



High performance anion exchange membrane with proton transport pathways for diffusion dialysis

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ABSTRACT

High performance anion exchange membranes (AEM) with proton transport pathways were fabricated through cationic functionalization of bromo-methylated poly (phenylene oxide) (BPPO) by a nucleophile dimethylamino pyridine (DMAP). The reaction was selectively occurred at dimethylamino functionalities of DMAP to form quaternary amine groups. The pyridine groups on DMAP having a dibasic nature promoted the formation of proton transport pathways and contributed to hydrophilicity of the membranes. The obtained membranes had the water uptake (W_U) in the range of 12–57%, the ion exchange capacity (IEC) from 0.84 to 2.07 mmol g⁻¹, acid dialysis coefficient (U_H) from 0.37 to 20.3 (10⁻³ m h⁻¹) at 25 °C. Interestingly, these membranes exhibited superior separation factor (S) values of 73–351 compared to a commercial DF-120 membrane and most reported membranes in literature. Moreover, the prepared membranes showed excellent thermal, chemical and mechanical stability.

1. Introduction

Ion exchange membranes (IEMs) defined as thin films composed of immobile positively or negatively charged moieties and counter ions, have received growing interests because they make separation based processes clean, efficient and cost effective. The immobile charged moieties are usually covalently bonded to the polymer architecture and are responsible for exchanging moveable ions (i.e. counter ions) and promoting hydrophilicity in the membrane matrix. Based on the nature of ionic groups in the polymer matrix, the IEMs can be classified into anion exchange membranes (AEMs) and cation exchange membranes (CEMs). The ion separation is directly related to the fixed charged moiety inside the membrane. Recently, AEMs are of great interest because they can be extensively utilized to recover acid wastes released from mining, metal processing, painting and agriculture industries.

Different from CEM, tailoring AEM is rather difficult and challenging. AEMs are prepared by covalently fixing the positively charged moieties on polymer structure such as $-NR_3^+$, imidazolium, pyridinium, phosphonium, or guanidinium, which permit favorably the negative ions to pass through, while restricting the passage of mobile positive ions. In contrast, an inverse pattern exists in the CEMs

containing negatively charge species [1]. Various hydrocarbon substrates have been used to fabricate AEMs including polysulfone [2], poly(tetrafluoroethylene) [3], polyvinyl alcohol (PVA) [4], chitosan [5] polybenzimidazole [6], and bromo-methylated poly (phenylene oxide) (BPPO) [7], etc. To meet the basic requirements for an industrial application, AEMs are considered to be good and effective when they show low electrical resistance, high ionic perm-selectivity, reasonable swelling degree, high chemical and mechanical stability [8]. These features make AEMs an appropriate candidate for various industrial separation processes, particularly in electrodialysis (ED) [9], pervaporation (PV) [10], and diffusion dialysis (DD) [11]. In comparison to other membranes based separation processes, DD process is thermodynamically favorable due to spontaneous nature and could be used to recover either acids or bases from industrial wastewaters. The most conspicuous and arresting features of DD process are: (i) no external power and thus low energy consumption, (ii) easy installation protocol, and (iii) less operating cost [1,12,13]. More importantly, DD process is considered to be more efficient for either acids or bases recovery [14,15].

For acid recovery, AEM should allow the passage of anions (i.e. Cl^- , SO_4^{2-}) while preventing the passage of cations (i.e. Fe^{2+}) [14], but to

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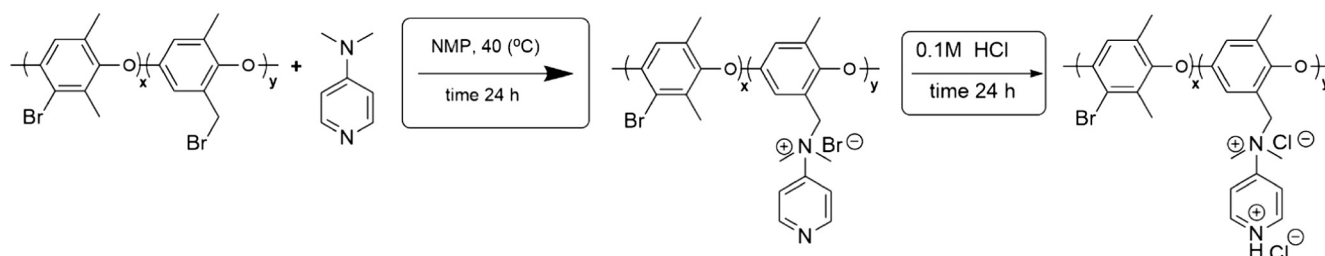
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Scheme 1. Nucleophilic substitution reaction of BPPO-P with dimethyl amino pyridine (DMAP) followed by acid treatment.

