Synthesis of polysulfone containing carboxyl side groups for hydrophilic and antifouling ultrafiltration membranes

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Abstract

This work focused on the synthesis of PSF and a series of carboxylated polysulfone (PSF-COOH) random copolymers with different carboxylation levels in direct copolymerization method and the preparation of antifouling PSF-COOH ultrafiltration membranes via the conventional immersion precipitation phase inversion method. The chemical structures of PSF and PSF-COOH copolymers were confirmed by FTIR. The morphologies of PSF and PSF-COOH membranes were investigated by SEM, and the morphology changes of these resultant membranes were explained in detail and verified by kinetic and thermodynamic theory. The pure water flux and protein solution rejection were measured through ultrafiltration experiments. The pure water flux increased with the increase of the carboxylation degree, suggesting superior hydrophilic performance.

Key word: Carboxylated polysulfone   Membrane morphology   Ultrafiltration   Hydrophilic

1. Introduction

Polysulfone (PSF) membranes were widely used in water treatment, bioengineering, chemical industry, medical service and other fields due to their prominent chemical and thermal stability, good oxidation resistance and durable mechanical strength [1-2]. However, the PSF membrane application in aqueous phase separation was limited by its inherent hydrophobic property. Consequently, when feed solutions containing substances like proteins were filtered, the hydrophobic interaction between the PSF membrane and protein molecules often caused nonspecific adsorption and deposition of proteins on the membrane surface or in pores, and resulted in serious membrane fouling [3-4].

A useful strategy to suppress the membrane fouling was used to enhance the membrane hydrophilicity by different methods. It was well known that introducing polar or hydrophilic groups to the molecules skeleton of membrane material was a straightforward and effective method to improve the membrane water permeability and meanwhile reduced membrane fouling. In the past studies, the sulfonation of membrane materials had been shown to effectively improve the separation performance and stain resistance of the membranes. However, excessive sulfonic acid groups can easily absorb large amounts of water and result in excessive swelling. Consequently, mechanical properties of the membranes declined significantly. In terms of acidic and water-absorbent, carboxylic acid groups was slightly weaker than sulfonic acid groups and was not easy to generate swelling. Thus, we designed 2-(Bis[4-hydroxyphenyl]methyl)benzoic acid(phenolphthalein, PPL) containing carboxylic acid groups to invert into the molecules skeleton of PSF. It is desirable to better improve the separation membrane performance and antifouling properties while retaining the mechanical properties of the ultrafiltration membrane by repeating hydrophilic units of the polymer chain as much as possible.

2. Experimental

2.1 Materials

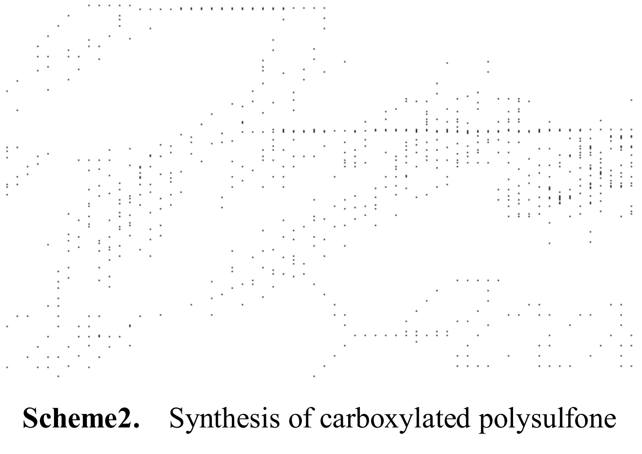
4,4-dichlorodiphenyl sulfone (DCDPS), 4,4-bisphenol A (BPA), Phenolphthalein (PPH) and anhydrous potassium carbonate were purchased from Sinopharm Chemical Reagent Co., Ltd. DCDPS and BPA were dried under vacuum at 100 ℃ for 24h before use. Anhydrous potassium carbonate was used as received. Phenolphthalin (PPL) was synthesized from PPH according to a procedure (Scheme 1) described in literature [5]. Poly (vinylpyrrolidone) (PVP k30), which was used as pore-former additives, was purchased from Sinopharm Chemical Reagent Co., Ltd. Bovine serum albumin (BSA, pI = 4.8, Mw = 67,000) and phosphate buffer solution(PBS, 0.1 mol/L, pH 7.4) were both purchased from Blue Season biological, Shanghai, China.Concentrated hydrochloric acid (38%), Zn powder Sodium hydroxide were purchased from Beijing Chemical Reagent, China. Dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and toluene were purchased from Shanghai chemical company, China, and were used as received.

