Accepted Manuscript

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PII: S0032-3861(15)30229-9

DOI: 10.1016/j.polymer.2015.09.024

Reference: JPOL 18110

To appear in: *Polymer*

Received Date: 13 July 2015

Revised Date: 2 September 2015

Accepted Date: 9 September 2015

Please cite this article as: Hou S, Zheng J, Zhang S, Li S, Novel amphiphilic PEO-grafted cardo poly (aryl ether sulfone) copolymer: synthesis, characterization and antifouling performance, *Polymer* (2015), doi: 10.1016/j.polymer.2015.09.024.

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Novel amphiphilic PEO-grafted cardo poly (aryl ether sulfone) copolymer: synthesis, characterization and antifouling performance

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Abstract: A series of comb-like amphiliphilic copolymers (PES-g-PEO) were synthesized through grafting poly(ethyleneoxide) (PEO) to cardo poly(aryl ether sulfone) (PES-NH) backbone. By controlling the ratios of PEO and cardo poly(aryl ether sulfone), amphiphilic copolymers with a range of PEO side chain were obtained and were employed to ultrafiltration (UF) membranes. The PES-g-PEO-XX materials showed high thermal stability (T_d >238 °C) and good mechanical properties especially elongation at break reached to 150% compared to 23% of PES-NH. The contact angle of PES-g-PEO-80 asymmetric membrane was decreased to a slow as 59° which was 30° lower than the value of PES-NH membrane (90°), indicating that PES-g-PEO-80 membrane exhibited remarkable hydrophilic property. No protein adsorption was found on the surface of PES-g-PEO-60 and PES-g-PEO-80 membranes, showing excellent antifouling properties compared to PES-NH. The results of this work suggest that PES-g-PEO copolymers are promising materials for the fabrication of fouling resistant membranes.

Keywords: PEO-grafted copolymers, membrane, Antifouling properties

1. Introduction

Polyethersulfone (PES) is one of the most favorable membrane materials in microfiltration (MF) and ultrafiltration (UF) for water treatment, and also it is one of the few biomaterials that can withstand all sterilization techniques as its excellent mechanical strength, suitable chemical resistance, good thermal stability, etc[1-4]. Nevertheless, fouling and in particular biofouling is still an important issue in the widespread implementation of PES membrane. The adsorption of serum proteins onto PES membranes used in medical areas can cause serious or life-threatening disease. The inherent hydrophobicity of PES membranes makes themselves easy to be fouled by biomacromolecules on membrane surfaces and pore walls during the membrane separation process resulting in high-cost. It is believed that the hydrophilic membranes are more resistant to fouling than hydrophobic membranes[5-8]. Therefore, improving the hydrophilicity of PES membranes is of great interest, as hydrophilic membranes can effectively reduce the interactions between the biological foulants and membrane surfaces.

In general, several methods including surface chemical grafting[9-14], surface coating[8, 15, 16] and adding hydrophilic molecules[17, 18] have been widely used to increase the hydrophilicity of membrane surface. However, many problems can arise with such surface modifications. Chemical grafting is a difficult operation to control and detrimental to membranes, and the same is true for surface coating using organic solvent in most cases. For adding hydrophilic molecules, hydrophilic molecules will leach out slowly from the membranes surface due to their water soluble properties, resulting in short-term effects. An alternative approach is the utilization of hydrophilic polymers for fabrication of membranes[19], as hydrophilic materials can overcome the chemical processes during the membrane fabrication processes and can stay steadily during the membrane separation processes.