meet the electrical neutrality, small size cations such as proton (H_3O^+) can establish hydrogen bonding with water molecules and easily pass through the membrane [16,17]. Literature review shows that for a commercially available membrane (DF-120), the acid recovery ratio has been reported in the range of 85 to 90%. Unfortunately, process capacity is very low ($11.3 \text{ L m}^{-2} \text{ d}^{-1}$) due to the low acid diffusion [18]. Therefore, several AEMs have been designed for DD process. For example, BPPO based membranes prepared by hydroxylation, quaternization and sol-gel reaction are reported to achieve the separation factor S and dialysis coefficient U_H in the 17–32 range and 5–11 (10^{-3} m h^{-1}), respectively [16]. Some other reported AEMs prepared from poly(VBC-co- γ -MPS) based on PVA showed S values in the 12–35 range [17]. From our group, we previously prepared pyridinium based AEMs for the acid recovery *via* diffusion dialysis and with improved U_H of 17–24 (10^{-3} m h^{-1}) and attained S range from 30 to 57 at 25 °C, respectively [19]. It is worthy to note that, both U_H and S depend on the morphology of a membrane. For instance, the porous ultra-filtration membranes fabricated *via* phase inversion technique, were employed for acid recovery *via* DD application [20]. Sun et al. prepared porous AEMs based on BPPO backbone *via* immersion of BPPO into solutions of multi-silicon and tertiary amine followed by a sol-gel reaction and they achieved U_H from 20 to 25 (10^{-3} m h^{-1}), while S value varied from 25 to 45.5 at 25 °C, respectively [21]. Similarly, Wang and co-workers prepared macro-porous asymmetric AEMs *via* phase inversion method and cross-linked with N,N -tetramethylethylenediamine to enhance the U_H value. The obtained TPPO-4h membrane demonstrated high U_H of 43 (10^{-3} m h^{-1}) and S 73.8 at 25 °C, respectively [22]. Because of large pores, the observed high U_H values of these prepared membranes were counterbalanced by the opposite influence of Fe^{2+} ions permeation. The increased permeation of Fe^{2+} ions was due to wide pores and high W_U . In the present scenario, this is indispensable to formulate AEMs with exceptional characteristics such as an easy preparation protocol, better mechanical, thermal and chemical properties with enhanced acid recovery plus salt rejection.

In present manuscript, we describe a novel approach to fabricate AEM through reaction of BPPO with 4-dimethyl amino pyridine (DMAP), a diamine based nucleophile. DMAP has been extensively used as a hyper-nucleophilic catalyst for acylation reaction [23], by taking the advantage of its high nucleophilic nature. Thus, the fabrication process for our AEM is flexible by using one-pot reaction. Moreover, DMAP possesses two nitrogen sites having different reactivity. By taking benefit of this difference, it is possible to direct reaction to one reactive nitrogen (dimethylamino group) to form quaternary amine with the bromo-methyl groups. On the other hand, the pyridine moiety was momentary quaternized with proton by immersing obtained membranes in HCl solution (or at the case of in-situ acid recovery) and created an additional repulsive site which led to high salt rejection. The obtained membranes were tested for acid recovery and ion separation *via* DD. We investigated and discussed in detail the variation behavior of ion exchange capacity (IEC), water uptake (W_U), thermal and chemical stability as a function of DMAP functionalities and as well as the morphology of the membranes.

2. Experimental section

2.1. Materials

4-(dimethylamino) pyridine (DMAP 99%) was purchased from Shanghai Aladdin Bio-Chem Technology Co. LTD (P.R China). N -methyl-2-pyrrolidolone (NMP, AR grade), dimethylsulfoxide (DMSO, AR grade), ethanol (AR grade), sodium chloride (NaCl, AR grade), sodium hydroxide (NaOH, AR grade), hydrochloric acid (HCl) aqueous solution (37%) and ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ 98%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, P.R China). Brominated poly (phenylene oxide) (BPPO) was obtained from Tianwei Membrane Corporation Ltd. (Shandong, P.R China). BPPO was designated pristine BPPO as BPPO-P. The benzyl bromide ($-\text{CH}_2\text{-Br}$) was about to 52% per repeating unit as confirmed by ^1H NMR (CDCl_3 , 400 MHz). Deionized (DI) water was used throughout the requirement.

2.2. Quaternization of BPPO-P

BPPO-P (1 g, 2.61 mmol) was dissolved in 10 mL of NMP at room temperature (i.e. 25 °C) and a calculated amount of DMAP (0.083 g, 0.68 mmol) was then added to the stirred solution of BPPO-P and further stirred for 24 h at 40 °C. The overall reaction is summarized in the Scheme 1. The reaction mixture was precipitated in toluene and purified several times to eliminate the traces of NMP. The obtained polymer was dried at 40 °C for 24 h and confirmed by ^1H NMR ($\text{DMSO-}d_6$, 400 MHz) analysis to examine the substitution of DMAP with BPPO-P.

2.3. Preparation of membranes

Well dried polymer was dissolved in NMP (10 wt%) to make a homogenous solution and cast over the glass plate at 60 °C for 24 h. The formed membrane was then peeled off and immersed in 0.1 mol L^{-1} HCl solution for further 24 h at 25 °C to allow the substitution of bromide ions by chloride ions and the creation of momentarily positive charge over pyridine nitrogen. The obtained membranes were designated as BPPO-A, BPPO-B, BPPO-C and BPPO-D with respect to the quantity of DMAP. Chemical compositions of obtained membranes are given in the Table 1.

2.4. Membrane characterization

2.4.1. ^1H NMR analysis

The chemical structures of BPPO-P and BPPO-D were investigated

Table 1
Chemical compositions of the obtained membranes.

S. No	Sample ID	DMAP (g)	BPPO (g)	NMP (mL)
1	BPPO-A	0.083	1.0	10
2	BPPO-B	0.161	1.0	10
3	BPPO-C	0.249	1.0	10
4	BPPO-D	0.319	1.0	10

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