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Preparation of high-capacity, weak anion-exchange membranes by surface-initiated atom transfer radical polymerization of poly(glycidyl methacrylate) and subsequent derivatization with diethylamine

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ABSTRACT

Ion-exchange membrane is of importance for the development of membrane chromatography. In this work, a high-capacity anion-exchange membrane was prepared by grafting of glycidyl methacrylate (GMA) onto the surface of regenerated cellulose (RC) membranes via surface-initiated atom transfer radical polymerization (SI-ATRP) and subsequent derivatization with diethylamine. Attenuated total reflectance Fourier-transform infrared (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to characterize changes in the chemical functionality, surface topography and pore morphology of the modified membranes. The static capacity of the prepared anion-exchange membrane was evaluated with bovine serum albumin (BSA) as a model protein. The results indicated that the anion-exchange membrane which could reach a maximum capacity of 96 mg/mL for static adsorption possesses a higher adsorption capacity, and the adsorption capacity increases with the polymerization time. The effect of pH and salt concentration confirmed that the adsorption of BSA followed ion-exchange mechanism. The established method would have potential application in the preparation of anion-exchange membrane.

1. Introduction

Membrane chromatography has attracted more attention in the separation and purification of the biomacromolecules, such as protein, virus, DNA, in the downstream processing of biotechnology. Compared with conventional chromatography, membrane chromatography combines the advantages of membrane technology and chromatography. Since solute is transported to the membrane binding sites primarily by convection, instead of diffusion, processing rates can be orders of magnitude higher for membrane chromatography systems [1,2], and the binding capacity of membranes is generally independent of flow rate [3]. In addition, membrane chromatography has several advantages, such as good penetration, fast mass transfer, lower pressure drop, easier to scale up. These properties make membrane chromatography a promising alternative for use in high-throughput separation and purification of biomacromolecules.

Although membrane chromatography has great potential application, its broad implementation may be limited by its process economy since membranes often have lower binding capacity than media used in packed-bed chromatography [4]. Thus, it is of significance to develop membranes with higher binding capacities. Building adsorptive functionality into membranes by coating or surface grafting polymerization is one valid strategy to increase binding capacities. Particularly, traditional surface grafting polymerization has been extensively explored and can be induced by free radical [5], ozone [6], γ-ray radiation [7], plasma [8,9], UV irradiation [10,11]. The binding capacity of membrane has been improved, but poor grafting controllability of these methods might cause the large changes of the pore structure of membrane. In comparison with the above-mentioned grafting methods, one of the currently fashionable living/controlled manners, atom transfer radical polymerization (ATRP), allows for the preparation of a well-defined polymer brushed with dormant chain ends on various types of substrates and thus has attracted a considerable attention in recent years [12–16]. Husson et al. [12–14] grafted 2-dimethylaminoethyl methacrylate and acrylic acid onto the surface of the commercial regenerated cellulose (RC) membrane separately to prepare anion-exchange and cation-exchange membrane in one step via ATRP. The microporous PVDF membrane was also converted into an ion-exchange membrane by grafting poly(2-vinylpyridine) onto the surface of the membrane via SI-ATRP [15]. Recently, our group prepared a strong cation-exchange membrane by grafting poly(sodium 4-styrenesulfonate) onto the RC membranes [16]. The reported results indicate that the membranes modified via ATRP show obvious improvement in binding capacity [12–16].

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Using a functional monomer is an easy way to directly prepare functional membrane via ATRP [12–16]. But in the case that the monomer is expensive or is not commercially available, the direct grafting method might account the difficulties. A two-step method might avoid this obstacle, in which ATRP is used to prepare the active membrane first and then subsequent derivatization with functional molecule. By using the two-step method, various functional membranes were prepared by grafting glycidyl methacrylate (GMA) [17–21] and 2-hydroxyethyl methacrylate [22,23] onto membranes or films via SI-ATRP, being followed by subsequent derivatization. This strategy could graft variety of functional groups onto the membrane surface easily due to the flexibility of the side chain, and the modified membranes often possess higher binding or adsorption capacity. In this work, GMA, a monomer containing the active epoxy group, was grafted onto the surface of commercial RC membrane via SI-ATRP and subsequent derivatization with diethylamine to produce a high-capacity anion-exchange membrane. Polymerization time was used as an independent variable to control the grafting degree (DG) of the monomer on the membrane surface, and BSA was used as a model protein to evaluate protein adsorption property of the so-prepared membranes.

2. Experimental

2.1. Materials

Regenerated cellulose membranes with a diameter of 47 mm, average pore size of 0.45 μm, and thickness of 160 μm were purchased from Sartorius (Göttingen, Niedersachsen, Germany). 2-Bromoisobutyryl bromide (2-BIB, Aladdin Inc., ≥98.0%), copper (I) bromide (Sinopharm, ≥98%), 2,2′-bipyridine (Sinopharm, ≥99.5%), glycidyl methacrylate (Aladdin Inc., ≥98.0%), diethylamine (Aladdin Inc., ≥99.0%), and BSA (Sigma, M_r = 61.7 kDa, 99%), as well as other chemicals were analytical grade.

