



Full Length Article

Preparation of hydrophilic and antifouling polysulfone ultrafiltration membrane derived from phenolphthalin by copolymerization method



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ARTICLE INFO

Article history:

Received 17 November 2016

Accepted 29 December 2016

Available online 30 December 2016

Keywords:

Carboxylated polysulfone

Ultrafiltration membrane

Hydrophilicity

Antifouling

ABSTRACT

In this task, carboxylated polysulfone (PSF-COOH) was achieved by introducing the monomer of phenolphthalin (PPL) containing carboxyl to the molecule backbone of polysulfone (PSF). And a series of PSF-COOH copolymers with different carboxylation degree was synthesized by adjusting the molar (%) of bisphenol A (BPA) and PPL in direct copolymerization method and was prepared as PSF-COOH ultrafiltration membranes *via* phase separation method. The effect of PPL molar (%) in copolymers on the morphology, hydrophilicity, permeation flux, antifouling and mechanical properties of membranes was investigated by scanning electron microscope (SEM), atomic force microscope (AFM), water contact angle, ultrafiltration experiments and universal testing machine, respectively. The results showed that with the increased carboxyl content in membranes, the hydrophilicity, permeation fluxes and antifouling properties of membranes gradually increased. When the molar (%) of PPL to BPA was 100:0, the membrane exhibited the highest pure water flux (329.6 L/m² h) and the maximum flux recovery rate (92.5%). When the content of carboxyl in the membrane was 80% or more, after three cycles of BSA solution (1 g/L) filtration, the flux recovery rate was basically constant or showed a slightly increase. Thus, it can achieve the goal of long term usage without compromising flux.

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1. Introduction

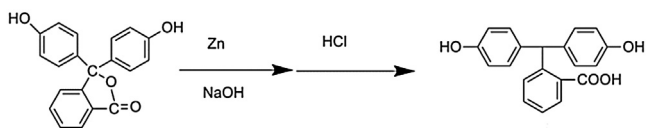
In recent decades, membrane separation technology was widely used in food [1], pharmaceutical [2], biotechnology [3], water treatment [4] and other fields [5–7] due to its outstanding performance like low energy consumption, good selectivity, no phase change, room temperature operation etc. [8]. The ultrafiltration membrane whose pore size varied from 1 nm to 100 nm can effectively separate and remove the macromolecules in waste water, such as humic acid and protein [9]. A lot of polymers like PSF, polyvinylidene fluoride (PVDF), cellulose acetate (CA), polyacrylonitrile (PAN) etc. were often used as ultrafiltration membrane materials [10]. Among these polymers, PSF and PSF based polymers played an increasingly important role in the field of ultrafiltration membrane materials because of their excellent performance such as good thermal stability, acid and alkali resistance, durable mechanical property and good film-forming property [11]. However, due to the inherent hydrophobic property of PSF membrane, organic or non-organic substances contained in waste water can easily adsorb or deposit on the membrane surface or in pores, causing the so-called membrane

fouling and then directly resulting in the flux decrease, shorter life expectancy of membranes. Accordingly, cleaning and handling costs also increased [12]. Consequently, the hydrophilic modification of PSF membrane to improve antifouling property seemed particular important.

Up to now, four methods, namely, coating [13], grafting [14], blending [15] and membrane based material modification [10] had been used to modify the hydrophilicity of membranes to improve the permeability and antifouling properties of membranes. Although the first three methods improved the hydrophilic of membranes to a certain extent, there were still some drawbacks: the coating can easily lead to the shedding and loss of the hydrophilic coating materials; the grafting *via* a redox reaction [16], plasma treatment [17] and UV irradiation [18] was prone to damage the properties of the membrane materials and it required tedious experimental procedures and harsh chemical environment [19]; the blending was likely to occur the incompatibility of organic additives [20] and the agglomeration of nanoparticle [21], which would limit the improvement of membranes hydrophilicity. The fourth method, membrane based material modification, was the introduction of hydrophilic substance or monomer containing a hydrophilic group into the molecule skeleton of the membrane based material by chemical reaction. This method can retain the excellent performance of the membrane material while improving the hydrophilic

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Scheme 1. Synthesis of the monomer of phenolphthalin (PPL).

property of the raw material. More importantly, it can not only realize the comprehensive modification of the membrane surface and the membrane matrix uniformly and firmly, but also achieve large-scale industrial production of hydrophilic membrane conveniently and concisely.

The introduction of hydrophilic substance or monomers containing polar groups (sulfonic acid group, carboxyl group, hydroxyl group, amino group) had improved the hydrophilicity and antifouling property of the membrane base material. For example, Ruikui et al. [22] reported the reaction between chloromethylated polysulfone (CMPSF) and polyethylene glycol monomethylether (PEGME) via nucleophilic substitution for preparing the copolymer PSF-g-PEG and the hydrophilicity and antifouling property of PSF ultrafiltration membrane were greatly improved; Liu et al. [10] synthesized a series of SPPSU with various controlled sulfonation levels by using sulfonated monomer in direct copolymerization method. When sulfonation degree of PPSU increased up to 20%, its hydrophilicity and antifouling property reached the maximum; it was also mentioned in another article [23] of Liu et al. that poly(arylene ether sulfone) containing hydroxyl groups (PES-OH) exhibited the smaller contact angle and the higher water flux compared with pure PES. Carboxyl, in terms of acidic and water-absorbent, is slightly weaker than sulfonic acid group, and unlike sulfonic acid group, the appearance of large amount of carboxyl can not cause swelling phenomenon. In addition, it often can be found that the substance containing carboxyl introduced into the membrane material by blending [24], grafting [25] and coating [26] can achieve the modification of hydrophilicity and antifouling, but the carboxyl which was introduced into the PSF molecular skeleton by a method of copolymerization was rarely seen.