It has been shown that poly(ethyleneoxide) (PEO) chains are highly resistant to hydrophobic or large molecules adsorption on membrane surfaces, as PEO is antifouling with the properties of uncharged and hydrophilicity. As a result, PEO materials have been extensively used for the surface modification of membranes in recent years for their remarkable antifouling properties[20-22]. However, there are still some trouble in PEO materials for membrane fabrication, such as poor mechanical and crystallinity properties. The use of PEO-grafted polymers is an especially convenient method to enhance the mechanical strength and minimize the crystalline regions in PEO[23, 24]. In our previous study, a series of cardo poly(aryl ether sulfone) materials have been synthesized[7, 24-28]. Grafting function group to cardo poly(aryl ether sulfone) is an especially convenient method to attain PES copolymers. Amphiphilic poly(ethylene oxide)-grafted cardo poly(aryl ether sulfone) copolymers were obtained by first grafting 1,2-epoxypropane group to cardo poly(aryl ether sulfone), and then by the reaction of glycidyl groups with methanamine-terminated poly(ethylene oxide)-methoxy (MeO-PEO-NHCH₃), showing improved hydrophilicity of the membranes[24]. However, the route of synthesis the copolymers which involved two grafting process to cardo poly(aryl ether sulfone) is hard to control, thus it is not suitable for prepare membrane materials.

In view of what has been previously outlined, we successfully synthesized a series of novel comb-like amphiphilic copolymers (PES-g-PEO) consisting of branch-like functional chains of poly(ethyleneoxide) (PEO) and cardo poly(aryl ether sulfone)(PES-NH)-based root-like hydrophobic chains. PES-g-PEO copolymers were obtained by one-step reaction between cardo poly(aryl ether sulfone) and tosylated poly (ethylene glycol)-methoxy as shown in Fig. 1. The properties of the PEO-grafted polymers were studied, such as the solubility, thermal stability and mechanical properties. Asymmetric membranes were successfully prepared using these different grafted PES-g-PEO copolymers. Interestingly, the PES-g-PEO membrane showed dramatically hydrophilicity compared to PES-NH. The antifouling performances of the membranes were determined using bovine serum albumin (BSA) as a model protein. It was worth to note that PES-g-PEO membranes exhibited excellent antifouling property.

2. Experimental

2.1 Materials

Phenolphthalein (PPH) was purchased from Beijing Chemical Reagent Company, and purified by recrystallization from mixed solvent of ethanol and water. 4, 4-Difluorodiphenyl sulfone (DFDPS) was purchased from Aldrich. Methoxy-terminated poly(ethylene oxide) (M=350) were purchased from

Aladdin and used as received. N-Methylpyrrolidinone (NMP) was firstly dried with CaH_2 and then distilled under reduced pressure before use. Anhydrous potassium carbonate was finely powdered prior to use. Bovine serum albumin (BSA, pI = 4.8, Mw= 67 kDa) was purchased from Sino-American Biotechnology Co., Ltd. All other chemicals were reagent grade and used as received.

2.2 Synthesis and characterization of PES-g-PEO



PES-g-PEO-XX

Fig. 1 Synthesis of tosylated poly (ethylene glycol)-methoxy and PES-g-PEO

2.2.1 Synthesis of 3, 3-bis (4-hydroxyphenyl)isoindolin-1-one (PPH-NH)

The monomer PPH-NH was prepared according to the method of Wang et al[29].

2.2.2 Synthesis of tosylated poly (ethylene glycol)-methoxy

A 500 mL three-necked round bottom flask was charged with a solution of PEO(CH₃(OCH₂CH₂)₇OH, 70 g, 0.20 mol) in 60 mL of tetrahydrofuran. Upon vigorous stirring at 0°C, sodium hydroxide (16 g, 0.40mol) dissolved in 60 mL of water was added. To this mixture, a solution of tosyl chloride (50 g, 0.27mol) in 80 mL of dry tetrahydrofuran was added dropwise over 1 h at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. Subsequently, 300 mL of dichloromethane was added and the organic layer was separated and washed with 1 M aqueous NaOH (3 x 50 mL). Again, the organic layer was washed with water (2 x 50 mL), dried over MgSO₄, followed by evaporation and drying *in vacuo*, to yield the title compound as a colorless liquid. ¹H NMR (CDCl₃, 500 MHz), δ (ppm): 7.82 (d, *J*=7.3 Hz, 2H), 7.4 (d, *J*=7.3 Hz, 2H), 4.13 (t, *J*=4.5 Hz, 2H), 3.6 (m, 26H), 3.25 (s, 3H), 2.4 (s, 3H).