Scheme1. Synthesis of 2-(Bis [4-hydroxyphenyl] methyl)benzoic acid(PPL).

2.2 Synthesis of carboxylated polysulfone copolymer(PSF-COOH)

The carboxylated polysulfone copolymers were synthesized via direct step polymerization.

The copolymer with different carboxylation degree were synthesized by varying the molar ratio of PPL to total monomers (Scheme2). The selected molar ratios (PPL/(PPL+BPA)) were 0, 20, 40, 60, 80and100 mol%. In one ratio (PPL/(PPL + BPA)=80/20), for example, the synthesis steps are as follows. Firstly, 0.9132 g (4 mmol) of BPA, 5.1254 g (16 mmol) of PPL, 5.7432 g (20 mmol) of DCDPS were added in a three neck flask equipped with a nitrogen inlet, DeaneStark trap and magnetic stirrer.And then 30.9654g DMSO was added into the three neck flask to obtain a 25% solid concentration. After anhydrous potassium carbonate (K_2CO_3,56 mmol,7.7398 g) and toluene were introduced to the system (DMSO/toluene=3/1 v/v). The reaction mixture was then heated until the toluene began to reflux. The temperature was maintained at 150℃ until no water was observed in the Dean-Stark trap. Then toluene was removed from the system, at the same time, the temperature was gradually increased to 160 ℃ and maintain for some hours until the viscosity did not increase further. Finally, the product was poured into deionized water to coagulation. The product was pulverized by a pulverizer , repeatedly washed with boiling deionized water to remove excess solvent and inorganic salt and was dried in a vacuum oven at 120℃ for 10 h.The copolymer was redissolved in a large number of DMF and then isolated by coagulation in a stirred 1 mol/L hydrochloric acid. The precipitated copolymer was then washed several times with ethanol, and dried in a vacuum oven at 120℃ for 24 h.



Scheme2. Synthesis of carboxylated polysulfone

2.3. Membrane preparation

PSF-COOH flat ultrafiltration membranes were fabricated via immersion precipitation phase inversion technique. The specific steps was as follow. The different of carboxylation degree copolymer of PSF-COOH were dried under vacuum at 100℃for 24 h prior to use ,and PSF-COOH and PVP were dissolved in DMF to form homogeneous and transparent casting solutions. The mass ratio of polymer, PVP, and DMF were 16 : 6 : 78. After filtering and degassing, the polymer solution was cast on a glass plate with a glass rod at room temperature. After staying in air for 30 s, then the glass plate was immerged in the deionized water to form asymmetric structure membranes. After complete coagulation and washing, the membranes were kept in deionized water for characterization. The thickness of the membranes was about 100 μm.

2.4. Characterization

2.4.1. Polymer characterization

Fourier transform infra-red (FTIR) spectroscopy of PSF-COOH copolymer was carryed out with a Bruker Vector 22 spectrometer at a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1}.

2.4.2. Membrane characterization

The membrane morphologies were observed by scanning electron microscopy (SEM). The membranes were needed fractured in liquid nitrogen to avoid destroying the structure of the pore. All specimens needed 30 s of gold coating before test .

The pure water flux (J_w) of the membrane was determined by direct measurement of permeate volume, which was calculated by the following equation:

Where V was the volume of permeation, A was the effective membrane area and t was the permeation time.

The membrane rejection ratio (R) was calculated by using the following equation:

$$R=1- C_p/ C_f$$

In which C_p (mg/L) is the permeate concentration and C_f (mg/L) is the feed concentration. The solute concentration of permeation was measured by a UV–vis spectrophotometer (UV3600, Shimadzu).

