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Novel antifouling positively charged hybrid ultrafiltration membranes for protein separation based on blends of carboxylated carbon nanotubes and aminated poly(arylene ether sulfone)

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ABSTRACT

In this study, an aminated hydrophilic poly(arylene ether sulfone) (APAES) multiblock copolymer was prepared from previously synthesized bromomethylated poly(arylene ether sulfone) (PAES-CH₂Br) block copolymer via *in situ* amination with triethanolamine. Novel positively charged hybrid ultrafiltration membranes were fabricated by film casting with non-solvent induced phase separation of blends of PAES and APAES block copolymers with carboxylated multiwalled carbon nanotubes (MWCNT-COOH). Fourier transform infrared spectroscopy in the attenuated total reflection mode, scanning electron microscopy as well as contact angle and outer surface zeta potential studies were performed to characterize the membranes in detail. The results confirmed that the fabricated membranes were porous, hydrophilic, positively charged, and had improved antifouling capacity. The hybrid membranes were used in ultrafiltration of ovalbumin and lysozyme model solutions (individually) at varied pH values. Membrane performance depended on the contents of MWCNT-COOH, which could be adjusted by varying its fraction in the membrane casting solutions. Due to the combined effects of size exclusion and charge repulsion, the permeability, antifouling properties and separation selectivity of the hybrid ultrafiltration membranes could be improved simultaneously by increasing of charge density and fraction of MWCNT-COOH.

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1. Introduction

Proteins concentration and purification is one of the most intensive separation processes for biotechnology, biomedicine and food production industries [1]. The research on protein concentration and purification is stimulated by the increasing demand for high-purity drugs [2]. Several separation techniques such as packed bed column chromatography [3], electrophoresis [4], electro-ultrafiltration [5], electrophoretic membrane contractor [6], membrane chromatography [7] and ultrafiltration (UF) [8,9] have been used to obtain high purity proteins from fermentation broth solutions. Packed bed column chromatography is widely used in the separation of protein mixtures [3]. However, the separation of proteins by chromatography is often limited by the slow protein diffusion into and out of the resin beads [2]. In addition, the scale-up cost for packed bed column chromatography can be very high [2,5]. Ion-exchange membrane chromatography has been implemented for protein concentration and separation

[7]. However, the use of this technique on large scale is limited because of relatively low binding capacity of typical membranes for proteins [2]. Therefore, efficient separation techniques to obtain high purity proteins at a low operation cost are still urgently required in biotechnology, pharmaceutical and food industries [2,5]. Among the aforesaid separation processes, ultrafiltration has received tremendous attention in concentration and purification as well as separation of proteins mixture in model solutions, fermentation broths and cell culture samples. This process is more efficient and easy to handle and could be scale up at low cost [2,8,9]. However, membrane fouling is the main obstacle for efficient use of ultrafiltration of protein mixture solutions [8,9]. Membrane fouling in protein ultrafiltration is mainly attributed to nonspecific protein adsorption and deposition on the surface or in the pores of the membrane by hydrophobic and electrostatic interactions between protein and membrane [10]. Reversible protein adsorption causes reversible fouling, which could be removed by simple hydraulic cleaning. On the contrary, irreversible fouling results from the strong adsorption of protein molecules on the surface or entrapment of protein molecules in the pores. This implies that the irreversible fouling typically dominates the total membrane fouling [8,10,11]. Various approaches such as surface coating, surface grafting via copolymerizations or blending hydrophobic membrane

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polymers with hydrophilic functionalized polymer or inorganic fillers have been explored to enhance the membrane fouling resistance and, hence, separation performance [12–17]. However, simple surface coating is often not an appropriate approach; due to weak adhesion of the modifying polymer to the membrane surface long-term stability is questionable. Surface grafting techniques such as graft copolymerization may lead to changes in the barrier pore structure of membrane what could reduce permeability [16]. Therefore, blending of membrane polymers with inorganic fillers has attracted considerable attention to fabricate antifouling ultrafiltration membranes [17,18].

Zirconium oxide, titanium oxide, zeolite, mesoporous silica and carbon nanotubes have been explored as inorganic fillers to fabricate ultrafiltration membranes with improved antifouling capacity [10,17–21]. Among these materials, carbon nanotubes have gained more attention in academia and industry because of their rapid mass transport behavior in combination with excellent mechanical, electrical and thermal properties. Hinds et al. had fabricated polymer–nanotube hybrid membranes by incorporating aligned MWCNTs across a solid polystyrene film; the hybrid membranes had four to five times higher water flow rate than conventional fluid flow predicted by Hagen–Poiseuille equation for the same barrier pore structure [22]. In another approach, chemical vapor deposition method has been applied to construct arrays of aligned carbon nanotubes in a silicon nitride matrix membrane, and analogously high water flow rates had been obtained [23]. Nevertheless, these studies do not provide immediate solutions for practical applications of membranes because the reported methods are tedious, difficult to scale up and therefore potentially very expensive. Various approaches have been explored to exploit the special barrier properties of (functionalized) carbon nanotubes by integrating the material in established polymer membrane manufacturing schemes (e.g. [24]).

