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# One-pot preparation of anion exchange membranes from bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) for electrodialysis

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## HIGHLIGHTS

- QPPO anion exchange membranes were prepared by the one-pot method.
- Membrane morphology is tunable by controlling the solubility parameter of solvent.
- Performances of one-pot prepared membrane are better than those of post-modified one.
- QPPO membranes are qualified for ED with low energy assumption.

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## ABSTRACT

Anion exchange membranes (AEMs) are commonly prepared by the heterogeneous post-modification of chloromethylated polymer films in trimethylamine (TMA) aqueous solution for the poor solubility of quaternary ammonium-functionalized polymers. This study reports the one-pot preparation of solvent-processable quaternary ammonium-functionalized poly (2,6-dimethyl-1, 4-phenylene oxide) (QPPO) solution by piping TMA gas into polymer solution directly. Solvents mixture with a proper solubility parameter is employed to ensure the dissolving of reactants and ammonium-functionalized products. Membrane morphology and properties, including ion exchange capacity, water uptake, area resistance, tensile strength and transport number, have been characterized to determine advantages of this strategy over the post-modification method. Moreover, the optimized membrane exhibits a better electrodialysis performance than that of post-modified membrane, suggesting the benefit of this strategy.

## 1. Introduction

Ion exchange membranes (IEMs), which were first reported by Juda and McRae (1950) in the last century, have stimulated both commercial and academic interests in water treatment and energy conversion processes (Buonomenna, 2013). For example, they can be used in electrodialysis (ED) to concentrate or deionize aqueous electrolyte solutions (Kim, 2011), and in diffusion dialysis to recover acid or alkali from waste acid or alkali solutions (Luo et al., 2011). They can also separate acidic gas via carrier transport (Way et al., 1987; Langevin et al., 1993; Adachi et al., 1998), or act as solid electrolytes in fuel cells (Sharaf and Orhan, 2014; Varcoe and Slade, 2005) and as sensing materials in sensors (Yasuda et al., 1990). Among these applications, separation of specific salts from aqueous electrolyte solutions through ED is one of the most important applications from the viewpoint of environmental protection and cleaner production (Strathmann et al., 2013).

As the key component of an ED device, tremendous IEMs have been extensively explored based on various backbones of engineering plastics for meeting requirements of high ion transport efficiency and stability. (Park et al., 2011; Wu et al., 2013). For commercially available IEMs, the most commonly utilized starting material is styrene-divinylbenzene copolymer, from which cation exchange membranes (CEMs) have already gotten a reliable production technology, but anion exchange membrane (AEM) still has technical problems during preparation, i.e. chloromethylation and quaternization. During chloromethylation, the mostly used chloromethyl methyl ether is a carcinogen (Warshawasky et al., 1984; Warshawasky and Deshe, 1985; Laskin et al., 1971). While for quaternization, the post-modification method is commonly employed by immersing films into trimethylamine (TMA) aqueous solution due to the lack of proper solvent for the dissolving of

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reactants and finally ammonium-functionalized products. The disadvantages include: (a) the efficiency of the solid–liquid heterogeneous reaction is very low. (b) The membrane quality is not stable, usually varied in different production batch, and membranes generally exhibit a loose morphology due to the erosion of TMA.

To date, increasing efforts have been devoted to the preparation of AEMs without using toxic chloromethylation reagents. Bromination of benzylmethyl and chloroacytlation of phenyl, are promising methods for avoidance of chloromethyl ether (Xu and Yang, 2001; Wu et al., 2006; Yan and Hickner, 2010). The less toxic modification allows for nearly quantitative conversion of benzylmethyl and chloroacytle groups to tetraalkylammonium groups. However, ammonium-functionalized products usually deposit during the quaternization process for its poor solubility. Hence, preparation of AEMs from solution-processable ammonium-functionalized ionomers is a challenging issue in industry-scale production of IEMs.

To overcome this obstacle, we develop a one-pot method to prepare AEM from ammonium-fuctionalized polymer solution, directly. It starts from the bromination of PPO and then quaternization. The key step is the choice of suitable solvents mixture which can dissolve both starting polymer PPO and finally ammonium-functionalized product QPPO. The final AEM is obtained by casting the reacting solution directly. Morphology investigation and properties characterizations, such as ion exchange capacity (IEC), membrane area resistance (Rm), ED performance, etc., are discussed extensively to show advantages of these membranes over that prepared by post-modification.