2.2. Surface modification of RC membrane

2.2.1. Preparation of initiator-functionalized membranes

RC membranes were first immersed in methanol for 15 min to eliminate glycerine and then dried prior to modification. The dried RC membranes were swelled in anhydrous tetrahydrofuran (THF) for 20 min, then 2-BIB (0.1 mol, 0.5 mL) and triethylamine (TEA) (0.1 mol, 0.5 mL) were added, and the reaction system was incubated in an ice bath for 3 h and then at 35 °C for 12 h. The obtained initiator-functionalized membranes were rinsed extensively with methanol and distilled water in sequence, then stored in a vacuum oven until next use.

2.2.2. Grafting of poly(GMA)

2-Propanol (30 mL), initiator-functionalized membranes and GMA (2.0 mL) were added into a two-necked flask and stirred with a magnetic stirring device. This mixture was purged with N_2 for 30 min to remove the dissolved oxygen, then 2,2′-bipyridine (0.30 g) and copper(I) chloride (0.10 g) were added under a nitrogen atmosphere. Polymerization was performed at 40 °C. After the reaction, the poly(GMA)-grafted membranes were washed with acetone to remove the homopolymer on the surface. Then the poly(GMA)-grafted membranes were immersed into 10% EDTA solution, stirred at room temperature to remove Cu^{2+} on the membrane surface, and then sequentially washed with water and methanol. The poly(GMA)-grafted membranes were dried under vacuum at 40 °C for 24 h until a constant weight was obtained.

Polymerization time was used as an independent variable to control DG of poly(GMA) on the RC membrane. DG was measured by the increase in the weight percentage of the initiator-functionalized membrane as described by Eq. (1).

$$DG = \frac{M_{PGMA} - M_{Br}}{M_{Br}} \times 100 \quad (1)$$

where, M_{Br} and M_{PGMA} are the weight of initiator-functionalized membrane and poly(GMA)-grafted membrane, respectively.

2.2.3. Derivatization of poly(GMA)-grafted membrane

The poly(GMA)-grafted membranes were immersed in 20% aqueous diethylamine solution, and the reaction mixture was raised to 55 °C for 6 h, under gentle stirring. Then the membranes were taken out and washed with deionized water, ethanol–water (1:1, v/v) and ethanol in sequence. Finally, the obtained anion-exchange membrane which contains tertiary amine groups was obtained.

2.3. Physicochemical characterization

2.3.1. Surface chemistry of membranes

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) (Thermo-Nicolet 5700, America) and X-ray photoelectron spectroscopy (XPS) equipped with Al Kα excitation radiation (1486.6 eV) (K-Alpha, VG Instruments, UK) were used to provide information on the surface chemistry of unmodified, initiator-functionalized, poly(GMA)-grafted and anion-exchange membranes.

For XPS the X-ray source was run at a power of 75 w, the high voltage was kept at 12.0 kV and the cathode current was 6 mA. The orbit signals of C and O were obtained at a photoelectron take-off angel of 45°. Binding energies were calibrated by using the containment carbon (C 1s = 284.6 eV).

2.3.2. Morphology of membrane

Scanning electron microscopy (SEM) (Quanta 200, Hong Kong) was used to investigate the morphology of unmodified, initiator-functionalized, and poly(GMA)-grafted membranes. Samples from each membrane were cut into 1 cm × 1 cm pieces and shadowed with platinum to make them conductive. SEM measurements were performed at an accelerating voltage of 20.0 kV. SEM image at 5000× magnification was taken for each membrane.

SEM images were taken of the porous surfaces and analyzed with the digital imaging technique (Image-Pro PLUS Analysis software) to estimate the surface pore sizes and to generate pore-size distributions for samples prepared at different polymerization times [15]. For each sample, data were used to calculate the average *surface* pore diameter.

2.4. Membrane performance

2.4.1. Flux measurements

The anion-exchange membranes, unmodified membrane and initiator-functionalized membrane were used to investigate the effect of DG on the water flux through the membrane. Each membrane sample was initially pre-compacted for 0.5 h until a constant flux was observed. Then the water flux was measured under 0.03, 0.06, 0.1 MPa, respectively. At each pressure the water flux was measured three times and the average value was obtained. The water fluxes were calculated in accordance with Eq. (2)

$$J = \frac{V}{A \times t} \quad (2)$$

where J is the water flux (L/m^2/h), V is the volume of the transmembrane water (L), A is the area of the membrane (m^2), and t is the ultrafiltration time (h).