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Preparation of a novel sulfonated polyphenlene sulfone with flexible side chain for ultrafiltration membrane application

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ABSTRACT

In order to mitigate the selectivity-permeability trade-off for ultrafiltration membranes, a series of polyphenylene sulfone (PPSU) with flexible negative charged sulfonated side chains (SPPSU-SC) were synthesized applied in ultrafiltration (UF) field. And tests results showed that the ultrafiltration performance was enhanced greatly. In short, the water flux increased to 380 $L{\cdot}m^{-2}h^{-1}$ at the sulfonation degree of 20%, which was as two and a half times high as PPSU membranes. However, the membrane SPPSU-SC20 still held a relatively high BSA rejection of 91.6%, which should be attributed to the enrichment of negative charged sulfonic groups on the membrane surface. More importantly, the antifouling properties were also promoted. The total fouling ratio (R_t), reversible fouling ratio (R_r), irreversible fouling ratio (R_{ir}) and flux recovery ratio (FRR) were all improved to some degree. Besides, compared to the main-chain sulfonated PPSU with the sulfonation degree of 20% (SPPSU-MC20) membranes, SPPSU-SC20 had a better separation structure caused by better phase separation during the membrane preparation period at the sane high sulfonation degree. In a word, the results showed that side-chain sulfonated PPSU possessed a potential bright horizon in ultrafiltration field.

1. Introduction

As time and technology change, people begin to realize the importance of shortage of water resources [1,2]. Therefore, finding methods to recycle waster water has attracted researchers' interests. Separation membranes, especially ultrafiltration membranes have gradually stepped into daily life to serve as an effective measure for the water initial treatment because it is environmental-friendly, cheap and developed devices are easy to operate [3–7].

Still, considerable researches have been carried out to further improve the ultrafiltration performance [8–10], most of which focus on the enhancement of surface hydrophilicity as it is closely associated to the permeability and anti-fouling properties of the membranes [8,9]. As an efficient modification, blending is always used to improve the performance [11–14]. Plenty of nanoparticles or modified nanoparticles including silicon dioxide [15–17], graphene [18], graphene oxide [19,20], carbon nanotubes [21–24] and so on have been applied as addictives to improve the performance of membranes. However the incompatibility between nanoparticles and the polymer membrane cannot be ignored [25–29]. In contract, application of polymer addictives especially sulfonated polymer is more desirable because of the better compatibility and low-cost [30–34]. By introducing sulfonated polymer addictives into the system, performance of membrane can be greatly improved. By preparing PES/SPSF composite membrane via H_2O-induced gelation phase separation, Li et al. achieved a high water flux of 858 $L{\cdot}m^{-2}h^{-1}$ and the concentration of SPSF in the casting solution was just about 3%. The strong interaction between H_2O molecules and the sulfonic groups, which led to the formation of sponge-like structure, attributed a lot to the amazing performance [35]. Besides, the sulfonated polymers can endow membranes with some specific functions. When blending SPES with polyrhodanine (PRh), because of the strong ionic bond and hydrogen bond, between sulfonic groups and PRh, the PRh would segregate to the interface between membrane surface and nonsolvent phase, Peyravi et al. finally got a nanocomposite membrane with both high water flux and excellent antibacterial character [36]. And it's well accepted that selectivity-permeability trade-off effect widely appears in separation membranes [37,38]. Usually, along with the increase of water flux, the rejection decreases. However, poly (m-phenylene isophthalamide) (PMIA) membranes prepared by Zhu et al. showed the tendency that flux and separation efficiency could get elevated at the same time. But the low operation pressure and low flux limited the practical application in daily use [39].

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In this work, to avoid the decrease of separation efficiency with the increase of sulfonation degree [40], a pre-synthesized monomer of which sulfonic group was attached by a flexible alkyl chain was synthesized [41] and introduced to the copolymerization system. As a result, a series of SPPSU-SC were synthesized. And the prepared membranes showed improved UF performance because of the existence of more negative charged sulfonic groups in the membrane. At the same time, compared to the enhancement of the water flux, the loss of BSA rejection could be ignored. In other words, the electivity-permeability trade-off was effectively mitigated. Compared to the complex blending or post-modification, our work provides a new method to prepare UF membranes with high performance.

2. Materials and methods

2.1. Chemical materials

Three kinds of commercial polysulphone membranes (US010, US020, US030) were purchased from RisingSun Membrane Technology (Beijing) Co., Ltd. N-methyl-2-pyrrolidinone (NMP, AR grade), ethanol (C_2H_5OH, AR grade), potassium carbonate (K_2CO_3, AR grade) and polyvinyl pyrrolidone (PVP K30, AR grade) were bought from Sinopharm Chemical Reagent Co., Ltd. 4,4-Biphenol (DOD, AR grade) and 4-fluorophenylsulfone (AR grade) were purchased from TCI (Shanghai) Development Co., Ltd. Tetramethylene sulfone (TMS, AR grade), polyethylene glycol (PEG, AR grade) and polyethylene oxide (PEO) with different molecular weights were bought from Aladdin Industrial Corporation. And bovine serum albumin (BSA, Mw = 66.4 KDa) was provided by Shanghai Bluegene Biotech Co., Ltd. Sulfonated Monomer Sodium 3-(4-(2,6-Difluorobenzoyl)phenyl)propane-1-sulfonate (SDFPPS) was synthesized and characterized in our previous work [41]. And 4,4′-dichlorodiphenyl sulfone (DCDPS) was synthesized on the basis of Chung's work [40].

