

Alternative preparative route for efficient and stable anion-exchange membrane for water desalination by electrodialysis



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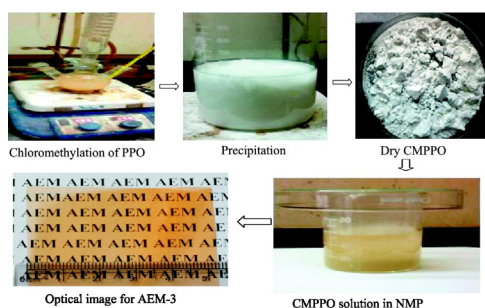
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HIGHLIGHTS

- Environmentally safe process for the functionalization of PPO
- Degree of chloromethylation increases with time.
- Improvement in conductivity of AEM-3 due to high degree of chloromethylation
- High current efficiency and low energy consumption for AEM-3

GRAPHICAL ABSTRACT



Different preparative steps for efficient and stable anion-exchange membrane.

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ABSTRACT

We disclosed an alternative method for controlled chloromethylation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) in presence of paraformaldehyde, tri-methyl chlorosilane and Lewis acid catalyst. About 35–74% degree of chloromethylation (DCM) of PPO was achieved under optimized conditions. Reported method avoids the use of hazardous chemicals (such as chloromethyl methyl ether, and bromine) during preparation of AEM. AEMs with varied DCM were extensively characterized by measuring their physicochemical and electrochemical properties. Reported AEM-3 (DCM: 74%), was designed to possess all the required properties such as good water uptake (26.2%), ion-exchange capacity ($1.61 \text{ meq}\cdot\text{g}^{-1}$), high permselectivity (0.98), and conductivity ($7.67 \times 10^{-2} \text{ S cm}^{-1}$) due to high molality of quaternary ammonium groups. Chronopotentiometry study of prepared membranes confirmed their homogeneous and alkaline nature suitable. Most optimized AEM-3 with splendid alkaline, oxidative and hydrolytic stabilities is a good candidate for electrodialysis.

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1. Introduction

Rapid growth of membrane science and technology for separation, purification and isolation of the molecules, production of salt from

seawater, water desalination by electrodialysis (ED), electro-deionization and other electrochemical devices, fuel the demand for non-hazardous preparative protocols for ion-exchange membranes (IEMs) [1–5]. During water desalination by ED, optimization of ED unit operation, in-built flow distributions in the stack, energy consumption and economics etc. are important factors, but improved membrane forming materials also play significant role for widespread utilization of

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the technologies [6,7]. Conductivity and permselectivity of cation- and anion-exchange membrane (CEM and AEM, respectively) for these electro-driven membrane separation technologies are key parameters and control the resistance of ionic current across the membrane along-with counter-ion transportation and co-ion exclusion [8–10]. High membrane permselectivity and conductivity are generally considered as desirable of IEMs. Membrane conductivity and permselectivity are sensitive to the polymer fixed charge concentration and volume fraction of water in the membrane phase [11,13]. Thus, a fine tuning between fundamental structural characteristics and membrane properties is quite essential to tailor an IEM desired electro-membrane applications, which may be achieved by controlled functionalization of the membrane matrix [1,12,14].

Different aromatic polymers such as polyethers, polysulfone, polyketone, poly(phenyl oxide) (PPO) and polystyrene, after functionalization with quaternary ammonium groups were explored as AEM [15–19]. Generally, functionalization of aromatic polymers was achieved via chloromethylation with chloro methyl ether (CME), while quaternary ammonium groups were introduced by Menshutkin reaction using triamine. This procedure leads to the poor control over concentration and position of the functional groups, while CME used for chloromethylation is carcinogenic and potentially harmful to human health [20–22]. Radical bromination of benzylic methyl groups on the aromatic polymer backbone was also achieved by liquid bromine or by azobis(isobutyronitrile) (AIBN) and *N*-bromosuccinamide (NBS) [23–28]. Utilization of liquid bromine is difficult to handle as well as bromination reaction is exothermic in nature [23]. Rate of bromination with NBS reported to be very slow and it depends on concentration and temperature of brominating agent [29]. An IEM should exhibit extremely low membrane resistance and high permselectivity, which may be achieved by high degree of functionalization [1,18,19]. Thus, high degree of grafting for quaternary ammonium group to the aromatic polymer backbone is necessary to fabricate highly suitable AEM. Further, electron withdrawing or donating characteristics of poly(arylene ether) such as PPO decides the brittleness nature of the AEM in alkaline

media due to cation activated polymer degradation [30]. To mitigate the cation triggered degradation, electron withdrawing substituents (such as bromine) should be completely eliminated from the PPO backbone. Hence, AEM based on PPO should be prepared via chloromethylation rather than free radical bromination to achieve the hydrolysis resistant backbone in the alkaline media.