## 2. Experimental methods

### 2.1. Materials

Bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) was kindly supplied by Tianwei Membrane Corporation Ltd. of Shandong (China). *N*-methyl pyrrolidone (NMP, AR grade), *N*,*N*-dimethylformamide (DMF, AR grade), chlorobenzene (CB, AR grade), dimethyl sulfoxide (DMSO, AR grade), trimethylamine (TMA, gas) were purchased from Shanghai-Sinopham Chemical Reagent Co. Ltd. (China). Cation exchange membrane (CEM, CJMC-2) was purchased from Hefei Chemjoy Polymer Materials Co., Ltd. Deionized water was used in all experiments.

### 2.2. Membrane preparation

A series of QPPO membranes were prepared via the solution-casting method. First, BPPO was dissolved in the solvents mixture (corresponding compositions are listed in Table 1) to form a 20 wt% BPPO solution. The solution is stirred at 50 °C for 2 h as TMA gas being piped into it slowly. After quaternization, the solution is cast onto a clean glass plate and dried at 60 °C to remove solvent completely to get the transparent and flexible membrane. Membranes in the $Cl^-$ form are obtained by immersing it in NaCl solution (0.5 mol/L) for 24 h and then washed thoroughly to remove residual ions and kept in deionized water for 48 h.

**Table 1**
Compositions of solvents mixture for different AEMs.

| Sample | BPPO (g) | NMP (g) | DMF (mL) | CB (mL) |
|---|---|---|---|---|
| M-1 | 20 | 80 | – | – |
| M-2 | 20 | – | 53 | 27 |
| M-3 | 20 | – | 60 | 20 |
| M-4 | 20 | – | 70 | 10 |

For comparison, BPPO membrane was prepared using a typical post-modification procedure: BPPO base membrane was immersed in the aqueous trimethylamine (TMA, 1 mol/$dm^3$) solution at 25 °C for 24 h to ensure the complete conversion of bromomethyl group to quaternary ammonium groups (Xu and Yang, 2001). The membrane is denoted as M-5.

### 2.3. Characterizations

#### 2.3.1. H NMR spectra

H NMR spectra were recorded on a DMX300NMR spectrometer at 300 MHz.

#### 2.3.2. Ion exchange capacity (IEC)

The membrane ($Cl^-$ form) was washed with deionized water and dried at 60 °C under vacuum for 24 h before the mass was recorded. Then the membranes were immersed into $Na_2SO_4$ (0.5 mol/L) solution for 8 h to convert it into the $SO_4^{2-}$ form. The amount of $Cl^-$ ions released from the membrane was titrated with $AgNO_3$ (0.1 mol/L) aqueous solution ($K_2CrO_4$ was used as colorimetric indicator). The IEC (expressed in mmol/g) values were determined by the amount of $AgNO_3$ consumed in the titration and the mass of the dry membrane.

#### 2.3.3. Water uptake and swelling ratio

A membrane sample (4 cm in length and 1 cm in width) was immersed in deionized water at a given temperature for 24 h. Then both surfaces were wiped with tissue papers. Mass and length were quickly measured. Water uptake was calculated as follows:

$$\text{Water uptake} = \frac{Wwet - Wdry}{Wdry} 100\% \tag{1}$$

where $W_{wet}$ presents the hydrated mass and $W_{dry}$ presents mass of the sample when dehydrated (recorded after the quaternary ammonium-functionalized poly (2,6-dimethyl-1,4-phenylene oxide) (QPPO) were dried until a constant weight at 60 °C).

The linear expansion ratio was similarly calculated as

$$\text{Swelling ratio} = \frac{Lwet - Ldry}{Ldry} 100\% \tag{2}$$

where $L_{wet}$ presents the length of hydrated sample and $L_{dry}$ presents the length of dehydrated sample.

#### 2.3.4. Scanning electron microscope

The surface morphology of membrane was observed by an environmental scanning electron microscopy (TM3000-2834, Hitachi).

#### 2.3.5. Membrane area resistance

Membrane area resistance was measured by a commercial cell-assembly (MEIEMP-I, Hefei Chemjoy Polymer Materials CO., LTD.) under a constant current mode (Larchet et al., 2008). It is composed of five compartments: two electrode chambers at both ends of the cell; two intermediate compartments equipped with two reference electrodes; one quadrate clip for membrane. Particularly, two pieces of Nafion-117 membranes were assembled between electrode and intermediate chambers, separately, to eliminate the influence of electrode reaction. Two intermediate chambers are separated by the membrane clip, and tips of the reference electrodes should be closely to the center of membrane. During the measurement, $Na_2SO_4$ solution (0.3 mol/L) was fed to electrode chambers, and NaCl (0.5 mol/L) is fed to intermediate chambers. A constant current is supplied by a direct current power supply (SHEKONIC, Yangzhou Shuanghong Co., Ltd.) and the potential between electrodes is read by a digital multimeter (model: GDM-8145, Good will instrument Co. Ltd., Taiwan).