2.2. Synthesis of side-chain sulfonated PPSU

The SPPSU-SC were synthesized by direct copolymerization. Briefly speaking, taking SPPSU-SC20 for an example where the number 20 is referred to the sulfonation degree, a 50 mL three-neck round-bottomed flask equipped with a nitrogen inlet and a dropping funnel was charged with SDFPPS (0.7246 g, 2 mmol), 4-fluorophenylsulfone (2.034 g, 8 mmol), DOD (1.8621 g, 10 mmol), potassium carbonate (1.6585 g, 12 mmol), toluene (5 mL), and tetramethylene sulfone (TMS, 11 mL). The mixture was kept at room temperature for 0.5 h and then heated to 155 °C for 3 h and to 190 °C for another 8 h. Finally, the mixture was poured into DI water to get white flakes. After being smashed and washed by DI water and ethanol for several times, the product was dried in a vacuum oven at 100 °C for 12 h. The PPSU, SPPSU-SC5, SPPSU-SC10 and SPPSU-SC15 were synthesized in the similar way by precisely controlling the feed ratio. As a contrast, SPPSU-MC20 was also synthesized. Similarly, DOD (2.7932 g, 15 mmol), 4-fluorophenylsulfone (3.4238 g, 13.5 mmol), DCDPS (0.7369 g, 1.5 mmol), potassium carbonate (2.4878 g, 18 mmol), toluene (10 mL), and tetramethylene sulfone (TMS, 17 mL) was loaded to a 100 mL three-neck round-bottomed flask equipped with a nitrogen inlet and a dropping funnel. The mixture was kept at room temperature for 0.5 h and then heated to 155 °C for 3 h and to 190 °C for another 6 h. The ejection of compact and purification of the product was the same as the SPPSU-SC. The synthesis route was shown in Scheme 1.

2.3. Characterization of the copolymers

Here hydrogen nuclear magnetic resonance spectrometry (^{1}H NMR, Bruker510, 500 MHz) with DMSO-d_6 as solvent and Fourier transform infrared spectrometer (FT–IR, Nicolet Impat 410, Nicolet, Co., USA) equipped with the spectra acquired with air as the background were used to characterize the synthesized copolymers. Besides, the viscosity of the synthesized copolymers was also tested with NMP as the solvent by Ubbelohde viscometer and the concentration of the solution was controlled at 0.5 g·dL^{-1}. And the thermal stabilities are studied with thermogravimetric analyses (Pyris 1TGA, Perkin-Elemer) from 50 °C to 800 °C at the heating rate of 10 °C·min^{-1} under nitrogen condition. The glass transition temperature (T_g) was determined by differential scanning calorimeter (DSC Q2000, TA instruments) from 50 °C to 400 °C at the heating rate of 10 °C·min^{-1} under nitrogen condition.

2.4. Membrane preparation

The UF membranes were prepared via non-solvent induce phase separation method (NIPs). First, the copolymer and PVP were dissolved in NMP under constant mechanical stirring at room temperature for over 8 h and then get degassed to get a homogenous solution. After that, the solutions were poured on a smooth glass plate and casted by a casted knife with a gap of 200 μm at 25 °C and evaporated for 30 s. Finally, the UF membranes were obtained after the solution film together with the glass plate were immersed into a water bath at 25 °C after fully solvent exchange. The composition of the casting solution was shown in the Table 1.

2.5. Membrane morphology and hydrophilicity

The surface and cross-section morphologies were detected by field emitting scanning electronic microscopy (FE-SEM, Nova Nanosem 450, FEI Co., USA). The membrane samples were dried at 120 °C for ten hours before test. And the surface hydrophilicity was characterized by testing the water contact angle (WCA) with Drop Shape Analyzer (DSA 100, Krüss GmbH, Hamburg, Germany). A water droplet of 4 μL was dropped on the dried membrane surface and 3 s later a photograph was taken by the equipped CCD camera, and the water contact angle was calculated by taking the average of no less than six independent test result on different sites of each membrane sample.

2.6. Ultrafiltration tests

The permeation and separation properties of prepared membranes and three kinds of commercial membranes were measured by a home-made cross-flow membrane performance evaluation equipment, which consisted of a water pump, solution storage containers, and a cross-flow filtration cell with an effective filtration area of 7.07 cm^2. And before the test, the purchased US020 was pre-soaked in DI water and ultrasounded for a certain time to recover the membrane performance. The test membranes were pre-compacted with a relatively high pressure of 0.15 MPa by deionized water for 1 h to obtain a steady permeation flux, and then the ultrafiltration experiments were carried out at a pressure of 0.1 MPa. The volume of filtrate was collected and recorded every 5 min. The pure water flux of the membrane (J_w, L/m^2 h) is defined as follows:

$$J_W = \frac{V}{A \times \Delta t} \tag{1}$$

where V (L) is the permeate volume; A (m^2) is the effective filtration area; Δt(h) is the collection time. In the following, BSA was dissolved in isotonic phosphate-buffered saline solution (PBS, pH = 7.4). The permeation flux of foulant feed solution was calculated as J_p (L·m^{-2}h) based on the permeated water quantity at 0.1 MPa. The rejection ratio (R) of BSA was calculated by following Eq. (3):

$$R = \left(1 - \frac{C_p}{C_0}\right) \times 100\% \tag{2}$$

where C_P and C_0 are the concentrations of BSA in the permeate and in the feed, respectively, which were analyzed via UV–Vis spectrophotometer (UV-2501, Shimadzu, Japan) at 278 nm. After BSA solution