to achieve both thermal stability and good mechanical property, and to maintain high permeability and good hydrophilicity, *etc.* The features mentioned above inspire the idea to synthesize the compound involving BPA and BHPF.

In this paper, we synthesized a novel co-polymer containing 9,9'-bis(4-hydroxyphenyl)fluorene (BHPF) to fabricate thermostable membrane for high temperature condensed water treatment. A series of poly(aryl ether sulfone ketone)s (PAESKs) obtained from both BPA and BHPF were synthesized through the nucleophilic substitution

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reaction. The influence of monomer composition on the chemical and thermal properties of the co-polymers was investigated. The ultrafiltration membranes of PAESKs were prepared using phase-inversion method, and the influences of molar ratio of monomers, polymer concentration, PVP concentration on the pure water flux (PWF), hydrophilicity, porosity, mechanical property and thermal properties of the membranes were studied.

EXPERIMENTAL

Materials

Bisphenol A (BPA) was purchased from Tianjin Guangfu Fine Chemical Research Institute (China). 9,9-Bis(4-hydroxyphenyl)fluorene (BHPF) was purchased from Wuhan Chi-Fi Chemical Co., Ltd (China). 4,4'-Difluorobenzophenone (DFB) was purchased from Sun Chemical Technology (Shanghai) Co., Ltd (China), and recrystallized from ethanol before use. 4,4'-Dichlorodiphenyl sulfone (DCS) was purchased from Alfa Aesar (Tianjin) Chemical Co., Ltd (China). Tetramethylene sulfone was purchased from Aladdin Co., Ltd (China), and refluxed over sodium hydroxide and activated carbon for 2 h, then distilled in vacuum. Tetramethylene sulfone and distilled water were used as the solvent and the nonsolvent agents, respectively. Poly(vinylpyrrolidone) [PVP (K30)] used as additive in the preparation of ultrafiltration membrane was obtained from Tianjin Damao Chemical Regent Factory (China). The bovine serum albumin (BSA, 68 kDa) used as a probe molecule for solute rejection test was obtained from Beijing Dingguo Changsheng Biotechnology Co., Ltd (China). All reagents used in the experiments were analytical grade and purified by conventional methods.

Synthesis of PAESK Co-polymers

The co-polymers described in this work were synthesized by the aromatic nucleophilic substitution reaction of BPA with BHPF, DFB and DCS. For the co-polymer synthesis, seven different molar concentrations of BPA and BHPF were used as described in Table 1.

Polymerization reaction was conducted in a 250 mL four-neck flask, which was generally equipped with a mechanical stirrer, nitrogen inlet, thermometer, Dean-Stark trap and condenser. A schematic representation of the reaction is

Table 1 Copolymer formulations used in the polycondensation reaction

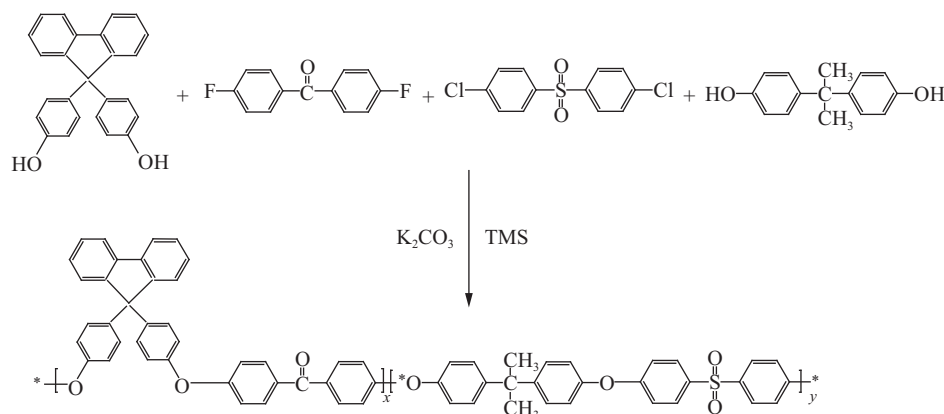
Polymer	BPA (mmol)	BHPF (mmol)	Molar ratio ^a (BPA:BHPF)
PAESK-10	20.00	0	1:0
PAESK-31	15.00	5.00	3:1
PAESK-21	13.33	6.67	2:1
PAESK-11	10.00	10.00	1:1
PAESK-12	6.67	13.33	1:2
PAESK-13	5.00	15.00	1:3
PAESK-01	0	20.00	0:1

^a Molar ratio of DCS and DFB is 1:1

given in Scheme 1. The reaction vessel was charged with solvent tetramethylene sulfone (30 mL), toluene (30 mL) as the dehydration solvent, and anhydrous potassium carbonate as the catalyst (3.3166 g, 24 mmol). In a typical copolymerization reaction, BPA:BHPF (1:1), a mixture of BPA (2.2829 g, 10 mmol), BHPF (3.5041 g, 10 mmol), DFB (2.1820 g, 10 mmol), and DCS (2.8716 g, 10 mmol) were added to the reaction system. The mixture was stirred under nitrogen atmosphere for 30 min, and then heated until the toluene began to reflux. The reflux temperature was kept between 135 and 140 °C until there was no water observed in the Dean-Stark trap. Then the system was heated to 180 °C during dehydration to remove the toluene from the reaction mixture to obtain the co-polymer. The viscous solution was poured into boiling distilled water to precipitate out polymer solid threads, and washed with ethanol for several times. The white fibrous co-polymer was then dried in a vacuum oven at 80 °C for 24 h with a yield over 95%.

