Towards improved antifouling ability and separation performance of polyethersulfone ultrafiltration membranes through poly(ethylenimine) grafting

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A B S T R A C T

The membrane fouling is one of the key issues in ultrafiltration (UF) process because it significantly reduces the membrane permeability and increases industrial cost. The challenge is to improve antifouling ability of UF membranes without compromising their separation performance. Here we report a facile strategy to prepare antifouling UF membranes via grafting of positively charged poly(ethylenimine) (PEI) chains onto brominated tetra-methyl polyethersulfone (TM-PES) membranes. The resultant PEI grafted TM-PES membranes show excellent antifouling ability with sufficient water permeability and outstanding separation performance. Typically, the grafted membrane with the bromination degree (BD) of 73% has not only a high water permeability of $72 \, \mathrm{L \, m^{-2} \, h^{-1} \, bar^{-1}}$ but also rejections of 96.3% for ferritin and 91.4% for bovine serum albumin (BSA). Specially, the water flux can be recovered nearly 90% after protein fouling. The developed strategy is suitable for preparation of antifouling UF membranes. Moreover, the fabricated membranes have a great potential application in biomacromolecule separation.

1. Introduction

Membrane fouling is considered one of the key issues in the membrane-based separation processes because it significantly depresses the membrane permeability and consequently increases high operating and membrane replacement cost [1–3]. This phenomenon is primarily caused by physical deposition and electrostatic adsorption of molecules on the membrane surface, as well as pore blocking, leading to the increase of filtration resistance [4,5]. Among those, fouling is more sensitive during UF process due to special asymmetric structure of UF membranes [6,7]. For example, about 27% loss of water flux was observed in poly(vinylidene fluoride) (PVDF) UF membranes during fouling experiment [8]. Polyethersulfone (PES) UF membranes have 34% loss of water flux [9]. This is the reason that antifouling ability is regarded as one of essential properties of UF membranes. Therefore, efficient approaches to improve the antifouling ability are required strongly in the production of UF membranes.

In general, the antifouling ability of UF membranes is influenced by surface roughness, surface hydrophilicity and surface charges [10,11]. Thus the antifouling ability can be improved by three common strategies, that is, reducing surface roughness, adding surface charges and increasing surface hydrophilicity [12–14]. Nowadays, most of UF membranes are produced from functional polymers with good mechanical strength and chemical stability, such as PES [15], PVDF [16], polyacrylonitrile (PAN) [17] and polyvinyl chloride (PVC) [18]. However, their antifouling ability is not well due to the electroneutrality and hydrophobicity of polymers. Up to now, many methods are developed to improve antifouling ability, such as blending with other polymers, filling with inorganic nanomaterials and grafting of polymer chains. The former two are simple strategies to adjust surface wettability and/ or charges for improving antifouling ability [19,20]. For example, the antifouling ability of PES membrane was improved to about two times by blending poly(arylene ether sulfide sulfoxide sulfone) [21]. Introduction of SAPO-34 nanoporous zeolite resulted in the 30% increase of antifouling ability for a PVDF membrane [22]. As a contrast, grafting charged groups into polymer chains before preparing membrane not only introduces surface charges but also improves surface hydrophilicity. For instance, the sulfonated PES membrane has better antifouling ability that increases with the sulfonation degree [23]. However, these methods usually result in the decrease of mechanical

strength and chemical stability of membranes.

Surface grafting of hydrophilic polymer chains has received much attention in recent years. It will decrease surface roughness, introduce surface charges and improve surface hydrophilicity, but not change properties of membrane matrix [24–26]. Polyethylene glycol (PEG) is the most widely-used material for surface grafting. For example, PEG chains were grafted onto the PES membrane and poly(etherimide) membrane by the low-temperature plasma method and the amidation reaction, respectively [27,28]. The membrane antifouling ability was improved largely, which is attributed to the increase of surface hydrophilicity. Very recently, polyelectrolyte grafting attracts the growing interest due to the introduction of charges onto the membrane surface. For example, negatively charged poly (methacrylic acid) chains were grafted to make the PES membrane have good antifouling ability, pH and temperature sensitivity [29]. Zwitterionic and hydrophilic poly (sulfobetaine methacrylate) polymer brushes were grafted onto the PVDF membranes for antifouling modification [30]. All of those modified membranes show good antifouling ability during UF process.

In this work, we report a facile strategy to prepare the antifouling UF membranes by grafting of PEI chains onto brominated TM-PES membranes, as shown in Fig. 1. PES is one of the most widely used membrane materials due to its good physical and chemical stability, however difficultly modified by surface grafting because of its inert chains [31]. The TM-PES has four benzyls in its repeat units other than the PES, which are easily brominated for grafting modification. Furthermore, the PEI has abundant positive charges and outstanding hydrophilicity, and thus should improve the antifouling ability of TM-PES membranes by quaternization grafting of tertiary amines with brominated benzyls [32,33]. In this work, a series of PEI grafted TM-PES membranes were prepared to study effects of the BD and PEI concentration on the separation performance. The structure, physic-chemical properties and separation performance were studied in detail.

