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Efficient and stable anion exchange membrane: Tuned membrane permeability and charge density for molecular/ionic separation

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ABSTRACT

Herein, we are reporting improved process for chloromethylation of polysulfone (PS) by in situ Friedel–Craft reaction without the use of chloromethyl methyl ether (CME). Further, in situ amination (Menshutkin reaction) was carried out to prepare quaternized ammonium polysulfone (QAPS). QAPS of varied degree of chloromethylation (DCM) (44.01–65.67%) was used for preparing anion-exchange membranes (AEMs) and it was observed that their pore morphology was highly dependent on membrane drying conditions (temperature and RH). As representative case, QAPS membrane (DCM: 44.01% and named as AEM-1(NF)_x; x indicates drying temperature) dried at low temperature (30 °C (RH: 75%); 45 °C (RH: 54%) and 60 °C (RH: 12%)) showed nano-porous nature with 5.28–1.89 L m⁻² h⁻¹ bar⁻¹ permeability corresponding to 59.31–80.23% salt rejection. Further, permeability of AEM-1(NF)_x followed the trend: AEM-1(NF)₃₀ > AEM-1(NF)₄₅ > AEM-1(NF)₆₀. Formation of porous structure of these membranes was attributed to the phase inversion of the QAPS polymer due to presence of atmospheric water at low temperature (high RH).

In addition, QAPS membranes (different DCM values) dried at 80 °C (RH: < 5%), exhibited completely dense nature with negligible permeability and named as AEM-1, AEM-2 and AEM-3 (DCM; 44.01; 53.87 and 65.67, respectively). Especially, AEM-3 (DCM: 65.67%) was designed to possess all the required properties such as high water uptake (22.20%), ion-exchange capacity (1.597 mequiv g⁻¹), and counterion transport number (0.96), along with reasonable conductivity (8.45 mS cm⁻¹) due to quaternary ammonium group functionality. Chronopotentiometric and *i-v* studies of AEMs revealed excellent electro-transport property for AEM-3, while its electro-dialysis (ED) performance confirmed the suitability for electro-membrane applications. Reported method is novel for preparing stable alkaline membrane with tuneable permeability and charged nature for separations of molecules/ions by pressure and/or electro-driven technologies.

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1. Introduction

Rapid growth in ion-exchange membrane (IEM) based technologies such as alkaline fuel cell, [1–3], water electrolysis, [4,5], ionic separation/isolation [6–9], storage batteries and sensors etc. [5], created huge demand for stable and efficient IEMs derived using non-hazardous chemicals. Depending on the nature of charged functional groups grafted with the membrane matrix IEMs were classified as cation exchange membranes (CEMs) and

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anion-exchange membranes (AEMs) [6,8,9]. During recent years, several types of AEMs based on polysulfones [10–11] poly(arylene ether ketones) [12,13] poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [14] copolymer of chloromethylstyrene and divinylbenzene [15] polyphenylenes [16] etc were extensively studied. To, these polymer back bones, generally quaternary ammonium groups were attached by chloromethylation [2,6,10,17] or radical bromination [10,18] followed by the Menshutkin reaction of benzyl halide with tertiary amine. In this process extensive optimization is required to achieve the desired degree of amination and also chloromethyl ether (CME) used for chloromethylation is carcinogenic and potentially harmful to human health [2,14,19]. The radical-initiated bromination of benzylic methyl groups of the aromatic polymer, is fast and polymer degradation is possible for targeted level of bromination. In addition, complete amination of

benzyl halide group is difficult and always unreacted benzyl halide residue is possible, which further react with hydroxide anion (strong nucleophile) under alkaline environment and reduced the extent of polymer functionalization.

Further, several other parameters such as conductivity, selectivity, thermal and mechanical stabilities, and acid–base resistance etc. for an AEM are essential requirements. Extent of functionalization and membranes morphology greatly affect these parameters and thus membrane preparation protocol should be critically optimized for specific requirements. Unfortunately, no attention was rendered to investigate relationship between membrane preparation conditions, morphology and properties [20]. For instance, various structures and pore sizes in the membrane matrix were achieved by controlled phase inversion (dry and wet) procedures. This may also possible by membrane drying at low temperature (high relative humidity). Thus, rationalization of synthesis–structure–property for an IEM is very urgent to achieve the desired separation efficiency.

Poly sulfone (PS) was considered as an excellent candidate for membrane preparation because of its feasible process-ability and low cost. Numerous reports are available regarding chloromethylation process for PES in non-aqueous medium using CME in presence of Friedel–Craft reaction catalysis (Lewis acid) [2,21–23]. Herein, we are reporting chloromethylation of PES, in which in situ produced CME was responsible for Friedel–Craft reaction in presence of paraformaldehyde, stannic chloride anhydrous (SnCl_4), and trimethylsilylchloride (TMSCl), using chloroform (CHCl_3) solvent. In second stage, in situ Menshutkin reaction of benzyl halide was achieved by tertiary amine, for preparing AEM. It was observed that membrane pore morphology was highly dependent on membrane drying conditions (temperature and RH) and it is possible to prepare highly water permeable porous IEM to quite dense AEM (negligible water permeability) by varying the drying conditions. In this case membrane porosity and charged nature, both can be finely tuned by controlling degree of chloromethylation (DCM) and membrane drying conditions.