Characterization of Co-polymers

Fourier transform infrared (FTIR) spectra of the polymers were recorded using a Nicolet Avatar-360 spectrophotometer. The proton nuclear magnetic resonance (¹H-NMR) spectra (400 MHz) were recorded on a Bruker AVANCE 400 instrument in CDCl₃ using tetramethylsilane (TMS) as the internal standard. Molecular weights and polydispersity index (PDI) were determined by gel permeation chromatography (GPC) with an Agilent 1100 instrument. Molecular weights were calculated from a calibration plot constructed using polystyrene (PS) standards and tetrahydrofuran (THF) was used as the mobile phase.



Scheme 1 Reaction route to the synthesis of PAESK co-polymer

The thermogravimetric analysis (TGA) was conducted on NETZSCH STA 449-C at a heating rate of 10 °C/min in air, and the glass transition temperature (T_g) was measured at the same heating rate in a nitrogen atmosphere. The obtained T_g values were recorded from the second scan after the first heating and quenching.

Membrane Preparation

PAESK membranes were prepared using phase inversion method. PVP was dissolved in DMAc in a 100 mL three-neck-round flask and stirred at 45 °C until a transparent solution was obtained. Then PAESK was added to the PVP solution in DMAc, and mixed by stirring for 6 h at 45 °C till the polymer solution became homogeneous. The composition of the casting solution was: 13 wt%–18 wt% (PAESK)/0 wt%–10 wt% (PVP)/72 wt%–87 wt% (DMAc). The lid of the container was kept closed to prevent the evaporation of solvent. Afterwards, the dope solution was cast on a smooth glass plate by a casting knife of 200 µm thickness at room temperature. After 20 s evaporation time in the air, the glass plate was immediately immersed in the coagulation bath (distilled water) to initiate the non-solvent induced phase separation. Then, the membrane was thoroughly rinsed with deionized water for complete solvent removal, and was stored in distilled water for 24 h to guarantee complete phase separation.

Membrane Characterization

Morphology observation

A scanning electron microscope (SEM, Hitachi S4800HSD) was used to observe the cross-section and surface morphology of the membranes. All the membranes were freeze-fractured under cryogenic condition using liquid nitrogen and sputter-coated with gold before being tested.

Mechanical properties

The mechanical properties of membranes were determined by Electron-Mechanical Universal Material Testing Machine (WD-1, China). Measurements were carried out at room temperature with a strain rate of 2 mm/min. The membranes were cut into rectangular strips with an effective dimension of 70 mm × 20 mm. An average of at least five individual measurements was used for each sample.

Hydrophilicity analysis

Hydrophilicity of membranes was evaluated by the contact angle between water and membrane surface by the surface wetting instrument (DSA10-MK2, KRÜSS, Germany). The contact angle was determined in 10 s after the water was dropped and measured at three different locations on the membrane surface and the results were reported as an average value.

Pure water flux (PWF)

Permeation flux studies were carried out by a dead-end stirred ultrafiltration (UF) cell (MSC-300, Shanghai, China). Effective area of the membrane in the module was 36.30 cm². The membranes were characterized in the module after pretreatment with pure water under 0.15 MPa pressure for 30 min. Then PWF was measured under a pressure of 0.10 MPa at ambient temperature. The PWF was calculated as Eq. (1):

$$J_w = \frac{Q}{A\Delta t} \quad (1)$$

where Q is the total volume (L) of the water during the experiment, A is the effective membrane area (m²), Δt is the sampling time (h), and J_w is the pure water flux (L·m⁻²·h⁻¹).

Molecular weight cut-off (MWCO) of membrane

Solute rejection measurements were carried out by the same instrument as pure water flux experiment. A concentration of bovine serum albumin (BSA, 68 kDa) was used to determine the membrane rejection (R , %), which was calculated as Eq. (2):

$$R(\%) = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (2)$$

where c_p and c_f are the concentrations of the permeate solution and the feed solution, respectively. The BSA concentrations in the permeation and feed solutions were measured by using a UV-Vis spectrophotometer (Persee TU 1901, Beijing) at a wavelength of 280 nm.

