Journal of Membrane Science 548 (2018) 481–489

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Antifouling polysulfone ultrafiltration membranes with pendent sulfonamide groups

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ARTICLE INFO

Keywords:
Sulfonamide
Ultrafiltration
Antifouling
Hydrophilicity

ABSTRACT

A series of polysulfones (PSfs) bearing sulfonamide groups were synthesized by chloromethylation and subsequently substitution with methanesulfonamide or benzenesulfonamide. The preparation of antifouling ultrafiltration (UF) membranes was achieved by the phase inversion method. The pure water flux of UF membranes was the in the range of 232–277 L m^{-2} h^{-1} bar^{-1}, which was much higher than that of pristine PSf UF membrane (116 L m^{-2} h^{-1} bar^{-1}). Importantly, the high protein rejections (> 97%) were retained for the sulfonamide-functionalized PSf UF membranes. The excellent hydrophilicity, high surface porosity and well vertically interconnected finger-like pores of the sulfonamide-functionalized PSf UF membranes confirmed by water contact angle and scanning electron microscopy (SEM) were believed to be the reasons of the high pure water flux. The antifouling properties were investigated by static protein adsorption experiments and ultrafiltration experiments using bovine serum albumin (BSA) as a foulant. All membranes with pendent sulfonamide groups showed lower BSA adsorption than the pristine PSf membrane because of the formation of the hydration layer near the surface via hydrogen bond between water molecules and the hydrophilic sulfonamide groups in polymer. Less irreversible fouling and thus higher flux recovery ratio (up to 95.1%) for sulfonamide-functionalized PSf UF membranes after three sequential dead-end filtration cycles were observed, which indicated their excellent antifouling properties. The results indicated that the PSf possessing pendent sulfonamide groups has the potential to alleviate the membrane fouling.

1. Introduction

Ultrafiltration (UF) membranes have been widely used for the separation of suspended solids or dissolved organic macromolecules [1,2], especially proteins [3], in food processing, wastewater treatment and pharmaceutical manufacturing thanks to their advantages such as low operating costs, high separation efficiency and simplicity [4,5]. Polysulfone (PSf) [6], polyethersulfone (PES) [7], cellulose acetate (CA) [8], polyacrylonitrile (PAN) [9] and polyvinylidene fluoride (PVDF) [10,11] are commonly employed as materials for commercial UF membrane. Among of them, PSf is a remarkable starting material for the preparation of ultrafiltration membrane due to its high chemical and thermal stability, adequate mechanical strength and excellent film forming ability. However, the hydrophobic nature of membranes made from PSf exacerbates their susceptibility to fouling due to the strong hydrophobic interactions between foulants and the membrane surface [12]. Therefore, membrane fouling has been a major problem in membrane filtration [13,14] and great efforts have been made to overcome the fouling issues [11,15].

It has been found that the highly hydrophilic membrane surfaces can attract a strongly bound water layer, which is effective to reduce membrane-foulant hydrophobic interactions and thus lessen the membrane fouling [16–18]. Various methods have been utilized to improve the surface hydrophilicity of PSf UF membrane such as surface coating [19], surface grafting [20,21] and additive blending [22–24]. The poly (methyl methacrylate) comb copolymers with oligoethylene glycol side chain were synthesized by Hyun et al. for the surface modification of PSf UF membranes [24]. The modified UF membranes exhibited a much greater response to cleaning cycles than unmodified membranes, which was explained by the excellent hydrophilicity of the modified membranes. A significant disadvantage of membrane surface modification by adsorption is that the antifouling modifiers may leach out from the surface over time [20]. Therefore, antifouling materials have been grafted onto/from membrane surfaces by various techniques including chemical treatment [25], UV irradiation [26], and plasma treatment [27]. Although these techniques for surface treatment or surface

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https://doi.org/10.1016/j.memsci.2017.11.064
Received 30 August 2017; Received in revised form 15 November 2017; Accepted 26 November 2017
Available online 27 November 2017

activation can be successfully applied for antifouling modification of PSf UF membranes, the aggressive treatments may cause PSf UF membrane damage [28,29]. Polymer blend is another common method to improve membrane hydrophilicity. Inorganic particles, hydrophilic polymers and amphiphilic copolymers are frequently used as additives. Wang and coworkers blended amphiphilic block copolymer, polysulfone-*block*-polyethylene glycol with PSf base polymer to prepare PSf UF membranes. The blend membranes exhibited simultaneously upgraded permeance, hydrophilicity, and fouling resistance [30]. However, the antifouling UF membranes obtained by surface modification or additive blending method were faced with a long-term stability problem of their antifouling ability.

Therefore, permanently hydrophilic modification of PSf, such as sulfonation [31,32] and quaternization [33], has been considered as a powerful method for anti-fouling UF membrane. Pozniak and coworkers has reported the sulfonated polysulfone UF membranes which showed improved anti-fouling ability [34]. Subsequently, Summers et al. prepared highly anti-fouling dipyridyl-functionalized PSf UF membranes [35]. High water flux and anti-fouling ability were observed for these hydrophilic-modification UF membranes. While all these systems demonstrated reasonable properties as UF membranes and established the feasibility for UF practical water treatment applications, the simultaneous improvement of membrane performance and anti-fouling ability is still a major challenge in the development of UF membranes.