In this study, we introduced PPL containing carboxyl into the molecule skeleton of PSF by the method of random copolymerization to synthesize a series of PSF-COOH copolymers with different carboxylation degree for preparing PSF-COOH ultrafiltration membranes. The chemical structures of PSF-COOH copolymers were thoroughly characterized by Fourier transform infra-red (FT-IR) and Nuclear magnetic resonance hydrogen spectrum (^1H NMR). And the morphology, surface roughness, surface hydrophilicity and the tensile strength of membranes were all characterized by SEM, AFM, water contact angle and universal testing machine, respectively. The ultrafiltration performance of membranes was also evaluated by the cycle ultrafiltration experiments in detail and each of antifouling parameters was also calculated accurately.

2. Experimental

2.1. Materials

4,4-dichlorodiphenylsulfone (DCDPS) was purchased from Yinsheng Chemical Co., Ltd. (Suzhou, China). 4,4-bisphenol A (BPA) and anhydrous potassium carbonate (K_2CO_3) were purchased from Acros., Shanghai. Phenolphthalein (PPL) was synthesized from phenolphthalein according to the steps (Scheme 1) mentioned in literature [27]. Poly(vinylpyrrolidone) (PVP, 30K) served as pore-former additives and was obtained from Sinopharm Chemical Reagent Co., Ltd. Bovine serum albumin (BSA, $\text{pI}=4.7$, $M_w=67,000$) was provided by Blue Season biological, Shanghai, China. Coomassie brilliant blue G250 was supplied by Aldrich

Table 1
Fundamental information of PSF-COOH copolymers.

Polymer	Feed molar (%)			DC	Viscosity η_{sp}/c (dL/g)
	BPA	PPL	DCDPS		
PSF	100	0	100	0	0.60
PSF-COOH-20%	80	20	100	0.20	0.61
PSF-COOH-40%	60	40	100	0.40	0.58
PSF-COOH-60%	40	60	100	0.60	0.57
PSF-COOH-80%	20	80	100	0.80	0.55
PSF-COOH-100%	0	100	100	1.00	0.58

Chemical Inc. Dimethyl sulfoxide (DMSO) and Dimethyl formamide (DMF) were both obtained from Tianjin Chemical Reagent Factory, and they worked as reaction solvent and casting solvent, respectively. Other reagents such as concentrated hydrochloric acid (HCl, 38%), toluene and ethanol were purchased from Beijing Chemical Plant, and pure water was obtained from the laboratory and used throughout the experiments. All reagents were used as received without further purification.

2.2. Synthesis of PSF-COOH copolymers

The PSF-COOH copolymers were synthesized via nucleophilic step polymerization (Scheme 2), and the different carboxylation degree were controlled by changing the feeding molar (%) of PPL and BPA, where PPL (%) / BPA (%) were 0:100, 20:80, 40:60, 60:40, 80:20 and 100:0, corresponding to the copolymers named PSF, PSF-COOH-20%, PSF-COOH-40%, PSF-COOH-60%, PSF-COOH-80%, PSF-COOH-100%, respectively (Table 1). The preparation of PSF-COOH-80% was used as a representative to illustrate detailed synthetic procedures. Firstly, 0.9132 g (4 mmol) of BPA, 5.1254 g (16 mmol) of PPL, and 5.7432 g (20 mmol) of DCDPS were added into a three neck flask equipped with a nitrogen inlet, DeanStark trap and magnetic stirrer. Then 30.9654 g of DMSO was added into the three neck flask to obtain a 25% solid concentration. Subsequently, 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 slowly heated to 150 °C and maintained for some hours. When no water was observed in the Dean-Stark trap, the temperature rose to 160 °C and maintained for some hours till the viscosity did not increase further. Finally, the product was poured into pure water to consolidation. After consolidation, the product was crushed into powder by crusher and repeatedly washed with boiling pure water to remove excess solvent and inorganic salt. Then the fine powder was immersed in a stirred 1 mol/L hydrochloric acid to reflux for 8 h. The precipitated copolymer was washed to neutral with pure water and dried in a vacuum oven at 120 °C for 24 h.

2.3. Membranes preparation

PSF-COOH flat ultrafiltration membranes were fabricated via immersion precipitation phase inversion technique. Specific steps were as follows. A series of PSF-COOH copolymers needed to be vacuum-dried at 100 °C for 12 h prior to use. Afterwards, the calculated amount of PSF-COOH and PVP were dissolved in DMF and mixed completely by magnetic stirring at 70 °C for 8 h to form homogeneous and transparent casting solutions, where the mass ratio (%) of the copolymer, additive, solvent was 16:6:78. After being filtered and vacuum-degassed, the casting solution was poured onto a cleaned glass plate and spread out using a casting knife with a gap of 100 μm at room temperature. Before the glass plates were immersed in pure water, the membranes stayed in air for 30 s. Immersed in the coagulating bath for some seconds, the membranes spun off from the glass plate to form nascent membranes. Then membranes were thoroughly precipitated and

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