Membrane porosity

Membrane porosity (P_r) has an important influence on the property of the membranes. The weight loss of wet membrane after its drying was used to measure membrane porosity. The membrane, stored with distilled water, was weighed after wiping away superficial water with filter paper. Then, the wet membrane was placed between two clean glass-plates until its drying before measuring the dry weight. The porosity of the membranes was calculated using Eq. (3):

$$P_r = \frac{W_0 - W_1}{\rho_w AL} \times 100\% \quad (3)$$

where P_r (%) is the membrane porosity, W_0 is the weight of the wet membrane, W_1 is the weight of the dry membrane, ρ_w is the density of distilled water, A is the membrane area, and L is the membrane thickness. The membrane porosity of each membrane was measured three times and the average values were reported.

Permeate flux of high temperature condensed water

The permeate flux experiments were carried out using high temperature condensed water in order to evaluate the filtration stability of membranes. The high temperature condensed water, prepared by dissolving a specified amount of Fe²⁺, SDS and diesel into distilled water, was fed to the membrane side. The membranes were characterized in the module after pretreatment with pure water under 0.16 MPa pressure for 20 min. Then PWF was measured under a pressure of 0.10 MPa at ambient temperature. After that, the membranes were pretreated by high temperature water (80 °C) for 20 min, finally, fed with high temperature condensed water (90 °C).

RESULTS AND DISCUSSION

Characterization of PAESKs

Three batches of PAESK-11 with varying polymerization time (5.5, 6.5 and 7.5 h) were synthesized. In a certain range, longer reaction time leads to higher polymerization degree, since fuller conversion results in higher molecular weight.

Table 2 GPC analysis for three different batches of polymers with different polymerization time

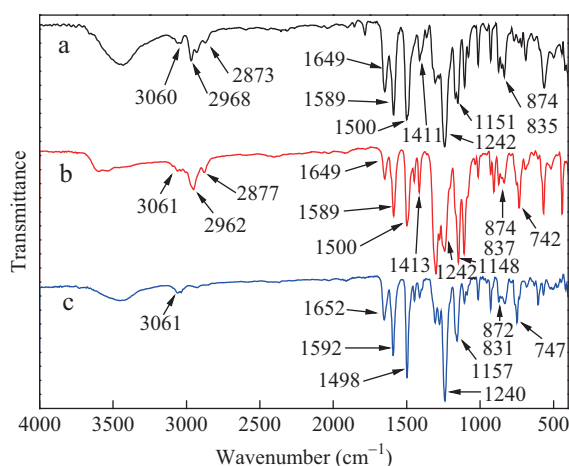
Polymer ^a	Polymerization time (h)	$M_n \times 10^4$ (g·mol ⁻¹)	$M_w \times 10^4$ (g·mol ⁻¹)	PDI
PAESK-11	5.5	2.26	3.73	1.65
PAESK-11	6.5	4.27	7.37	1.73
PAESK-11	7.5	3.27	5.39	1.65

^a Molar ratio of DCS and DFB is 1:1

The molecular weight and polydispersity index (PDI) obtained by GPC relative to polystyrene standards are given in Table 2. It is obvious that longer reaction time leads to the higher molecular weights. However, excessive time (7.5 h) can cause decrease of molecular weight. The molecular weight for 6.5 h is the highest, and the PDI is increased a little bit. Hence, the polymerization time of 6.5 h was employed to produce polymers.

The FTIR spectra of the polymers (PAESK-10, PAESK-11 and PAESK-01) are shown in Fig. 1. From Fig. 1(a), the peaks located at 3060, 1598 and 1500 cm⁻¹ are assigned to the benzene rings. The peaks appearing at 2968, 2873 cm⁻¹ can be assigned to the methyl group (—CH₃) from BPA. The absorption bands at 1649 and 1151 cm⁻¹ are assigned to the stretching vibration of carbonyl group and sulphone group, respectively. The strong peak at 1242 cm⁻¹ is associated with the bending vibration of the Ar—O—Ar bond. The two peaks at 873 and 875 cm⁻¹ are attributed to the 1,4-*para*-substituted benzene stretching vibrations. This indicates that PAESK-10 was synthesized by the monomers of BPA, DCS and DFB through the nucleophilic displacement polymerization reaction. The peak at 747 cm⁻¹ in Fig. 1(c) corresponds to the 1,2-*ortho*-substituted phenyl rings in BHPF, which is not present in Fig. 1(a). It is revealed that PAESK-01 contains all the characteristic peaks of PAESK-10, except those at 2968, 2873 cm⁻¹ (methyl group, —CH₃). From Fig. 1(b), the FTIR spectrum of PAESK-11 displays the characteristic absorption peaks in Figs. 1(a) and 1(c), which indicates that PAESK-11 containing BPA and BHPF was synthesized successfully. Therefore, in this study, a series of PAESKs derived from BPA, BHPF, DCS and DFB were obtained.