3. Results and Discussion

FTIR was used to verify the incorporation of the carboxyl groups and chemical structures of the carboxylated polysulfone copolymers. As shown in Fig. 1, the absorption peaks was clearly observed at 1720 cm^{-1} for all carboxylated copolymers from PSF-COOH-20% to PSF-COOH-100%, which was attributed to the vibration of C=O group. Additionally, the density of the characteristic peak of the C=O group vibration increased with the increased carboxylation degree. The FTIR spectrum aids in concluding that the carboxylated monomers are introduced into the copolymers successfully as expected.

Fig. 2 presented the cross-section SEM images of membranes with different carboxylation degree. This images showed that the PSF-COOH membranes have typical asymmetric structures, which include the dense skin layer and the finger-like structure sub-layer. As shown in Fig. 2 ,with the increase of carboxylation degree, the membrane occurred more and wider finger-like pores and showed the trend of from finger-like structure to sponge-like (PSF-COOH-80%,PSF-COOH-100%). Another obvious phenomenon among these membranes is the increment of their pore sizes in the inner of sub-layer macrovoids. This was probably due to the intensity of the interaction between PSF-COOH and DMF increases with the increase of the hydrophilic carboxyl group. The strong interactions between PSF-COOH and DMF restrict the diffusion process of water and suppress the exchange rate of DMF and water, which increase the time to reach precipitation and induce the delayed liquid–liquid dimixing process take place and eventually result in the formation of larger porous structure [6-7]. However, the thickness of the dense skin layer were gradually decreased, the possible reason was that when lower carboxyl group content, interaction between copolymer and DMF is small, and DMF overflew at a faster rate without coagulating agent flowing in, which resulting in the formation of polymer-rich phase. Thus ,this is benefit to the formation of a thick dense skin. Vice versa.Ultrafiltration experiments were carried out to investigate the separation performance of a series of PSF-COOH membranes. Fig. 3 shows the changes in water permeation and protein rejection of the different membranes. The pure water flux was gradually increased from 124.20 L/m^2 h to 307.64 L/m^2 h with an increase carboxylation degree, However, BSA rejection ratio was slightly decreased from 99.7% to 94.6% as the carboxylation degree increase from 0 to 1. This result may be attributed to the increase of surface hydrophilicity and porosity of the PSF-COOH membranes.

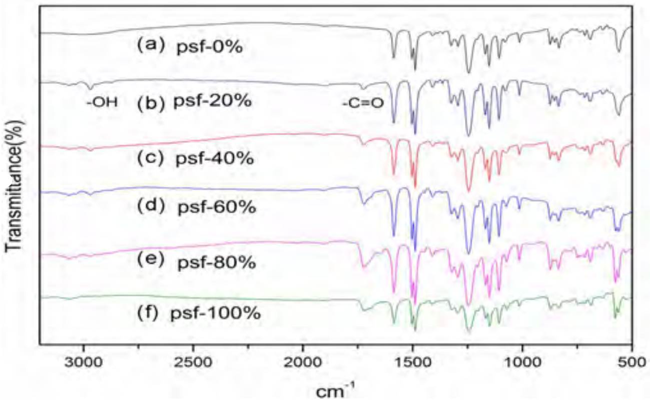


Fig.1. FTIR spectrum of the PSF-COOH copolymers: (a) PSF, (b) PSF-20%, (c) PSF-40%, (d) PSF-60%, (e)PSF-80%and (f) PSF-100%.