2.2.3 Synthesis of cardo poly(aryl ether sulfone)s (PES-NH)

To a 1000 mL three-necked round bottom flask equipped with mechanical stirrer and N₂ inlet, PPH-NH (38.05g, 0.12 mol), DFDPS (30.51g, 0.12 mol), anhydrous K_2CO_3 (41.16 g, 0.3 mol), 340 mL NMP and 170 mL cyclohexane were added. The reaction mixture was heated with stirring at 120 °C for 4 h. After the cyclohexane and water had been removed by azeotropic distillation, the temperature was raised to 145 °C and allowed to react at this temperature for 8 h. The system was cooled to room temperature and diluted with NMP. The solution was filtrated to remove inorganic salts. The filtrate was poured into water to give white flake of the product, which was washed with hot water several times and extracted with ethanol. The resulting product was dried under vacuum at 120 °C for 24 h.

The yield was 97%. ¹H NMR (DMSO-d₆, 300 MHz), δ(ppm): 9.80 (s, 1H), 7.87 (m, 4H), 7.78-7.56 (m, 4H), 7.07-7.10 (m, 8 H).

2.2.4 Synthesis of cardo poly(aryl ether sulfone)s with poly (ethylene oxide) group (PES-g-PEO-XX)

The PEO grafted cardo poly(aryl ether sulfone)s are denoted as PES-g-PEO-XX, where XX represents the molar percent of PEO groups. A typical synthetic procedure for PES-g-PEO-60 is illustrated as follows. PES-NH (8.0 g, 0.015 mol) and NaH (0.43 g, 0.018 mol) were added to 80 mL of DMAc at room temperature and stirred for 30 min. Then tosylated poly (ethylene glycol)-methoxy (4.5 g, 0.009 mol) was added and the reaction was allowed to proceed at room temperature for 24 h. The viscous solution was precipitated into deionized (DI) water. The polymer was separated by filtration and dried in a vacuum oven at 100 °C for 24 h.

2.3 Membrane preparation

2.3.1 Dense membranes

In a typical dense membrane preparation process, the polymer was dissolved in DMAc to form a 10.0 wt% solution. After filtrated and degassed, the solution was cast onto a clean glass substrate, and the solvent was evaporated over 24 h at 60°C. The as-cast membrane was dried further under vacuum for 24 h at 120 °C. Then the membrane was immersed into deionized water and peeled off. Finally, the resulting dense membrane was dried for another 24 h at 120 °C under vacuum. The as-made dense membrane was used to tensile measurements.

2.3.2 Asymmetric membranes for antifouling performance

Asymmetric membranes were prepared by the well-known phase inversion process. The dope solutions with polymer concentration of 18.0 wt% in DMAc were cast onto clean glass plates using a casting knife with a 150 µm gate gape, and the glass plates were then immersed immediately into a coagulation bath of deionized water. The film samples were kept in deionized water prior to testing. 2.4 Measurements

¹H NMR was recorded on Varian Unity spectrometer at 300 MHz with tetramethylsilane (TMS) as the internal standard and DMSO-d₆/CDCl₃ as the solvent, respectively. Inherent viscosities of all polymers were determined at 30 ± 0.1 °C using Ubbelodhe viscometer with 0.5 dL/g concentration in DMAc. Attenuated total reflectance infrared (ATR-IR) characterization was made with a Bio-Rad digilab Division Fst-80 spectrometer. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin Elmer TGA-2 thermogravimetric analyzer (Inspiratech 2000 Ltd., UK) at a heating rate of 10 °C/min. All the samples were first vacuum-dried and kept in the TGA furnace at 150 °C in a nitrogen atmosphere for 30 min to remove water before TGA characterization. Thermal behaviors of PEO-grafted cardo poly (aryl ether sulfone) copolymers were evaluated by differential scanning calorimetry (DSC) (TA Instruments DSC Q20 USA) at a heating rate of 10 °C/min under N₂ atmosphere. Tensile measurements were performed with a mechanical tester Instron-1211 instrument (Instron Co., USA) at a speed of 2 mm/min at ambient humidity.