The chemical structures of PAESK-10, PAESK-11 and

**Fig. 1** FTIR spectra of PAESKs: (a) PAESK-10, (b) PAESK-11, (c) PAESK-01

PAESK-01 were characterized by ¹H-NMR (Fig. 2). The resonance signals in the range of 7.90–7.70 ppm correspond to the aromatic hydrogen atoms at the *ortho*-position of the carbonyl group. The signals in the range of 7.45–7.30 ppm are attributed to the fluorene groups, which cannot be found in PAESK-10. The resonances at 7.18–7.32 ppm belong to the aromatic hydrogen atoms close to sulfone group. The signals appearing at 7.05–6.80 ppm are associated with the aromatic hydrogen atoms at the *ortho*-position of the ether bond. A specific signal of the methyl group (—CH₃) protons, which is attributed to the BPA, is observed at about 1.70 ppm. Meanwhile, the signal of the methyl group cannot be detected in PAESK-01. The signal assigned to the CDCl₃ appears at 7.26 ppm, while the signals appearing at 2.25 and 3.05 ppm belong to the residual solvent of tetramethylene sulfone. Combining the spectra of FTIR and ¹H-NMR, it can be known that the reaction has occurred as expected.

PAESK is a co-polymer with aromatic structure and rigid fluorene group moieties. The ratio of BPA to BHPF has an influence on the thermal properties of the PAESK co-polymers. Fig. 3 illustrates the results of thermal gravimetric analysis of different PAESK co-polymers in air. Decomposition in the range of 150–200 °C is associated with the residual solvent and absorbed water, which can also be proven in Fig. 3. The thermal properties of the PAESKs are summarized in Table 3. Judging from the decomposition temperature (*T*_d, defined as the temperature at 5% and 10% weight loss) of the PAESKs, increase in the rigid BHPF fraction can improve their thermal stability. It can also be found that the *T*_g of PAESKs (243–285 °C) changes with the increase of fluorene group moieties to some extent due to the incorporation of rigid fluorene moieties. The 5% and 10% weight loss values of PAESK-13 are the highest among the PAESKs. But PAESK-13 shows a little brittle because of the increasing fraction of fluorene group. It is not as tough as other PAESKs. *T*_g values of all the PAESKs are close to that of poly(phthalazine ether sulfone ketone) (PPESK) (263–305 °C), which is often applied in the treatment of high temperature condensed water[12–14].

The solubility of PAESKs in selected solvents is shown in Table 4. As expected, the obtained PAESKs can readily be dissolved in DMAc, DMSO, chloroform, THF, NMP, and pyridine at room temperature, and also in DMF upon heating. However, PAESKs are insoluble in some polar solvents, such as water, ethanol, methanol and acetone.

Characterization of the PAESK Membranes

Pure water flux (PWF) and rejection (R) of membranes

PAESK-12 was used to prepare membrane, as it has high 10% weight loss temperature and is tough enough. PWF and BSA rejection of the prepared membranes are shown in Fig. 4. As we know, reducing the polymer concentration in

