



Chiral resolution by polysulfone-based membranes prepared via mussel-inspired chemistry



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ABSTRACT

Reported herein is a chiral resolution polysulfone membrane prepared via mussel-inspired chemistry. Polysulfone membranes were modified with dopamine, which underwent in situ polymerization on the membrane substrate, and β -cyclodextrin was used as a chiral selector. The preparation conditions were optimized and the resultant membrane obtained under these conditions showed desirable water permeability (~ 24.0 L/(m²·h·bar)) and surface hydrophilicity (contact angle is lower than $37.1 \pm 3.4^\circ$). The polydopamine layer exhibited desirable stability in a series of aqueous solutions with pH values ranging from 4.0–6.0 or in isopropanol for less than an hour (detachment ratio was lower than 1.2%). Characterization of the surface morphology and XPS elemental analysis revealed that the membrane surface was fully coated by polydopamine and a β -cyclodextrin monolayer formed on the surface of the polydopamine coating. The grafting density of β -cyclodextrin calculated from the XPS results was ~ 11.5 mg/m². The optimal pH value for the resolution of D- or L-tryptophan feed solution was 5.90 and a low concentration of the feed solution provided a high resolution efficiency. The enantiomeric excess (e.e.) value of the membrane for Trp racemic mixture achieved to $\sim 3.2\%$ with the feed solution of tryptophan racemic mixture was 5×10^{-5} mol/L and the operating pressure was 0.1 MPa. After 3 times of isopropanol-washed regeneration processes, the e.e. value was still stable around to $\sim 3\%$. The mussel-inspired chemically modified membrane exhibited the same mechanical properties as the purely polysulfone-based membrane. The methods and results provided in this paper may facilitate the large-scale production of chiral resolution membranes or other chiral separation membranes with higher performance.

1. Introduction

Enantioseparation technology has been developed rapidly in response to demand for optically pure compounds with a wide variety of applications in the last two decades [1]. Crystallization resolution, kinetic resolution, chromatographic separation, membrane-based separation and other technologies have been popular approaches to prepare optically pure chiral compounds [2–5]. The use of solid chiral separation membranes has been considered as a promising method for achieving large-scale enantioseparation due to their low energy consumption, simplicity and continuous operability [5,6]. Based on the previous work, there are two strategies for preparing a solid chiral resolution membrane. The first strategy involves forming a membrane from a natural or synthetic polymer that contains chirally active carbons on its backbone, such as cellulose and its derivatives, sodiu-

malginate, chitosan and etc. [7–9]. Another strategy is to directly introduce the modified-chiral selectors onto the substrate [10]. Although the formation of a chiral resolution membrane directly from a mixture of chiral selectors and a substrate is a simple method, the miscibility between a chiral selector and a substrate is a critical issue because it can determine whether the resultant composite membrane has suitable interfacial properties. The hydrophilic chiral selectors may be prone to detach from the surface of the composite membrane after prolonged exposure to water [11].

The modification of post-prepared substrate membranes is another promising method. Some physical techniques have been utilized on the surfaces of substrate membranes to generate polar species, such as plasma-grafting, irradiation grafting, photo-grafting and other strategies [12–15]. Although these widely reported methods were suitable for the modification of substrate membranes, they still had disadvantages

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in certain situations. For example, the main disadvantage of plasma-treatment is the high cost of high vacuum systems [16]. In addition, the irradiation with high energy may cleave the chemical bonds of the substrate membrane, it is difficult to modify the internal surface of hollow fiber membranes via photo-grafting and the UV irradiation may weaken the membrane's performance [17,18]. Furthermore, various thermolabile chiral selectors, such as proteins and DNA, also have high affinities toward the enantiomer, and mild conditions are required to accommodate their introduction onto the surface of the substrate membrane [19,20]. Thus, a mild and convenient surface modification technology is also required to enable to preparation of novel and applicable chiral resolution membranes.

Dopamine (DOPA), an important neurotransmitter in the human body, can form a self-polymerized coating on various substrates under alkaline and aerobic conditions [21]. The resultant polydopamine (PDA) coatings have been widely used as intermediate layers for composite membranes and they can conjoin organic or inorganic chemicals on the surface of various substrates because the catechol groups in the DOPA unit can further react with thiol- and amino-containing compounds via Michael addition or Schiff-base reactions [21–25]. As has been demonstrated in previous reports, many thermoplastic polymers, such as polysulfone (PSf), poly(ether sulfone) (PES), poly(vinylidene fluoride) (PVDF) could be modified by PDA to form various functional composite membranes with desirable chemical and mechanical properties [26–28]. Meanwhile, the hydrophilicity of the substrate is also enhanced due to the excellent hydrophilicity of PDA coatings [29]. The hydrophilicity of a PDA coating protects the resultant membrane against bio-fouling and enhances the diffusion rate of hydrophilic materials during the separation process [5,30].

