



Poly(2,6-dimethyl-1,4-phenylene oxide) containing imidazolium-terminated long side chains as hydroxide exchange membranes with improved conductivity

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ABSTRACT

Hydroxide exchange membrane fuel cells (HEMFCs) receive growing interest due to the usability of non-precious metal catalysts in the basic operating environment. The applications of HEMFCs are hindered by the trade-off between high hydroxide conductivity and good dimensional stability of the HEMs. Here, a novel poly(2,6-dimethyl-1,4-phenylene oxide) with imidazolium-terminated long side chains (PPO-COC₅H₁₀-Im) was synthesized by simple and controllable acetylation reaction of PPO and 6-bromohexanoyl chloride in a moderate condition (at room temperature), followed by the Menshutkin reaction with 1,2-dimethylimidazole. The introduction of long chains between imidazolium groups and polymer main chains facilitates the formation of good hydrophilic/hydrophobic micro-phase separation structure, which is illustrated by TEM. The hydroxide effective mobility in PPO-COC₅H₁₀-Im membrane is almost 2-fold that in short side chain imidazolium functionalized PPO (PPO-CH₂-Im) membrane at a certain IEC. Given similar swelling ratios (25% vs. 27%), PPO-COC₅H₁₀-Im membrane shows much higher hydroxide conductivity than PPO-CH₂-Im membrane (62 vs. 42 mS cm⁻¹) at 60 °C. It indicates that the PPO-COC₅H₁₀-Im membranes prepared here exhibits highly enhanced conductivity without sacrificing the dimensional stability.

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1. Introduction

Hydroxide exchange membrane fuel cells (HEMFCs) have received growing interest because of their advantages over proton exchange membrane fuel cells (PEMFCs) [1]. Operating in the alkaline environment, HEMFCs exhibit enhanced kinetics of both the fuel oxidation and oxygen reduction, which allow non-precious metals to be used as active catalysts (e.g. silver and nickel) [2,3]. In addition, the catalysts could be more stable in the basic medium than in the acidic one. Therefore, HEMFCs have the potential to solve the problems of catalyst cost and durability while achieving high power and energy density [4].

As a critical component in HEMFCs, hydroxide exchange membranes (HEMs) serve as both hydroxide conductors and fuel/oxidant separators simultaneously, controlling HEMFCs'

performance [5]. HEMs possess lower conductivities compared to proton exchange membranes (PEMs), due to the intrinsically lower mobility of hydroxide ions compared to protons [6]. Thus many efforts have been made aiming to develop highly conductive HEMs. The most frequently used route is grafting hydroxide conducting groups onto the high-performance polymers. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has extensive applications in hydroxide exchange membranes (HEMs), due to its excellent physicochemical properties including good mechanical strength, thermal stability and chemical stability [7–9]. PPO based HEM materials are commonly prepared via introducing halogenomethyl groups onto PPO polymer matrix, followed by the functionalization reaction [10–13]. As the functional groups are connected to the PPO backbone via short links, it is hard to form good hydrophilic/hydrophobic micro-phase separation structure which is necessary for well-interconnected hydroxide transporting pathways. Therefore, the PPO based membranes prepared by this method showed low hydroxide conductivity.

There are two approaches which could enhance the hydroxide conductivity of HEMs: increasing the ion exchange capacity (IEC)

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and improving the ionic mobility [14]. Higher IEC could offer the ability to absorb more water uptake, which make hydroxide conducting channels more connected, thus enhancing hydroxide conductivity [15,16]. However, high water uptake inevitably expands the overall hydrophilic domains, and eventually induces excessive swelling of these membranes, even loss of dimension stability [17–19]. Crosslinking is usually applied in the design of polymer architecture to obtain mechanically robust HEMs with improved dimensional stability [20]. However, the degree of crosslinking is usually not easily controlled. Hence an effective strategy to boost hydroxide conductivity of HEMs is to improve the hydroxide mobility by promoting hydrophilic/hydrophobic micro-phase separation structure to construct hydroxide conducting highway [21]. Enhancing the mobility of functional groups by introducing long side chains [22] and designing a natural aggregation of functional groups by introducing multiple functional groups in one side chain [16,23] could enhance the micro-phase separation ability of PPO based HEMs. Compared to multiple functionalization, the synthetic processes of introducing long side chains are easier to be controlled, but still need harsh reaction conditions.

Herein, a novel PPO with imidazolium terminated long side chains was synthesized by simple and controllable acetylation reaction of PPO under moderate reaction conditions (at room temperature), followed by a Menshutkin reaction with 1,2-dimethylimidazole. Compared to the literatures [22], the reaction condition used here is much more mild. The effects of long side chains on water uptake, swelling ratio, hydroxide conductivity, thermal and alkaline stability for the membranes were comprehensively investigated. The introduction of the flexible long side chain enhances the mobility of the terminated imidazolium groups, promoting the formation of hydrophilic/hydrophobic micro-phase separation structure. Given similar swelling ratios, the long side chain type PPO membrane exhibits much higher hydroxide conductivity than the short side chain type one.