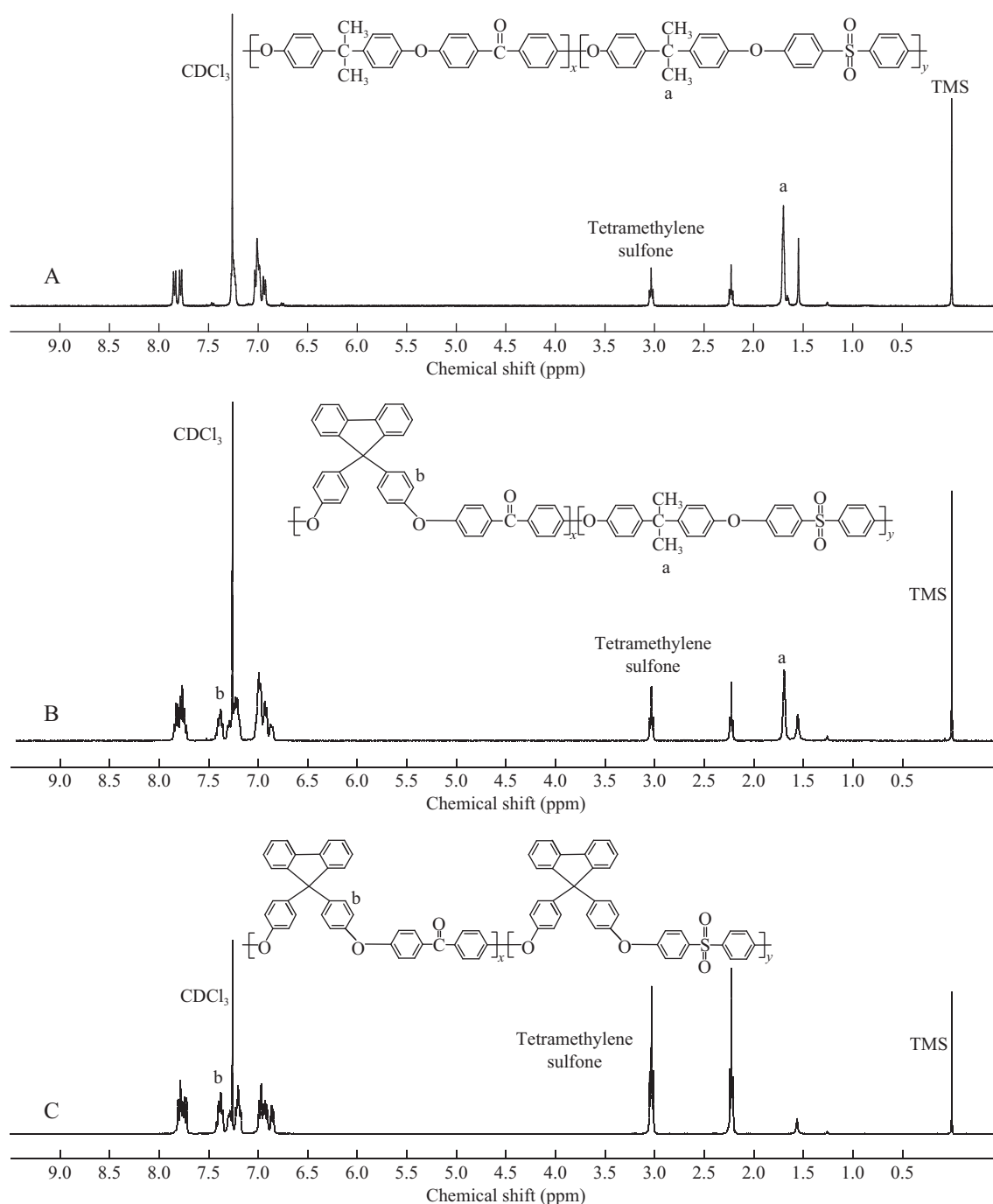


Fig. 2 ^1H -NMR spectra of (A) PAESK-10, (B) PAESK-11 and (C) PAESK-01

the casting solution, which results in instantaneous demixing, produces large pores on the surface of membrane. The exchange between the non-solvent and solvent during the membrane formation is restrained by the long chains of the polymer in the casting solution^[18]. From Fig. 4, it can be found that with increase in the polymer concentration, the PWF of PAESKs membranes decreases dramatically from $493.29 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ to $194.56 \text{ L}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$, and the BSA rejection of membranes lowers slightly. This indicates that increasing the polymer concentration in the casting solution leads to the formation of membrane with denser structure. The membrane with a polymer concentration of 13 wt% in

casting solution shows high PWF and good BSA rejection, but it is too brittle and easy to be damaged during the permeation measurement. So we choose the polymer concentration of 15 wt% to prepare membrane.

Water-soluble polymers, such as poly(vinyl pyrrolidone) (PVP), have been extensively used as additives during the preparation of ultrafiltration membranes *via* phase inversion method due to their good solubility in water and organic solvent, low toxicity, high complexing ability, and good film-forming characteristics^[19]. Generally, PVP is favorable to the increase of membrane surface pore size and porosity due to their pore-forming effect^[20, 21]. The effects of PVP

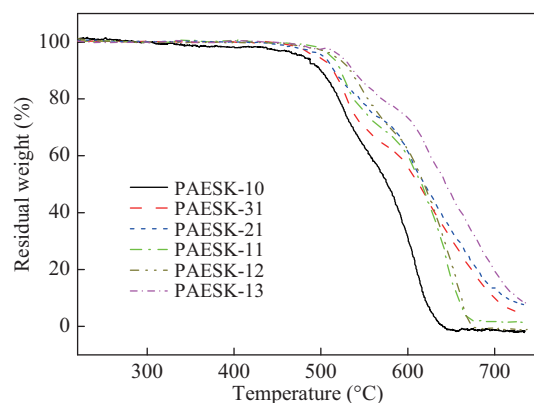


Fig. 3 TGA curves of PAESKs (in air)

Table 3 Thermal properties of PAESK co-polymers

Polymer	^5T_d (°C)	$^{10}T_d$ (°C)	T_g (°C)
PAESK-10	480.10	500.10	188
PAESK-31	495.00	513.79	243
PAESK-21	503.10	515.29	275
PAESK-11	513.10	522.89	277
PAESK-12	516.10	532.70	279
PAESK-13	523.60	537.29	285

Table 4 The solubility of the PAESK co-polymers

Solvent	Molar ratio (BPA:BHPF)						
	1:0	3:1	2:1	1:1	1:2	1:3	0:1
Water	—	—	—	—	—	—	—
Ethanol	—	—	—	—	—	—	—
Methanol	—	—	—	—	—	—	—
Acetone	—	—	—	—	—	—	—
DMAc	+	+	+	+	+	+	+
DMF	±	±	±	±	±	±	±
DMSO	+	+	+	+	+	+	+
Chloroform	+	+	+	+	+	+	+
THF	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	+
Pyridine	+	+	+	+	+	+	+

0.05 g sample in 5 mL solvent: +, soluble at room temperature; ±, soluble on heating; —, insoluble. DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; NMP, *N*-methyl-2-pyrrolidone.