2.5 Water contact angles

The static contact angle measurements were carried out to evaluate the hydrophilicity of the membranes by a contact angle goniometer (JC2000C Contact angle Meter, Powerach Co., Shanghai, China). Distilled water was dropped onto the surface of the membrane samples, and the contact angles

of the drops were measured at several spots on the same membrane piece for at least three pieces of each membrane at room temperature. Finally, the average contact angle was calculated.

2.6 Protein fouling test

FITC-labeled BSA (BSA-FITC) was prepared according to reported method[30]. Asymmetric membranes (1 cm \times 1 cm) were washed three times with PBS (phosphate buffer saline) solution, and then immersed in 1 mL 1 mg/mL FITC-BSA PBS solution at room temperature for 4 h to allow protein surface adsorption. After the protein incubation, the membranes were then rinsed gently with PBS buffer to remove any loosely bound surface BSA. Finally, membrane surface fluorescence was visualized using Leica TCS SP2 Confocal fluorescence microscopy.

2.7 Ultrafiltration experiments

Ultrafiltration membranes were tested using a cross flow filtration cell, and the effective area of the membranes was 23.7 cm². At first, each membrane was compacted at 0.2 MPa for 1 h. Then the operation pressure was lowered to 0.1 MPa. After compacted, deionized water was passed through the ultrafiltration membranes for 0.5 h to obtain the beginning pure water flux J_1 (L/(m²h)), which was calculated by the following equation:

$$\boldsymbol{J}_{1} = \frac{V}{A\Delta t} \qquad (1)$$

Where V was the volume of permeated water (L), A was membrane area (m²) and Δt was permeation time (h).

The rejections of BSA were calculated according to the feed and the permeate concentration via UV spectrophotometer at 280 nm according to the following equation:

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

Where C_p and C_f (mg/mL) refer to the concentration of BSA in permeate and feed solutions respectively.

3. Result and discussion

3.1 Synthesis of amphiphilic polymer

In our former work, a series poly(ethylene oxide)-grafted cardo poly (aryl ether sulfone) copolymers were synthesized through multiple-step process. First, epoxide group was introduced to the cardo poly(aryl ethyl sulfone), and then methylamine-terminated monomer (MeO-PEO-NHCH₃) obtained through two-step process was grafted to the epoxide-grafted cardo poly(aryl ethyl sulfone). This proposal is not suitable to prepare the membrane materials due to it was laborious and difficult to control the two grafting processes. In this work, poly(ethylene oxide)-grafted cardo poly (aryl ether sulfone) copolymers were synthesized via the reaction of amide group with tosylated poly(ethylene glycol)-methoxy which are more active than mesylated poly(ethylene glycol)-methoxy. Synthesis of tosylated poly (ethylene glycol)-methoxy was accomplished using tosyl chloride (1.3 eq) and NaOH as the base in a yield of 90%. Fig. 2 shows the hydrogen signal assignment in the ¹H NMR spectra of MeO-PEO-OH and tosylated poly(ethylene glycol)-methoxy. The -OH peak at 2.9 ppm disappeared, and three typical peaks of tosylate group were observed at δ 2.4 ppm, 7.4 ppm and 7.8 ppm. The peak of -CH₂- near the tosylate group moved to 4.1 ppm from 3.6 ppm, indicating the successful synthesis of

tosylated poly(ethylene glycol)-methoxy.