PPO based dense electrolytic membranes were reported for fuel cells, electrodialysis, pervaporation, diffusion dialysis etc. due to high glass transition temperature (T_g) [31–34]. PPO was modified by electrophilic substitutions including bromination, carboxylation and methyl esterified carboxylation, sulfonation and acylation [35,36] and by an introduction of trialkyl-silyl, hydroxyl ethylene and ethyleneoxy-trialkyl-silyl groups in the polymer backbone [37]. Herein, we are reporting chloromethylation of PPO by Friedel–Craft reaction in presence of paraformaldehyde, stannic chloride anhydrous (SnCl_4), and trimethylsilylchloride (TMSCl) in chloroform (CHCl_3) solvent. Reaction proceeded by in-situ produced CME. In second stage, in situ Menshutkin reaction of benzyl halide was achieved by tertiary amine, for preparing AEM. AEMs with varied degree of chloromethylation (DCM) (35–74%) were prepared and assessed for their suitability in electro-dialytic water desalination.

2. Experimental section

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was obtained from Sigma-Aldrich Chemicals. Chloroform (CHCl_3), methanol (CH_3OH), stannic chloride (SnCl_4), trimethyl chlorosilane (TMCS), para formaldehyde (HCHO), sodium hydroxide (NaOH), sodium chloride (NaCl), silver nitrate (AgNO_3), *N*-methyl pyrrolidone (NMP), and trimethylamine (TMA) of AR grade were received from SD fine-Chemicals Limited, India and used without further purification. Deionized water (resistivity: $18.2 \text{ M}\Omega \text{ cm}$) was used for all experiments.

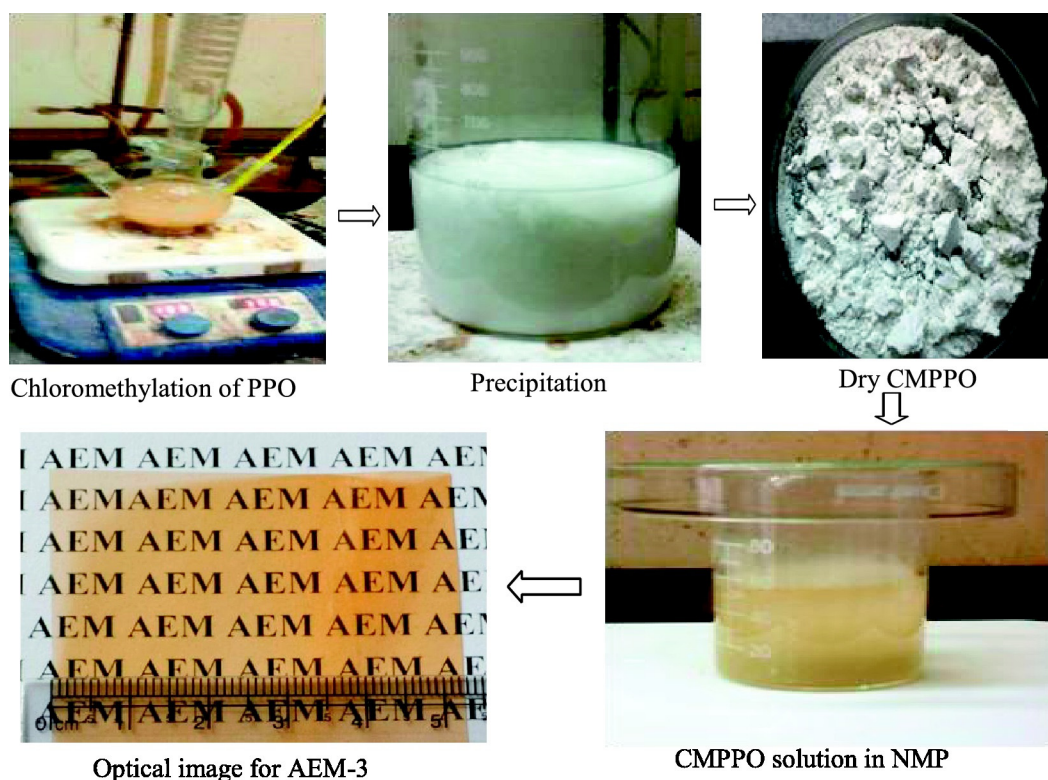


Fig. 1. Different reaction steps for the preparation of QPPO based AEM.

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