concentration on the permeation of PAESK-12 membranes are shown in Fig. 5. It can be observed that the PWF increases from $71.87 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ to $247.65 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ as PVP concentration increases from 0 wt% to 10 wt%. Meanwhile, the BSA rejection decreases from 99.01% to 96.17%. According to Fig. 5 and Table 5, increasing PVP fraction can increase the porosity, which is good for PWF; meanwhile, BSA rejection decreases slightly. Table 5 also shows that the PWF and BSA rejection of the PAESK-12 are higher than those of the PAESK-21 with the same PVP concentration

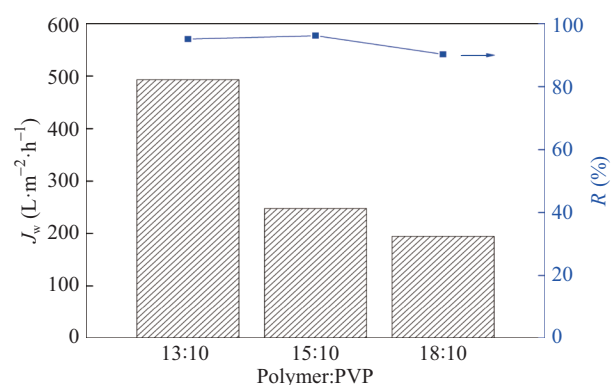


Fig. 4 Effect of the polymer concentration on the pure water flux (PWF) and BSA rejection of PAESK membranes (BPA:BHPF = 1:2)

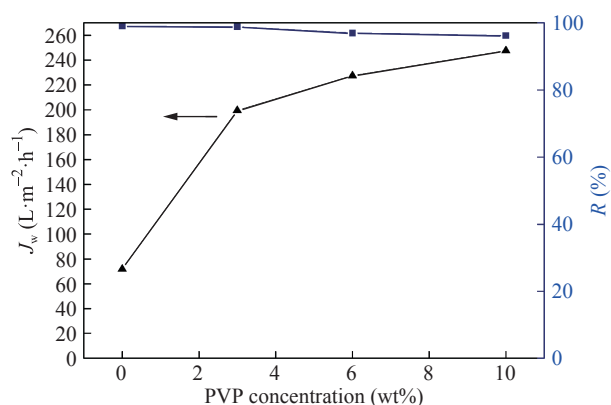


Fig. 5 Effect of the PVP concentration on the pure water flux (PWF) and the BSA rejection of PAESK membranes (polymer:PVP = 15:10, BPA:BHPF = 1:2)

and similar P_r . This can be explained by the fact that the addition of BHPF can improve the hydrophilicity of the membrane^[16]. As a result, an appropriate concentration of 10 wt% PVP is adopted to improve the PWF of PAESK-12 membrane.

Membrane morphology

SEM images of the top surface and cross-section morphologies of PAESK-12 and PAESK-21 membranes (with the same PVP concentration of 10%) are shown in Fig. 6. With increased portion of BHPF, the penetrated finger-like structure in sublayer is developed, and sponge-like structure begins to be suppressed (a2 and b2). And data in Table 5 show that the porosity of PAESK-12 and PAESK-21 are 85.81% and 83.81%, respectively. There is a slight increase with the portion of BHPF increased. According to the results by Smolders *et al.*^[22], the formation of macrovoids structure in sublayer is initiated from nucleation of polymer-lean phase. The growth or suppression of macrovoids is

Table 5 Effect of the dope solution composition on the permeation property of membranes

Polymer	Polymer composition (wt%)	PVP concentration (wt%)	J_w ($\text{L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$)	R (%)	P_r (%)	Contact angle θ (°)
PAESK-12	15/85	0	71.87	99.01	63.06	82.1
PAESK-12	15/82	3	199.52	98.78	74.34	77.0
PAESK-12	15/79	6	227.38	96.96	80.21	64.1
PAESK-12	15/75	10	247.65	96.17	85.81	55.4
PAESK-21	15/75	10	243.23	95.85	83.81	59.0

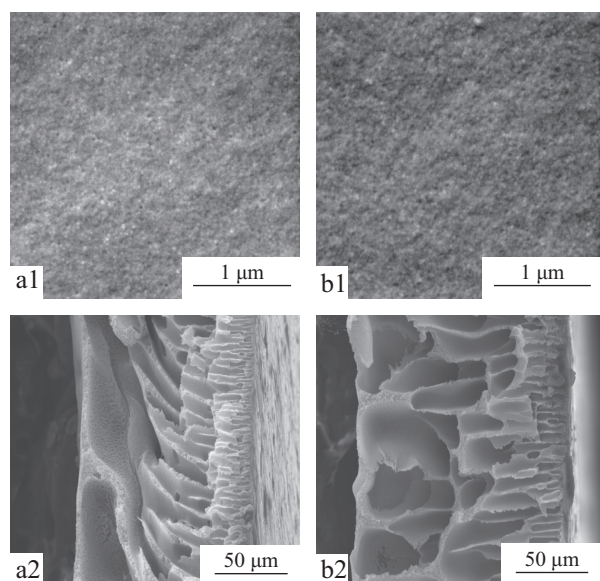


Fig. 6 SEM micrographs of PAESKs membranes with the same PVP concentration 10 wt%: (a1, a2) PAESK-21, (b1, b2) PAESK-12 (1, top surface; 2, cross-section)

determined by the relative diffusion rates between solvent and non-solvent. Therefore, the PAESK-12 membrane shows a dense and thin top layer, probably due to the bulky fluorene groups and cardo structure of BHPF that can bring much free volume in the polymer chain, leading to an increased exchange rate between solvent and non-solvent.