Fig. 2 ¹H NMR spectra of MeO-PEO-OH, and tosylated poly (ethylene glycol)-methoxy in CDCl₃

The cardo poly(aryl ether sulfone) (PES-NH) copolymer containing amide groups was synthesized using PPH-NH and DFDPS. Different graft ratio PES-g-PEO-XX copolymers were obtained by treatment of PES-NH copolymer with NaH in NMP in the presence of tosylated poly (ethylene glycol)-methoxy. The mole ratios of amide groups to tosylated poly(ethylene glycol)-methoxywere set to 1:0.2, 1:0.4, 1:0.6, 1:0.8 respectively. The chemical structure of the amphiphilic copolymers PES-*g*-PEO-XX were analyzed by ¹H NMR as shown in Fig. 3. The chemical shifts at δ =3.01 ppm, δ =3.32 and δ =3.63 could be assigned to -N-CH₂-, -O-CH₃ and -O-CH₂- of PEO respectively. The peaks observed at δ =6.99 and δ =7.02 were assigned to the protons ortho to the diphenyl ether unit. The unit number (XX) of PEO in PES-g-PEO-XX was calculated using the equation:

 $XX = [I_{\delta=3.01} / 2] / [(I_{\delta=6.99} + I_{\delta=7.02}) / 8]$

Where $I_{\delta=3.01}$, $I_{\delta=6.99}$ and $I_{\delta=7.02}$ are proton peak intensities of -N-CH₂-, protons ortho to phenolic bridge, respectively. The value of XX is 78.4% with the mole ratio of amide group to tosylated poly(ethylene glycol)-methoxy was 1:2, which indicated that PEO is grafted to the PES backbone successful. Table 1 shows the molecular weight, grafting degree, and inherent viscosity of each polymer.



Fig. 3 ¹H NMR spectra of amphiphilic polymer PES-*g*-PEO in CDCl₃ Table 1. Molecular weight, grafting degree, viscosity of polymers

Polymer	Mn	Mw	Grafting	Viscosity
	(10 ⁴)	(10 ⁴)	degree(%)	(dL/g)
PES-NH	5.9	13.0		0.53
PES-g-PEO-20	6.3	14.5	18	0.58
PES-g-PEO-40	6.6	15.9	33	0.62
PES-g-PEO-60	7.0	17.8	52	0.67
PES-g-PEO-80	7.2	20.1	78	0.72

In agreement with the NMR results, the ATR-IR spectra of PES-g-PEO-80 (Fig. 4) revealed a new vibrational band at 1105 cm⁻¹, due to the C-O stretch of the PEO side chains. The new absorptions at 1372 and 1409 cm⁻¹ were the aliphatic C-H bends of the PEO. Other new absorptions at 2870 and 2925 cm⁻¹ were assigned to the aliphatic C-H stretch of the PEO side chains. In conclusion, both ¹H NMR and ATR-IR spectra indicated that the PEO side chains were successfully grafted onto the poly(aryl ether sulfone) backbone.



Fig. 4 ATR-IR spectra of the membranes

3.2 Physical and chemical properties

Solubility is very important for polymers, as it determines the applications of polymer materials. The solubility properties of the copolymers were qualitatively tested in various organic solvents, and the results are summarized in Table 2. None of the polymers were soluble in methanol or water. As shown in Table 2, both PES-NH and PES-g-PEO-XX were soluble in polar aprotic solvents, such as NMP, DMF and DMAc. However, PES-g-PEO-XX (XX \geq 60) showed significantly different solubility properties compared with the PES-NH. PES-g-PEO-XX (XX \geq 60) copolymers were soluble well in low boiling point solvents, such as tetrahydrofuran, CHCl₃, CH₂Cl₂, or acetone. The solubilities increased in low boiling point solvent with the increased PEO amount. The good solubilities of PES-g-PEO-XX polymers were attributed to the PEO side chains.