2. Experimental section

2.1. Materials

Polysulfone (PS) (poly[oxy-1,4-phenylensulfonyl-1,4-phenylensulfonyl-1,4-phenyleneoxy-1,4-phenylene (1-methylethyli-dene)-1,4-phenylene]) ($M_w=85,157$, $M_n=38,721$; $M_w/M_n=2.199$) was obtained from Sigma-Aldrich Chemicals. Para formaldehyde (HCHO)_n, stannic chloride anhydrous (SnCl_4), trimethylsilylchloride (TMSCl), chloroform (CHCl_3), 2-propanol ($\text{CH}_3\text{CHOHCH}_3$), methanol (CH_3OH), water, N-methyl 2-pyrrolidone (NMP), tri-methylamine (TMA), di-chloro methane etc. were obtained from S.D. fine Chemicals, India.

2.2. Synthesis of chloromethylated polysulfone (CMPS)

Chloromethylation of PS was carried out in a three-neck round-bottom flask with mechanical stirrer according to the procedure depicted in (Fig. S1, ESI). PS (10 g) was dissolved in chloroform (5 wt%) under stirring. In-situ chloromethylation was achieved by drop-wise addition of SnCl_4 (0.7 mL), paraformaldehyde (13.5 g) and TMSCl (57 mL). Reaction mixture was stirred for 72 h at 45–50 °C, and product was precipitated in 2-propanol. Obtained CMPS (white solid polymer) was washed with solvent, water and finally hot methanol to remove catalyst and impurities.

By varying reaction conditions, different degree of chloromethylation (DCM) for PS were achieved and three types of CMPS (namely AEM-1, AEM-2 and AEM-3) were prepared with 44.01,

53.87 and 65.67% DCM value.

2.3. Preparation of AEM-1(NF)_x and AEMs with tunable water permeability

To prepare quaternized ammonium polysulfone (QAPS), CMPS was dissolved in N-methyl 2-pyrrolidone at 50–60 °C in the presence of di-chloro methane, followed by addition of tri-methyl amine (20 wt%). Reaction mixture was stirred for 15–18 h at 45–50 °C to obtain QAPS-Cl.

Three types of AEM-1(NF)_x membranes (x denotes membrane drying temperature in °C) were prepared by casting of QAPS-Cl (DCM: 44.01%) viscos solution onto a clean, flat glass plate. Casted membrane thin films were dried at varied temperature (30 °C (RH: 75%); 45 °C (RH: 54%); 60 °C (RH: 12%) and 80 °C (RH: < 5%)) for 24 h, to obtain the membranes with varied water permeability (porosity). It was observed that structural morphology and pore size of the membrane highly tuneable with membrane drying temperature and relative humidity (RH).

QAPS-Cl (DCM: 44.01, 53.87 and 65.67%) membranes were dried at 80 °C (RH: < 5%) for 24 h and designated as AEM-1, AEM-2, and AEM-3, respectively, due to their dense nature. Finally, AEM membranes were as immersed in KOH solution (1.0 M) for 24 h to replace the Cl^- , and washed with deionized water until the pH of the residual water became neutral.

2.4. Instrumental characterizations

The ^1H NMR spectra were recorded by spectrometer (Bruker, 200 MHz for ^1H NMR). Fourier transform infrared (FTIR) spectra were recorded with spectrum GX series 49387by ATR techniques. Thermal analysis was carried out by thermo gravimetric analyzer (TGA) (Mettler Toledo TGA/SDTA851e with star^c software) under nitrogen atmosphere at 10 °C/min heating rate (50–350 °C). Differential scanning calorimetric was performed between –30 and +30 °C. In dynamic mechanical thermal analysis (DMTA), an oscillatory strain is applied to a sample and the resulting stresses are determined as a function of frequency, temperature, or both. The burst strength (Kg cm^{-2}) of the prepared composite membranes was measured by Burst Strength Tester machine provided by Test Techno Consultant, Vadodara, Gujarat, India.

2.5. Membrane stabilities

Oxidative, hydrolytic, acidic and alkaline stabilities of prepared AEMs were assessed by long-term aging experiments in respective mediums. Under strong oxidative water splitting and formation of oxy active radicals at electrodes during ED in over-limiting current density, assessment of membrane's oxidative stability served as an accelerated test to avoid the degradation [24,25]. Oxidative stability of QAPS membranes was evaluated in Fenton's reagent at for 3 h. Membrane hydrolytic stability was assessed under boiled water condition for 24 h in a pressurized closed vial. Membrane Acidic/alkaline stabilities of prepared AEMs were assessed by treating it in HCl/KOH (5.0 M) for 24 h at 100 °C. Membrane stabilities were evaluated by loss in weight, IEC, and conductivity of samples [26].

2.6. Physicochemical characterizations

Detailed procedures adopted for the measurement of water uptake (WU) and ion exchange capacity (IEC) have been included in (Section S1, ESI). Procedure for the estimation of membrane surface charge density (χ^m) has been included in (Section S2, ESI). Methodology for the measurements of water permeability and salt rejection for AEM-1(NF)_x membranes also have been included in (Section S3, ESI).

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