Hydrophilicity of membranes

Water contact angle is used to evaluate the hydrophilicity of membrane, which is an important indicator of membrane application. Variation in the contact angle of different PAESK membranes is displayed in Table 5 and Fig. 7. As shown in Table 5, the contact angles of the membranes decrease gradually when the amount of PVP is increased in the casting solutions. The contact angle of PAESK membrane without PVP is 82.1° because of the inherent hydrophobicity. When the concentration of PVP increases from 0 wt% to 10 wt%, the porosity increases from 63.06% to 85.81%, while the contact angle decreases from 82.1° to 55.4°, which means that the addition of PVP has improved the membrane porosity. The higher porosity may also play a role in obtaining higher permeate flux due to decreased intrinsic membrane resistance. For PAESK-21 and PAESK-12 membranes in Fig. 7, the contact angles are 59.0° and 55.4° with the same concentration of PVP (10 wt%), respectively, while the porosity of PAESK-12 and PAESK-21 membranes are similar (seen from Table 5). Above results indicate that the addition of BHPF can improve the hydrophilicity of PAESK membrane.

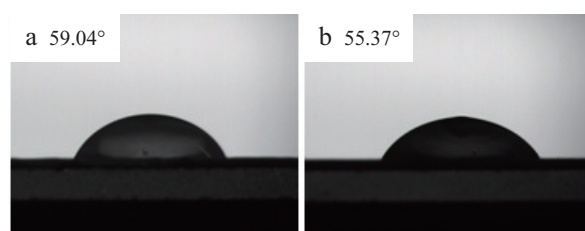


Fig. 7 Contact angle measurement image of PAESK membranes with the same PVP concentration of 10 wt%: (a) PAESK-21; (b) PAESK-12

Mechanical properties of membranes

In industrial applications, the mechanical strength of the membrane is very important for long duration and stable performance. In order to investigate the effect of PVP on the mechanical properties of PAESK-12 membranes, three parameters including tensile strength, Young's modulus and elongation at break were measured and the results are listed in Table 6. The results demonstrate that the mechanical properties of the PAESK-12 membrane deteriorate with increasing PVP concentration. The tensile strength, Young's modulus and elongation at break of the membrane containing 10 wt% PVP reduce to 1.36 MPa, 28.51 MPa and 4.78%, respectively. The variation in mechanical properties of the membranes could be attributed to the augment of porosity and the restriction of polymer chains.

Thermal properties of membranes

Fig. 8 illustrates the results of thermal gravimetric analysis of PAESK-12 membranes in air with different addition of PVP. With the concentration of PVP increasing from 0 wt% to 10 wt%, the decomposition temperatures at 5% and 10% weight loss increase slightly, which indicates that PVP can improve the thermal stability of PAESK membranes. The thermal properties of membranes are summarized in Table 7.

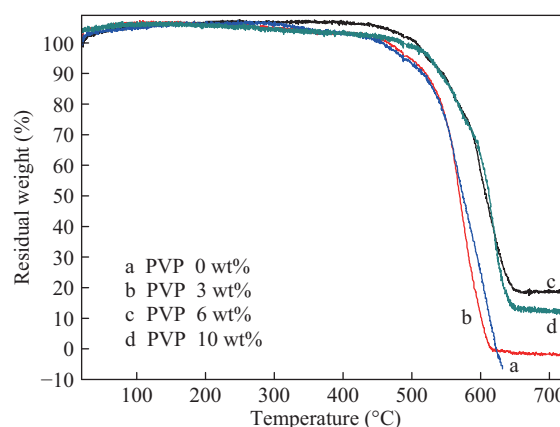


Fig. 8 TGA curves of PAESK-12 membranes with different addition of PVP

Table 6 Effect of PVP concentration on mechanical properties of PAESK-12 membranes

Polymer	Polymer/solvent composition (wt%)	PVP (wt%)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
PAESK-12	15/85 PAESK/DMAc	0	2.97	5.71	51.96
PAESK-12	15/82 PAESK/DMAc	3	2.77	5.49	50.40
PAESK-12	15/79 PAESK/DMAc	6	1.81	5.20	34.73
PAESK-12	15/75 PAESK/DMAc	10	1.36	4.78	28.51

It can be found that all the membranes show good thermal stability; the decomposition temperatures of all the membranes are about 500 °C. Compared with the PAESK-12 co-polymer in Table 3, the obtained membrane with 10 wt% addition of PVP shows the highest decomposition temperature.