However, it would be also appealing if hydrophilic ultrafiltration membranes with rapid mass transport could be prepared by dispersing carbon nanotubes in the polymer matrix using non-solvent induced phase separation method [20,25–28]. To achieve this goal, hybrid ultrafiltration membranes with improved antifouling properties have been fabricated by dispersing MWCNTs in the polymer membrane matrix [10,20,24,25,27–32]. Liu et al. had fabricated protein resistant hybrid UF membranes from amphiphilic-polymer-modified MWCNTs and polysulfone; membranes had high protein resistance capacity and water permeability [25]. Wu et al. prepared hybrid ultrafiltration membranes by incorporating MWCNTs into the matrix of brominated polyphenylene oxide what had been functionalized with triethanolamine; the membranes had improved antifouling capacity and water permeability [30]. Although, one drawback of such hybrid ultrafiltration membranes was that they do not have high selectivity in protein separations. This problem could be ameliorated by anchoring anionic or cationic groups in the barrier layer of membranes [33–35]. Mehta et al. reported that the membrane performance in proteins concentration and separation can be significantly improved by controlling the surface charge density because charged membranes provide high retention of proteins with the same charge by exploiting repulsive electrostatic interactions [35]. The combination of size and charge based selectivity will be helpful for improving the separation performance of membranes in ultrafiltration processes. Moreover, significant improvements in the UF of the proteins solutions could be achieved by controlling the solution pH and ionic strength [2,9,35–37]. Thus, selective separation of proteins using charged hybrid UF membranes is, in principle, possible at a controlled pH and applied transmembrane pressure.

Recently, a poly(arylene ether sulfone) (PAES) multiblock copolymer had been synthesized and then converted by block-selective reaction to the bromomethylated derivative (PAES-CH₂Br). Positively

charged UF membranes had then been obtained by film casting with non-solvent induced phase separation of blends of PAES and PAES-CH₂Br and subsequent heterogeneous quaternization with trimethylamine [37]. To the best of our knowledge, positively charged hybrid ultrafiltration membranes with improved antifouling capacity (especially irreversible fouling) based on homogeneously synthesized aminated PAES block copolymer and carboxylated multiwalled carbon nanotubes have not been reported till now. In this study, efforts have been made to fabricate such novel hybrid UF membranes with varied charge density from blends of PAES and APAES block copolymers with functionalized MWCNT-COOH by solution casting and non-solvent induced phase separation (“phase inversion”) method. The fabricated membranes have been evaluated in the selective UF transport of the model proteins ovalbumin and lysozyme at varied solution pH. It is demonstrated that the hybrid membranes at an optimal fraction of MWCNT-COOH in the polymer matrix containing quaternary ammonium groups have superior protein separation performance based on combined size and charge interactions with the selective barrier at low fouling.

2. Experimental section

2.1. Materials

The 4,4'-fluorophenyl sulfone (FPS), 4,4'-isopropylidenebis(2,6-dimethylphenol) (IBDP) and 9,9'-bis(4-hydroxyphenyl) fluorene (BHF) monomers were purchased from Sigma-Aldrich. N-bromosuccinimide (NBS), benzoyl peroxide (BPO) and disodium hydrogen phosphate were received from Acros Organics. Anhydrous potassium carbonate (K₂CO₃), calcium carbonate (CaCO₃), toluene and triethanolamine (TEOA) were purchased from Sigma-Aldrich. N,N'-dimethyl acetamide (DMAc), sodium dihydrogen phosphate monohydrate, and N-methyl pyrrolidone (NMP) were obtained from Merck Chemicals Co. 1,1,2,2-Tetrachloroethane (TCE) was purchased from Alfa Aesar. Ovalbumin (OVA) was purchased from Sigma-Aldrich and lysozyme (LYZ) was received from Fluka Chemicals. Carboxylated multiwalled carbon nanotubes (MWCNT-COOH) (purity > 95%, -COOH content 3.86 wt%, average diameter 9.5 nm and length < 1 μm) were purchased from Nanocyl, Belgium. MWCNT-COOH were treated with 1 M aqueous HCl solution for 24 h at room temperature (RT) to remove the metallic impurities. Thereafter, acid treated MWCNT-COOH were washed with deionized (DI) water to reach neutral pH and dried in vacuum oven at 60 °C for 8 h. DMAc was dried over 4 Å molecular sieve before further use. FPS monomer was crystallized from toluene whereas IBDP and BHF monomers were crystallized from toluene–ethanol mixture (4:1). Other solvents and reagents were commercial grade and used as acquired. DI water and water purified with a Milli-Q system (Millipore) were used throughout the study.

2.2. Synthesis of bromomethylated poly(arylene ether sulfone) block copolymers

The step-wise synthesis of the oligomeric building blocks A₁₆ from FPS and IBDP and B₁₂ from FPS and BHF as well as the polymerization of A₁₆ and B₁₂ to PAES had been described before [37]. PAES-CH₂Br block copolymer was synthesized by allylic free radical substitution reaction on the IBDP units of PAES block copolymer [37]. The synthesis of PAES-CH₂Br via allylic free radical substitution reaction on that particular precursor polymer was performed because it allows selective functionalization in one (A₁₆) of the two blocks and avoids the use of a carcinogenic and banned chemical, i.e. chloromethyl methyl ether, which is generally used in chloromethylation of aromatic polymers [38]. The ¹H NMR spectra of block copolymers were recorded in CDCl₃

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