Sulfonamide (compound) which is a compound that contain -S$(=O)_2$-NH_2, an amine group attached to a sulfonyl group has been widely used as an synthetic antimicrobial or antibacterial agents in medical chemistry. However, there is not any report about sulfonamide-functionalized PSf for anti-fouling ultrafiltration membrane. Herein, PSf with pendent sulfonamide group was firstly synthesized by the chloromethylation of PSf and subsequently substitution with methylsulfonamide or benzenesulfonamide. A detailed investigation on the properties of sulfonamide-functionalized PSf UF membranes was performed. Their hydrophilicity, water flux and anti-fouling ability are described and compared to those of UF membranes from commercial PSf.

2. Experimental

2.1. Materials

A commercial available PSf (P-1001A, M_n = 41000) was received from Solvay. Chlorotrimethylsilane [$(CH_3)_3SiCl$, > 98%], tin tetrachloride ($SnCl_4$, > 99%), paraformaldehyde [$(CH_2O)_n$, > 96%], bovine serum albumin, methanesulfonamide (99%) and benzenesulfonamide (98%) from Energy Chemical were used without further purification. All the other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis and characterization of sulfonamide-functionalized PSf

Chloromethylated PSf was obtained according to the previous reports [36]. In a round bottom flask with a reflux condenser and magnetic stirring, 20 g (45.2 mmol) PSf was dissolved in 670 mL of $CHCl_3$. 14.13 g (452 mmol) paraformaldehyde, 58 mL (452 mmol) $(CH_3)_3SiCl$ and $SnCl_4$ (1.1 mL, 9 mmol) were added to the PSf solution. The mixture was heated to 60 °C and reacted at this temperature for a period of time. The reaction mixture was precipitated in methanol and washed with methanol for three times. The polymer was filtered and dried in a vacuum drying oven at 50 °C for 24 h. The reaction was carried out at different experiment time such as 3, 7 and 14 h leading to chloromethylation degree (the value of “x” in Scheme 1) of 7, 13 and 21 mol %, respectively. They are named with the chloromethylation degree as CMPSf-7, CMPSf-13 and CMPSf-21.

Sulfonamide-functionalized PSf was prepared as following [37]. CMPSf-13 (4.5 g) in DMF (50 mL) was slowly added dropwise to the mixture of benzenesulfonamide (5.5 g) or methanesulfonamide (3.2 g), finely powdered K_2CO_3 (1.6 g) and DMF (50 mL) at ambient temperature (25 °C) with efficient stirring. After addition had been completed (2 h), stirring was continued at ambient temperature for 5 h. The resultant mixture was then precipitated in diluted hydrochloric acid. The product was washed with deionized water for three times and dried in a vacuum drying oven at 60 °C for 24 h. The reaction product of benzenesulfonamide or methanesulfonamide with CMPSf-13 was named as BSAPSf-13 or MSPSf-13. BSAPSf-7, BSAPSf-21, MSPSf-21 and MSPSf-7 were synthesized similarly (MSPSf-21 was found brittle and unfit for UF membranes preparation).

^{1}H NMR spectra were obtained with a Bruker AVANCE III 400 MHz spectrophotometer at room temperature using $CDCl_3$ or DMSO-d_6 as the solvent. The thermogravimetric analysis of PSf, BSAPSf-13 and MSAPSf-13 was conducted under a nitrogen atmosphere with a Perkin-Elmer TGA-7 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} from 40 to 700 °C.

2.3. Membrane preparation

The UF membranes of PSf, MSAPSf and BSAPSf were prepared by the nonsolvent-induced phase inversion process. A solution of 16 wt% polymer (PSf, BSAPSf for MSAPSf) and 16 wt% ethylene glycol monomethyl ether (EGM) as pore-forming agent in NMP (68 wt%) was cast onto a clean glass plate and obtain a liquid film with the thickness of ~ 100 μm with a casting knife. The cast film was allowed to stand in air for 10 s and then immersed in deionized water at room temperature. Phase inversion took place and UF membrane was obtained. The membrane was washed thoroughly with fresh deionized water before it was tested.

Dense membranes of PSf, MSAPSf and BSAPSf were prepared to measure the hydrophilicity of the polymers. The polymer (1 g) was thoroughly dissolved in NMP (9 g) to obtain a homogeneous solution after filtration and degassing. The solution was cast onto a clean glass plate and then dried in a forced-air drying oven at 80 °C for 12 h and in vacuum at 100 °C for 24 h.

2.4. Membrane characterization

The membrane porosity (ε) was determined by wet and dry weight method [38]. Square pieces of membranes that had been dipped in deionized water at room temperature for 24 h were weighted after removing excessive water with a filter paper. The wet membrane samples were dried in a vacuum oven at 60 °C for 24 h and then the dried membrane samples were weighted. The porosity was calculated using Eq. (1):

$$\varepsilon = \frac{w_1 - w_2}{V\rho_w} \qquad (1)$$

where w_1 is the weight of the wet membrane, w_2 is the weight of the dry membrane, ρ_w is the density of water (1.0 g/cm^3) and V (m^3) is the volume of the membrane which is calculated with the membrane thickness and membrane area.

The membrane structures, including surface and cross-section morphologies, were observed by scanning electron microscopy (Hitachi S4800). The samples for cross-section observation were prepared by freeze-fracturing the membranes in liquid nitrogen. Prior to imaging by SEM, all the samples were sputtered with gold. The surface SEM images were analyzed using ImageJ 1.48v software (National Institutes of Health, USA1.48v) to calculate quantitatively the surface pore size and surface porosity of the membranes according to the literature of Masselin et al. [39]. Atomic force microscopy (Veeco Multimode V) imaging was used to analyze the membrane surface roughness.

The contact angle was measured by the sessile drop method using KINO SL 200KB at ambient temperature. A camera was used to capture the image of the droplet which was dropped onto the surface of