Table 7 Thermal properties of PAESK-12 membranes with different addition amounts of PVP

Code	PVP concentration (wt%)	^5T_d (°C)	$^{10}T_d$ (°C)
a	0	486.30	513.79
b	3	497.00	518.39
c	6	522.89	545.60
d	10	528.20	544.10

Permeate flux for high temperature condensed water

Fig. 9 shows the flux stability measurement of PAESK-10, PAESK-12 and PAESK-21 for high temperature condensed water at 90 °C. The permeate flux of PAESK-10 declines with time increasing, indicating that PAESK-10 is hydrophobic and could cause protein or microorganism fouling. So, it is not suitable to deal with high temperature condensed water. On the other hand, high performance of PAESK-12 and PAESK-21 can keep unchanged for a long time; the permeate flux are almost constant after 12 h at 90 °C. And with the content of BHPF increasing, the permeate flux increases observably. That means the PAESK membranes containing more BHPF can improve hydrophilicity and display high stability for high temperature condensed water due to the fact that BHPF segment improves the hydrophilicity and thermal stability of membranes. So it can be used for high temperature condensed water treatment.

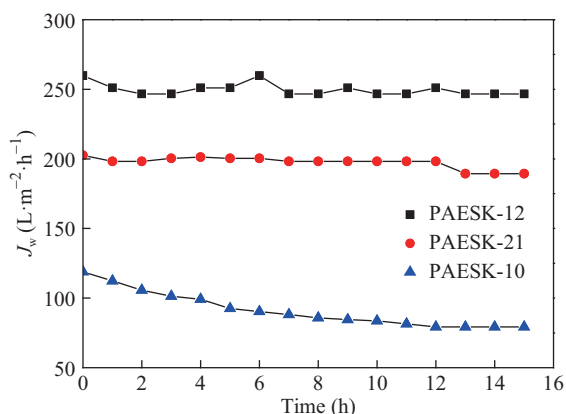


Fig. 9 Permeate stability of the membranes for high temperature condensed water at 90 °C

Antifouling properties of PAESK membrane during BSA filtration

In order to investigate the antifouling properties of the PAESK-12 membrane, dynamic filtration tests were conducted at room temperature using BSA as a model protein. Filtration measurements are designed into three stages. The first stage is 20 min pure water permeation. The second stage is 20 min ultrafiltration of BSA solution and the third stage is the pure water flux of the cleaned membrane by

deionized water for another 20 min. The typical time-dependent permeation flux of membrane is depicted in Fig. 10. It can be clearly seen that the initial water flux value is about 240 L·m⁻²·h⁻¹, then the permeation flux of BSA solution undergoes a dramatic decline, owing to the adsorption or deposition of protein molecules on the membrane pore wall or surface, which reduces the pore size and causes membrane fouling^[23]. It is clear from the third stage that the pure water flux recovers to some degree, but not completely reverts. The flux recovery ratio (FRR) is only about 43.2%. This result suggests that although the addition of BHPF could improve the hydrophilicity of PAESK membrane, the membrane is still hydrophobic and needs to be modified to increase the hydrophilicity.

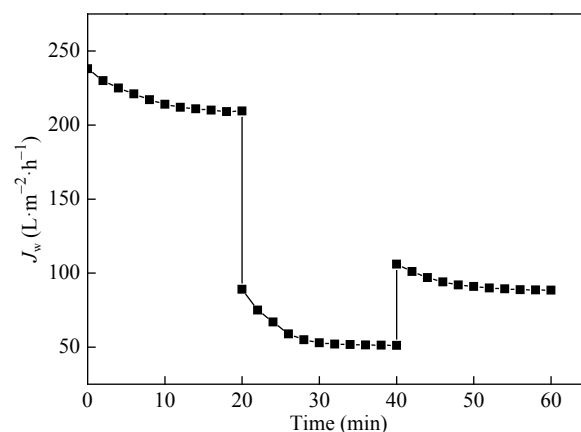


Fig. 10 The antifouling properties of PAESK-12 membrane

CONCLUSIONS

In this paper, PAESK co-polymers containing fluorene group were successfully synthesized through the nucleophilic substitution polymerization, and PAESK UF membranes were prepared by phase inversion technique. The addition of BHPF improves the thermal stability of polymers. Especially, PAESK-12 shows the highest decomposition temperature and the glass transition temperature is up to 295 °C. The effects of polymer concentration and PVP concentration were investigated during the membrane preparation. 15 wt% of PAESK-12 and 10 wt% of PVP were found to be the optimal condition to fabricate membrane, where the contact angle of the obtained membrane is 55.59°, and the PWF and BSA rejection are up to 247.65 L·h⁻¹·m⁻² and 96.17%, respectively. And the PAESK-12 membrane with 10 wt% addition of PVP shows the highest thermal stability. Permeate flux for high temperature condensed water at 90 °C shows that the permeate flux of PAESK-12 is the highest and stable. The antifouling test shows that the PAESK membrane needs to improve the hydrophilicity. We believe that the as-prepared membranes have great potential for high temperature condensed water treatment.

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