We are not aware of any reports describing the preparation of chiral resolution membranes via mussel-inspired chemistry. This is a facile method for introducing chiral selectors onto the surface of a substrate membrane without requiring any costly pre-treatment. Meanwhile, the enhanced hydrophilicity of the substrate membrane can facilitate the absorption or desorption of an enantiomer which has a stronger binding affinity for certain chiral sites over others and enhances the resolution efficiency during a gradual transport process [5]. Thus, we used PDA to bind the chiral site onto the surface of the substrate membrane to prepare a diffusion-selective chiral resolution solid membrane in this work. Polysulfone and β -cyclodextrin were selected as the substrate and chiral selector, respectively. The membrane's water permeability, stability, surface chemical composition, and enantioselectivity for tryptophan (Trp) enantiomers, were evaluated and discussed. The facile and mild strategy reported in this work may be useful for the large-scale preparation of solid chiral resolution membranes or other chiral separation membranes with higher performance.

2. Experiments section

2.1. Materials and reagents

PSf (Udel®P1700 NT LCD, $M_n = 39,000 \text{ g}\cdot\text{mol}^{-1}$) was purchased from Solvay Specialty Polymers. Polyethylene glycol (PEG, $M_n = 2000 \text{ g}\cdot\text{mol}^{-1}$), dopamine hydrochloride (98%), D -Trp (98%) and L -Trp (99%) were all supplied by Aladdin Reagents., Shanghai, PR China, ethylenediamine modified β -cyclodextrin (EDA- β -CD) was synthesized according to a previously reported procedure, and original PSf membrane was prepared via a method described in our previous work [12,31]. Other reagents were used as received without any pretreatment.

2.2. Membrane preparation

2.2.1. PSf@PDA membrane

First, unmodified PSf membranes were immersed in isopropanol for 0.5 h until the membrane pores were wetted adequately. Subsequently,

the membranes were thoroughly washed with deionized water. Second, the wet membranes were immersed into and stirred in a Tris buffer solution of DOPA (concentration was 0.25 g/L and pH \approx 8.5) for a predetermined time. Third, the PSf@PDA membranes were washed with deionized water for another 12 h and the resultant membranes were dried with a nitrogen flow.

2.2.2. PSf@PDA@CD membrane

First, PSf@PDA membranes which had been modified by PDA for 24 h were immersed into an aqueous H_2O_2 solution (1 wt%) for 1 h, and then the membranes were thoroughly washed with deionized water. Second, the membranes were immersed into an aqueous EDA- β -CD solution (10 mmol/L) and stirred for a predetermined time. Subsequently, the membranes were washed with deionized water to remove any residual EDA- β -CD and the resultant membranes were dried with a nitrogen flow.

2.3. Measurements

2.3.1. Water contact angles (WCAs)

The WCAs of the dried membranes were measured using a contact angle measuring instrument (Powereach Digital Technology Equipment Co., Ltd., Shanghai, China). Deionized water droplets (5 μL in volume) were allowed to fall onto the surface of the membranes at room temperature. The photographs were captured immediately and the WCAs were measured.

2.3.2. Water permeability

The water permeability of all the samples were evaluated in a stirred ultrafiltration cell (8010, Millipore) at 25 °C. A circular membrane sample was affixed onto the bottom of an ultrafiltration cell and pressurized with deionized water for 30 min at 0.1 Mpa. The water permeability (J) was calculated according to the Eq. (1).

$$J = \frac{V}{At} \quad (1)$$

where V corresponds to the volume of the permeate (mL), A is the effective area of the membrane ($4.2 \times 10^{-4} \text{ m}^2$), and t is the sampling time (h).

2.3.3. Fourier transform infrared (FT-IR) spectroscopy

The ATR-IR spectra of dried membranes were directly recorded using a FT-IR (Perkin-Elmer Spectrum One) spectrophotometer equipped an attenuated total reflection (ATR) probe.

2.3.4. X-photoelectron spectroscopy (XPS)

XPS measurements were performed using a Surface Science Instruments X-ray Photoelectron Spectroscopy/ESCA (ESCALAB 250, Thermo Fisher Scientific) at a pressure of 2×10^{-9} mbar. X-ray source: monochromatic Al K α (1486.6 eV, 15 kV, 150 W, 500 μm); Scanning mode: CAE; Lens mode: Large Area XL; Survey spectra passing energy: 150 eV.

2.3.5. Scanning electron microscopy (SEM)

SEM images of the membranes were characterized using a field emission scanning electron microscope (FESEM, Hitachi, S-4800) that was operated at an accelerating voltage of 2.0 kV. The samples were then coated with a thin layer of gold using a Hummer I sputter coater prior to observation.

2.3.6. Atomic force microscopy (AFM)

Surface topographies of the dried membranes were observed by a SPE AFM (Multimode 8, Bruker) that was operated in the tapping mode.

2.3.7. Stability of PDA layer

The dried PSf@PDA membranes were cut into squares with dimen-

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