2. Experimental

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, GFN2-701) was obtained from SABIC Innovative Plastics (USA), with a molecular weight of about 50,000. Chloromethyl octyl ether (CMOE) was synthesized according to the Ref. [24]. Aluminum chloride anhydrous, tin chloride anhydrous, 6-bromohexanoyl chloride, 1,2-dimethylimidazole, n-octanol, polyoxymethylene, calcium chloride anhydrous, hydrochloric acid (37–38%), ethanol, and N-methyl-2-pyrrolidone (NMP) were commercially obtained and used as received without further purification. All the used chemicals in the

experiments were analytical grade. Dichloromethane and chloroform was dried over molecular sieves (4 Å, 8–12 mesh) before use. In order to reduce the possible effect of CO₂ dissolved in deionized water on the membrane characterization, the deionized water was boiled to completely degassed prior to use.

2.2. Preparation of long-side-chain imidazolium functionalized PPO membranes

A long side chain was grafted onto the PPO by the acetylation reaction of PPO and 6-bromohexanoyl chloride. 1 g PPO was dissolved in 10 mL dichloromethane to form a PPO solution in a 25 mL round-bottom flask with strenuous stirring. 0.67 g of aluminum chloride anhydrous was added into 15 mL dichloromethane with stirring in a three-neck flask under nitrogen. The flask was chilled in an ice/water bath, then 0.77 mL 6-bromohexanoyl chloride was added dropwise into the stirring solution. After that, the PPO solution was added into the flask, and the reaction mixture was stirred at room temperature for 1.5, 2.0, 2.5, and 3 h. The final PPO containing bromide terminated long side chains (PPO-COC₅H₁₀-Br) was obtained by depositing the reaction solution in ethanol and the solid was dried at room temperature under vacuum.

Long-side-chain imidazolium functionalized PPO was prepared from the reaction between PPO-COC₅H₁₀-Br and 1,2-dimethylimidazole. 0.76 g PPO-COC₅H₁₀-Br and 3 equivalents 1,2-dimethylimidazole were dissolved into 12 mL NMP with stirring, then the solution was heated to 80 °C and kept for 24 h. After cooling to room temperature, the solution was filtered and poured onto a glass casting plate. After curing and drying at 80 °C for 48 h, the long-side-chain imidazolium functionalized PPO (PPO-COC₅H₁₀-Im) membrane was obtained and peeled off the glass plate. The final PPO-COC₅H₁₀-Im membranes in OH⁻ form were immersed in 1 M KOH solution at room temperature for 24 h to exchange the ion from Br⁻ to OH⁻. The resulted membranes were washed and immersed with deionized water until neutral. The synthetic processes are shown in Fig. 1.

2.3. Preparation of short-side-chain imidazolium functionalized PPO membranes

Short-side-chain imidazolium functionalized PPO was synthesized by the typical two-step chloromethylation-functionalization method. The synthetic procedures illustrated in Fig. 2. 1 g of PPO was added to 50 mL chloroform at room with stirring, followed by addition of 0.05 mL anhydrous tin chloride and CMOE (1, 1.5, 2, and 2.5 mL, respectively). The reaction was kept at room temperature for 30 min. The final chloromethylated PPO (PPO-CH₂-Cl) was obtained by depositing the reaction solution in ethanol and drying at room temperature under vacuum. Then, 0.9 g PPO-CH₂-

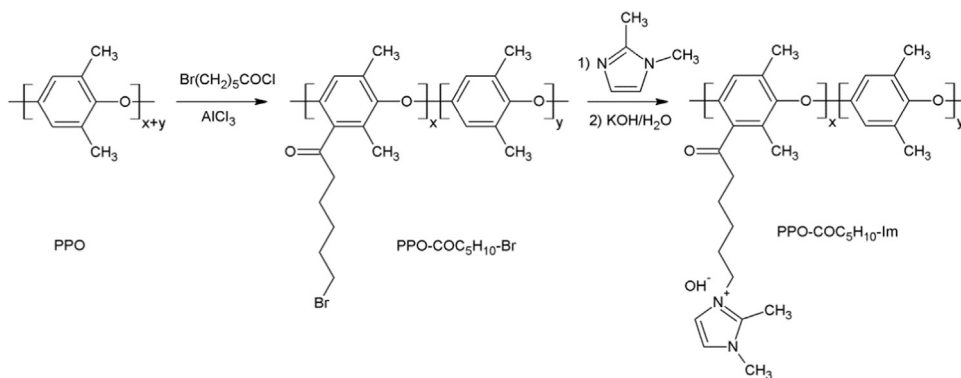


Fig. 1. Synthesis of long-side-chain imidazolium functionalized PPO.

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