



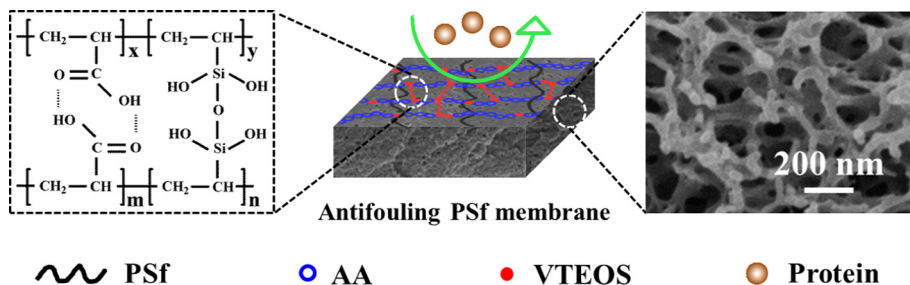
Regular Article

Negatively charged polysulfone membranes with hydrophilicity and antifouling properties based on *in situ* cross-linked polymerization

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GRAPHICAL ABSTRACT



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ABSTRACT

Polysulfone (PSf) membrane has been widely used in water separation and purification, although, membrane fouling is still a serious problem limiting its potential. We aim to improve the antifouling of PSf membranes via a very simple and efficient method. In this work, antifouling PSf membranes were fabricated via *in situ* cross-linked polymerization coupled with non-solvent induced phase separation. In brief, acrylic acid (AA) and vinyltriethoxysilane (VTEOS) were copolymerized in PSf solution, then directly casted into membranes without purification. With the increase of monomers concentration, the morphology of the as-cast membranes changed from a finger-like morphology to a fully sponge-like structure due to the increased viscosity and decreased precipitation rate of the polymer solutions. Meanwhile, the hydrophilicity and electronegativity of modified membranes were highly improved leading to inhibited protein adsorption and improved antifouling property. Furthermore, in order to further find out the different roles player by AA and VTEOS, the modified membrane without VTEOS was prepared and characterized. The results indicated that AA is more effective in the membrane hydrophilicity improvement, VTEOS is more crucial to improve membrane stability. This work provides valuable guidance for fabricating PSf membranes with hydrophilicity and antifouling property via *in situ* cross-linked polymerization.

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1. Introduction

With water scarcity occurring globally, water purification and reuse are playing an increasingly important in human and industrial activities. Nowadays, membrane technology has emerged

and dominated in water purification technologies due to its low cost and high efficiency [1,2]. In comparison to other types of membranes, polysulfone membrane is one of the most popular due to its good processability and high flexibility. However, serious membrane fouling restricts their potential in water purification. Membrane fouling often caused by adsorption and deposition of colloidal particles, macromolecules, ions and biological substances on the membrane surfaces and in the membrane pores, leading to

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decreased flux and altered product quality and increased operating costs [3,4]. It has been reported that the highly hydrophilic membrane surfaces are effective to inhibit the adsorption and deposition of pollutants, thus reducing fouling [5,6]. Therefore, extensive efforts have been carried out to develop functional materials and efficient techniques for controlling and reducing membrane fouling by improving membrane hydrophilicity.

Surface modification and blending modification are usually used to improve membrane hydrophilicity and antifouling [7,8]. In comparison to surface modification, blending method is easier and more convenient to prepare membranes in large scale, meanwhile, membrane structures and performances can be adjusted in a single step. Poly(ethylene glycol) (PEG) and poly(vinyl pyrrolidone) (PVP) have been used as additive to improve membrane hydrophilicity and antifouling [9,10]. Up to date, amphiphilic copolymers with both hydrophobic hydrocarbon chains and hydrophilic chains are favorable due to their good compatibility with the PSf matrix and excellent comprehensive properties. For instance, polysulfone-*block*-polyethylene glycol (PSf-*b*-PEG) were synthesized and blended with PSf [11,12]. Zhao et al. [13] improved the hydrophilicity of PSf membrane via surface zwitterionization from the additive of polysulfone-*block*-poly(N,N-dimethylamino-2-ethylmethacrylate) (PSf-*b*-PDMAEMA), and the results revealed highly fouling-resistance of the prepared membranes. Shi et al. [14] also reported modified PSf membranes using polysulfone-*graft*-poly(glycidyl methacrylate) (PSf-*g*-PGMA) as additive, and the blend membranes had more hydrophilic surfaces, more open porous structures, higher permeation flux and better antifouling properties. Generally, amphiphilic copolymers were first synthesized via living polymerization, then purified and dried, last blended with polymer matrix. It is expensive and time consuming. Therefore, a simplified and advanced blending method is expected.