2. Experimental

2.1. Materials

2,2-Bis(4-hydroxy-3,5-dimethylphenyl)propane (also named as tetra-methyl bisphenol A, TMBPA, 98%) and bis(4-fluorophenyl) sulfone (FPS, 99%) were purchased from *Tokyo Chemical Industry*. Hyperbranched PEI (M_w~25000), ferritin (from equine spleen), BSA and ovalbumin (OVA) were obtained from *Sigma-Aldrich*. 10 nm gold colloids were purchased from *British Biocell International*. Potassium carbonate (K_2CO_3, 99%), benzoyl peroxide (BPO, 99%), N-bromosuccinimide (NBS, 99%), 1,1,2,2-tetrachloroethane (TCE), dimethylacetamide (DMAc), and other chemicals were provided by *Sinopharm Chemical Reagent Co. Ltd*. All chemicals were not purified before usage.

2.2. Synthesis of brominated TM-PES

Firstly, TM-PES was synthesized by TMBPA and FPS under K_2CO_3 as catalysis (Fig. 2) [34,35]. TMBPA (0.010 mol), FPS (0.010 mol) and K_2CO_3 (0.030 mol) were dissolved in the DMAc/toluene (75 mL/15 mL) mixture in a three-necked, round-bottomed flask with a magnetic stirrer, a Dean-Stark trap and a nitrogen inlet and outlet. The resulting solution was stirred sostenuto at 140 °C for 3 h and at 165 °C for another 12 h. After that, the resultant was dropwise added into the methanol
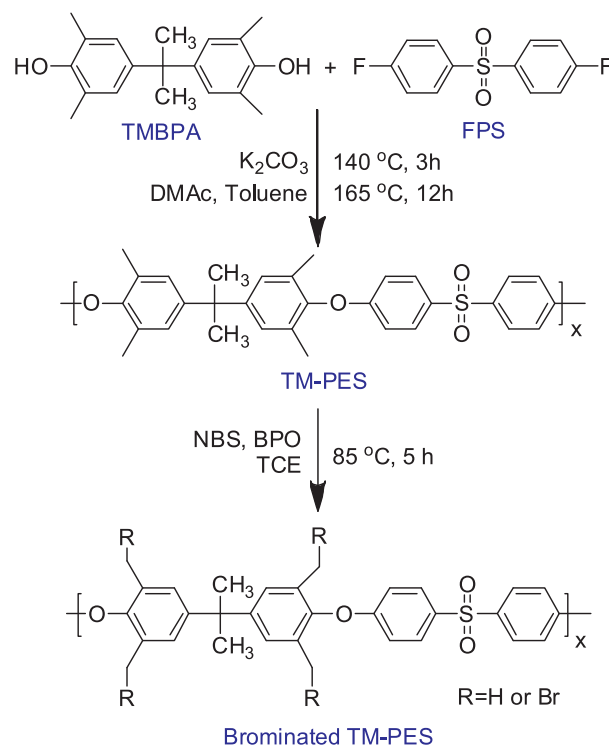
Fig. 2. Synthesis process of brominated TM-PES.

aqueous solution (1:1 v/v). The precipitate was washed with methanol for three times and dried in a vacuum oven at 80 °C for 24 h. Finally, the molecular weight of the obtained TM-PES was characterized by a gel permeation chromatography (GPC) system (*Waters*, USA) equipped with three Styragel columns (HT4, HT5E and HT6, *Waters*, USA) at 30 °C.

The obtained TM-PES was brominated by the nucleophile substitution reaction with NBS, as shown in Fig. 2. A given amount of NBS and BPO were added into the TM-PES (2.50 g) solution with TCE (50 mL) as a solvent. The resulting mixture was stirred at 85 °C for 5 h, and then precipitated in methanol. The resulting brominated TM-PES powders were washed with methanol and dried in the vacuum oven at 60 °C for 24 h. The BD was adjusted by amounts of NBS and BPO. For example, the TM-PES with 30% BD can be obtained by using 0.9925 g of NBS and 0.0900 g of BPO. Further chemical structure of brominated TM-PES was recorded on ^1H nuclear magnetic resonance (^1H NMR) (Avance III 500 MHz, *Bruker*, Switzerland) with chloroform-d (CDCl$_3$, (D,99.8%) + 0.03% V/V TMS, *Aladdin*) as solvent.

2.3. Preparation of PEI grafted TM-PES membranes

Asymmetric brominated TM-PES membranes were prepared *via* non-solvent induced phase separation (NIPS), as shown in Fig. 1. Brominated TM-PES was dissolved in DMAc at room temperature with a magnetic stirring. The resulting homogenous solution was cast and formed a 100 μm-thick film on a glass plate by a casting knife after removing bubbles *via* ultrasonication, and immediately moved to the pure water non-solvent bath for precipitation at 20 °C for 2 days. After
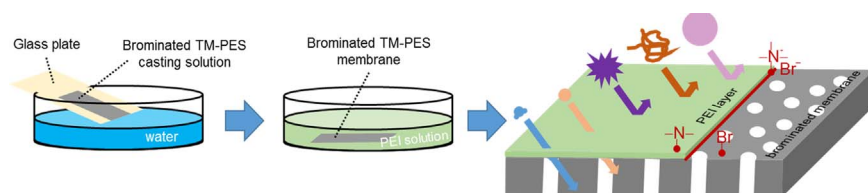
Fig. 1. Schematic process of PEI grafted TM-PES membranes.