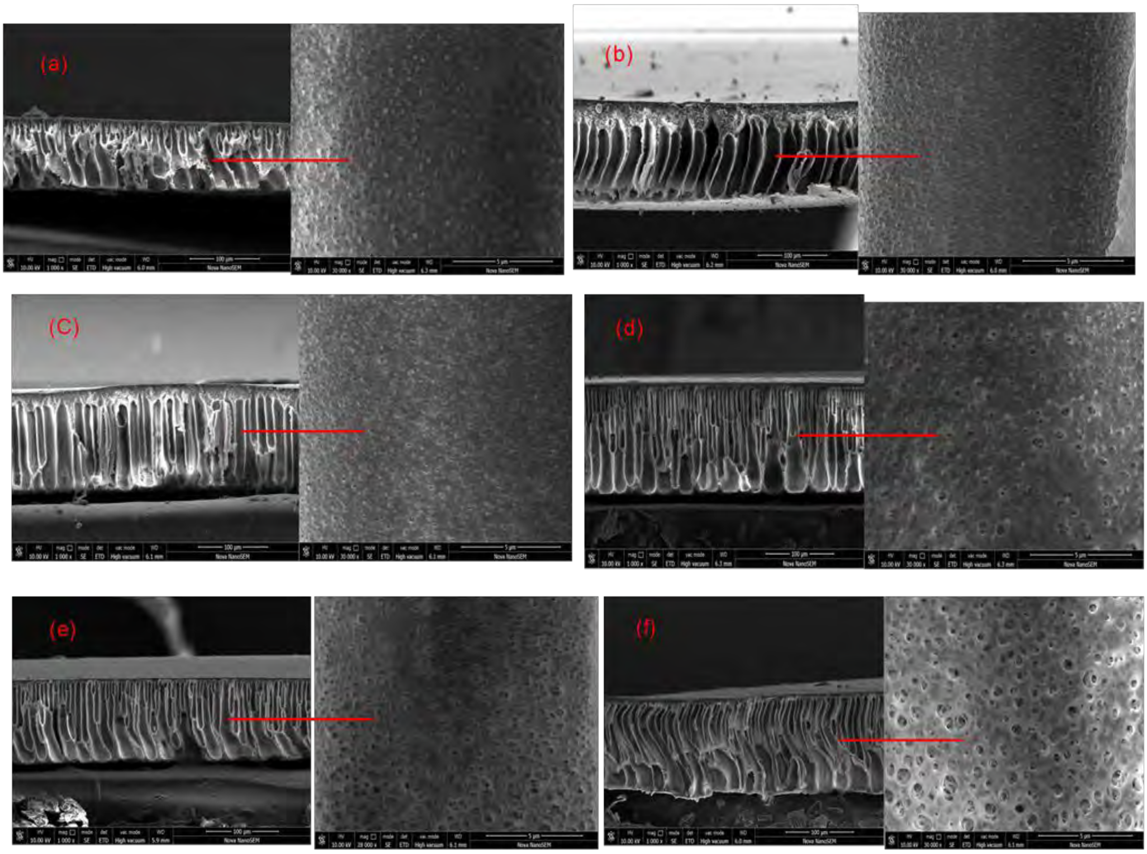


Fig.2. SEM images of the cross-sectional of the PSF-COOH membranes: (a) PSF, (b) PSF-20%, (c) PSF-40%,(d) PSF-60%, (e) PSF-80% and (f) PSF-100%.

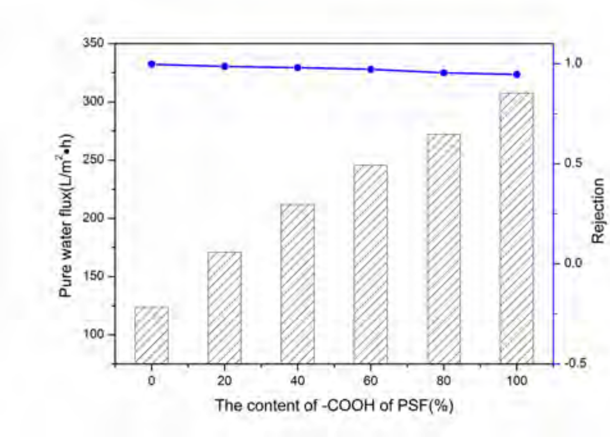


Fig 3. Pure water flux and BSA rejections of the PSF-COOH membranes.

Conclusions

In this study, we successfully synthesized different degrees carboxylated polysulfone copolymer by nucleophilic substitution reaction, and prepared a series of ultrafiltration menbranes by immersion precipitation phase inversion method. IR spectra confirmed the structures of PSF and PSF-COOH. SEM can observe morphology change of different carboxylation degree film and can reasonably explain this change in the kinetics and thermodynamics view. Ultrafiltration experiments results showed that with the increase of the carboxylation degree, the pure water flux of the membranes increased from the 124.20 L/m^2 h to 307.64 L/m^2 h, which proved the introduction of hydrophilic carboxyl group can successfully realize the hydrophilic modification of polysulfone ultrafiltration membranes, this was consistent with expectations.

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