Table 2. Solubility of the polymer

Polymer	Acetone	Tetrahydrofuran	CHCl ₃	CH ₂ Cl ₂	NMP	DMSO	DMF	DMAc
PES-NH	_	_	_	_	+	+	+	+
PES-g-PEO-20	_	-	_	_	+C	+	+	+
PES-g-PEO-40	±	±	+	+	+	±	+	+
PES-g-PEO-60	±	+	+	+	+	±	+	+
PES-g-PEO-80	+	+	+	+	+	±	+	+

The tests were performed at concentration of 0.05 g/mL (+) soluble; (\pm) partially soluble; (-) insoluble

The thermal properties of the PES-NH and PES-g-PEO-XX copolymers are shown in Fig. 5. PES-NH exhibited a single decomposition event and the starting decomposition temperatures of 498 °C, corresponding to the decomposition of the polymer backbone. Two major steps of degradation were found in PES-g-PEO-XX copolymers. The first decomposition starts at 238 °C, corresponding to the cleavage of PEO side chains. The second decomposition stage was observed at 450 °C and was assigned to the degradation of the main chains.



Fig. 5 TGA traces of PES-NH and PES-g-PEO-XX recorded under a nitrogen atmosphere.

The mechanical properties of the PES-NH and PES-g-PEO-XX membranes were measured as shown in Table 3. The PES-NH membrane yielded a tensile strength at 48.6 MPa, Young's modulus of 1677 MPa, and elongation at break of 23%. After introducing the flexible PEO side chains, the tensile

strength, Young's modulus, and elongation at break of the PES-g-PEO-XX membranes ranged over 22-43 MPa, 1480-794 MPa, and 50-150%, respectively, which indicated that the materials possessed sufficient strength for membrane application. With the increasing PEO amount, the tensile and the modulus of the membranes decreased and the elongation at break increased, indicating that the mechanical properties could be controlled by grafting different amount of PEO. The glass transition temperature (Tg) of the graft polymers were also measured using DSC. The Tg value of the PES-NH was 294 °C. After grafting the flexible PEO side chain, the Tg value of PES-g-PEO-80 decreased to 173 °C (Table 3), indicating the increase in chain mobility of grafted polymers.

Table 3. Mechanical properties and Tg values of the PES-NH and PES-g-PEO-XX dense membranes in the dry state

Polymers	Tensile	Young's	Elongation	Tg (°C)
	strength (MPa)	modulus	at break (%)	
		(MPa)		
PES-NH	48.6	1677	23	294
PES-g-PEO-20	43.2	1480	50	232
PES-g-PEO-40	37.5	1266	83	190
PES-g-PEO-60	30.8	1038	115	178
PES-g-PEO-80	22.5	794	150	173

Hydrophilicity of membrane surface has an effect on membrane fouling and other vital properties. Water contact angle measurement provided an effective approach to measure the hydrophilicity of a membrane surface. Thus static water contact angle of asymmetric membranes was measured in order to investigate the hydrophilicity of the surfaces and the results were shown in Fig. 6. It can be seen that the contact angle of membranes decreased with the increasing the PEO amount. The contact angle of PES-g-PEO-80 was decreased to as low as 59° which was lower than the value of PES-NH and other reported membranes such as PSf (90.6°)[29], PES (89°)[30], PVDF(93.8°)[31], indicating that membranes exhibited remarkable hydrophilic property. The decrease of the water contact angle can be attributed to the increased surface coverage of hydrophilic PEO domains on the asymmetric membrane. In a word, these results revealed that grafting PEO to PES-NH backbone could effectively enhance the hydrophilicity of membranes.



Fig. 6 The contact angles of (a) PES-NH, (b) PES-g-PEO-80, (c) PES-NH, and PES-g-PEO-XX. 3.3 Protein antifouling