In situ cross-linked polymerization has been reported as a special blending method to prepare poly(vinylidene fluoride) (PVDF) membranes [15–17] and polyethersulfone (PES) membranes with improved hydrophilicity and antifouling properties [18–20], barely for PSf membranes. Usually, the functional (co)polymers were directly synthesized in polymer matrix solution via free radical polymerization, then the solution without further purification was casted into membranes, avoiding any tedious or post-synthetic treatment. In addition, compared with the conventional blending, the miscibility of the polymer matrix and synthesized modifier increases, leading to a promising advance in membrane fabrication and modification in large-scale [18,21].

In this work, a series of modified PSf membranes were prepared via *in situ* cross-linked polymerization of acrylic acid (AA) and vinyltriethoxysilane (VTEOS) in polymer solution and non-solvent induced phase separation. The PAA chains in the copolymer provided hydrophilicity, electronegativity and antifouling [22,23], and the VTEOS chains supplied active site for cross-linking reaction to improve membrane stability [16]. In addition, the effect of monomers addition on the membrane chemistry, morphology, electronegativity and hydrophilicity were investigated systematically. The ultrafiltration experiments of pure water and BSA solution were used to explore the antifouling property of the as-cast membranes.

2. Experimental

2.1. Materials and reagents

Commercial polysulfone (PSf, Ultrason S 6010, $M_w = 78.0 \times 10^3$ g/mol, $M_n = 22.3 \times 10^3$ g/mol) was purchased from BASF SE. Acrylic acid (AA), vinyltriethoxysilane (VTEOS), bovine serum albumin (BSA, $M_w = 66.4 \times 10^3$ g/mol) and azobisisobutyronitrile

(AIBN) were bought from Aladdin, China. VTEOS and AA were purified with basic alumina and vacuum distillation to remove the inhibitors before use, respectively. Deionized water was used throughout the experiments. All other reagents were brought from Sinopharm Chemical Reagent Co., Ltd, China.

2.2. Membrane preparation

In this work, the casting solutions were synthesized via *in situ* cross-linked polymerization of AA and VTEOS in PSf solutions, which were applied to prepare the modified PSf membranes by the classical non-solvent induced phase separation (NIPS) technique. In a typical procedure, PSf, AA and VTEOS were dissolved in DMAc. Then AIBN (2 mol% with respect to AA and VTEOS) was added into the homogeneous solution. After bubbling nitrogen for 1 h, the *in situ* cross-linked polymerization of AA and VTEOS in PSf solution was carried out with stirring under nitrogen at 80 °C for 10 h, then terminated by quenching in ice water. The synthesized casting solution was degassed to release bubbles, then coated on a clean glass plate. Immediately, the liquid film was immersed into deionized water 30 °C, in which the solvent and non-solvent exchanged leading to phase separation. The prepared solid PSf membrane was peeled off and rinsed in deionized water at 80 °C to remove residual solvent and unreacted monomers, and dried via freeze drying. As a control, neat PSf membrane was prepared using the same procedure. The sample informations and the compositions of the cast solutions for the prepared PSf membranes are shown in Table 1, in which the molar ratio of AA to VTEOS was about 4 for $M_{2-1.3}$ to $M_{8-5.3}$. It should be noted that the polymer solution after polymerization of 10 wt% AA and 6.6 wt% VTEOS in PSf solution was difficult to be casted into membranes. Therefore, in this work, the adding limitation of the AA and VTEOS was 8 and 5.3 wt%, respectively.

2.3. Dope solution and membrane characterization

The shear viscosity of the synthesized polymer solutions was measured by a rotational rheometer (Physica MCR-301, Anton Paar GmbH, Austria) at 30 °C in a shear rate range of 1–1000 s⁻¹. The phase separation rate of the casting solutions was investigated by light transmittance experiment. In brief, the dope solution was casted onto a slide with a thickness of 150 μm, then immersed into a quartz cuvette holding water. The light transmittance at 525 nm was recorded by a UV-vis spectrophotometer (Lambda 950, PerkinElmer, USA). Membrane surfaces chemistry was characterized by X ray photoelectron spectrometer (XPS, Shimadzu Axis Ultradrid, Japan) with a take-off angle of 45° and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Thermo-Nicolet 6700, US). The membrane surface zeta potential (ζ) was measured by a SurPASS electrokinetic analyzer (Anton Paar GmbH, Grza, Austria) equipped with an adjustable gap cell using 1 mmol/L KCl solution as the testing solution. The surface and cross-section morphologies of the prepared PSf membranes were imaged by a field-emission scanning electron microscope (FESEM, Hitachi S-4800, Japan). Average pore size of the membranes was analyzed according to the binary image transformed from the SEM images by Image J software. The mechanical properties of the membranes were characterized by a tensile tester (Instron 5567, US) at a constant tensile speed of 10 mm/min at room temperature.

2.4. Hydrophilicity measurements

Water contact angle was applied to characterize the hydrophilicity/hydrophobicity of the membranes, and carried out a contact angle measurement (OCA20, Dataphysics, Germany)

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