The biofouling formation onto the surface of a membrane is critical issue for most filtration processes such as water treatments and membrane bioreactor applications. It is generally believed that the non-specific, irreversible attachment of protein can cause the membrane fouling. To test the ability of PES-g-PEO-XX membranes to resist protein fouling, a protein adsorption assay was carried out to measure the nonfouling property of the membranes. PES-NH was used as controls in the assay. Bovine serum albumin was used as a model to investigate the ability of protein adsorption on membrane surface. All the membranes were briefly rinsed with PBS, and then soaked in 1 mg/mL Fluorescein Isothiocyanate labeled bovine serum albumin (FITC-BSA) for 4 h. After the socking, membranes were gently washed again with PBS to remove any loosely bound surface BSA. Finally, the pictures of five membranes were taken under a fluorescent microscope with the same excitation light intensity and exposure time. The images of accumulated BSA on the membrane surfaces are shown in Fig. 7. The PES-NH membrane exhibited a high protein attachment after 4 h, which could be attributed to its hydrophobic property. Significant quantitative decreases protein adsorptions were observed on PES-g-PEO-XX membranes compared to the PES-NH membrane. There were no protein adsorptions on membrane surface when the XX reached 60. The high protein antifouling performance of the membranes was ascribed to its hydrophilic nature. In view of these results, it can be concluded that the incorporation of PEO side chains to PES-NH backbone greatly improves the hydrophilicity and protein fouling resistance of PES-NH, and therefore PES-g-PEO-XX are suitable for their intended purpose such as processed as UF membranes.



Fig. 7 Confocal microscopic images of FITC-BSA adsorption on the surfaces of the (a) PES-NH,(b) PES-g-PEO-20, (c) PES-g-PEO-40, (d) PES-g-PEO-60, (e) PES-g-PEO-80 membranes.3.4 Pure water permeation and BSA rejection

The rejections for BSA and the pure water flux of the asymmetric membranes with different PEO content in PES-*g*-PEO-XX (0, 20, 40, 60) were plotted in Fig. 8. According to Fig. 8, it could be concluded that PES-*g*-PEO-XX had a good performance on BSA rejection. It was also observed that pure water flux increased as the content of PEO increased. The water flux of PES-*g*-PEO-60 was as high as 338.6 L/m²h compared to 98.5 L/m²h of PES-NH, which was in agreement with the results of water contact angle and surface hydrophilicity. All these results indicated that PES-*g*-PEO-XX copolymers are promising materials for ultrafiltration membrane.



Fig. 8 Pure water flux and rejection for BSA of PES-NH and PES-g-PEO-XX membranes

4. Conclusion

In conclusion, a series of comb-like amphiliphilic copolymers (PES-g-PEO) were synthesized using cardo poly(aryl ether sulfone) as hydropholic backbone and PEO as the hydrophilic side chains.

By controlling the ratios of PEO and cardo poly(aryl ether sulfone), amphiphilic copolymers with a range of PEO side chain were obtained. The graft copolymers showed excellent solubility, high thermal stability and good mechanical properties. It is found that the hydrophilicity of PES-g-PEO-XX membranes increased as the content of PEO increased. The contact angle of PES-g-PEO-80 asymmetric membrane was 30° lower than the value of PES-NH membrane (90°), indicating that membrane exhibited remarkable hydrophilic property. Furthermore, it is also found that protein adsorption decreased dramatically with the increasing the content of PEO. No protein adsorption was found on the surface of PES-g-PEO-60 and PES-g-PEO-80 membrane, indicating PES-g-PEO membranes exhibited very good antifouling properties compared to PES-NH. The results of this work indicated that PES-g-PEO copolymers are promising materials for the fabrication of fouling resistant membranes.

5. Acknowledgments

We thank the National Basic Research Program of China (2015CB655302), the National Science Foundation of China (No. 51473163, 51321062, 51133008). Chinese Academy of Sciences-Wego Group High-tech Research & Development Program (ZKYWG2013-02), Science and Technology Service Network Initiative (KFJ-EW-STS-047), and Scientific Development Program of Jilin Province (Project number: 20130204027GX).

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- A series of novel comb-like amphiliphilic copolymers (PES-g-PEO) were synthesized.
- The PES-g-PEO copolymers are promising materials to fabricate ultrafiltration membranes.
- The PES-g-PEO membranes exhibited remarkable hydrophilic properties and antifouling performances.