



Preparation of anion exchange membranes by an efficient chloromethylation method and homogeneous quaternization/crosslinking strategy



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ABSTRACT

A novel chloromethylation method and homogeneous quaternization/crosslinking strategy for a series of polymers are demonstrated in this paper. The chloromethylation is accomplished by using 1, 4-bis (chloromethoxy) butane (BCMB) as the chloromethylating reagent and concentrated sulfuric acid as the solvent and catalyst. BCMB is a kind of high-efficient, non-carcinogenic and inexpensive chloromethylating reagent, and concentrated sulfuric acid replaces toxic halogenated hydrocarbon. Study results indicated that BCMB had higher reactivity than chloromethyl octyl ether under similar reaction conditions. The chloromethylated poly (phthalazinone ether sulfone ketone) (PPESK) was then crosslinked and quaternized by using N, N, N', N'-tetramethyl-1, 6-hexanediamine (TMHDA) as the homogeneous quaternizing and crosslinking agent during the solvent evaporation. The ion exchange capacity (IEC) of the crosslinked membranes (C-QAPPEK/OH) was very close to the theoretical value, higher than that of the membranes quaternized by trimethylamine (TMA) aqueous solutions (QAPPEK/OH). In addition to higher IEC, C-QAPPEK/OH membranes possessed greater hydroxide conductivity and chemical stability than that of QAPPEK/OH membranes. The results suggest that this efficient chloromethylation together with the homogeneous quaternizing and crosslinking method is a time-saving strategy with potential application in the preparation of anion exchange membranes.

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1. Introduction

Recently, considerable attention has been paid to anion exchange membrane fuel cells (AEMFCs) because of their numerous advantages in comparison with polymer electrolyte membrane fuel cells (PEMFCs), such as faster electrode kinetics, desirable applicability of non-precious metals as catalyst and milder corrosion environment [1]. Therein, the anion exchange membrane (AEM) plays an inherently significant role in improving fuel cell performance, thus it is attracted special research interests [2]. AEMs are usually composed of polymer matrix and cationic charged groups. Up to now, chloromethylation followed by quaternization and alkalization is one of the most frequently used methods to fabricate AEMs [2]. Among them, chloromethylation and quaternization are the most important steps.

Chloromethylation introduces chloromethyl groups onto the phenyl ring via electrophilic substitution reaction between chloromethylation reagents and polymers [2,3]. Chloromethyl methyl ether (CMME), paraformaldehyde/HCl and trimethylchlorosilane are the commonly used chloromethylation reagents. Nevertheless, the activity of paraformaldehyde/HCl and trimethylchlorosilane is low, thus prolonged

reaction time is required [2]. Despite the high activity, chloromethyl methyl ether is a well known toxic and carcinogenic compound. As a consequence, long acyclic chloromethyl octyl ether (CMOE) with low toxicity and volatility was used to conduct chloromethylation [3–8]. Unfortunately, the activity of CMOE is lower than that of CMME, because the molecule size of CMOE is larger than that of CMME, leading to the difficulty for CMOE to attack polymers caused by steric blocking effects. Additionally, the chloromethylation reaction reported in literature was usually carried out in halogenated hydrocarbon (e.g., chloroform) with Lewis acid (e.g., SnCl₄) as the catalyst [2,8,9]. Generally, the halogenated hydrocarbon should be dried before use and the Lewis acid is humidity sensitive, so air and water free conditions are required, resulting in the complication of facilities and production process. Furthermore, the halogenated hydrocarbon solvent is prone to volatilize and the vapor is harmful to environment and human health. Therefore, a “green” chloromethylation method needs to be developed in urgency.

Followed by chloromethylation, quaternary ammonium (QA) groups are introduced to the polymer by quaternization process. This is usually accomplished by treating the pre-formed chloromethylated polymer membranes in trimethylamine (TMA) aqueous solutions [3,4,6–11]. This is a heterogeneous quaternization method which proceeds in solid membranes and takes prolonged time. Meanwhile, TMA is highly volatilizable and carcinogenic, which makes the membrane fabrication process not environmental friendly. Consequently, the homogeneous quaternization

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method, i.e., the transformation of chloromethyl groups to QA was accomplished before or during the membrane formation, is desirable [12–15]. N, N, N', N'-tetramethyl-1, 6-hexanediamine (TMHDA) can be used to quaternize chloromethyl groups [13,15,16] and it is less volatilizable, thus TMHDA can be utilized as a safer and homogeneous quaternization reagent. More importantly, the crosslinking of membranes will be realized simultaneously if diamines are used. Crosslinking has been proved to be a simple and effective method to improve the mechanical and chemical stability of QA-based AEMs [13,14,17–19], which is required for the fuel cell applications.

Herein, we demonstrated a new chloromethylation and crosslinking method to prepare anion exchange membranes. The chloromethylation was accomplished by using concentrated sulfuric acid and 1, 4-bis (chloromethoxy) butane (BCMB) as the solvent and chloromethylating reagent, respectively. In addition to the nonvolatile nature, concentrated sulfuric acid has good solubility for many polymers and it can be also used as catalyst in the chloromethylation reaction [6,8]. BCMB is a non-carcinogenic and inexpensive chloromethylating reagent [20,21]. Then we adopted N, N, N', N'-tetramethyl-1, 6-hexanediamine (TMHDA) to quaternize and crosslink chloromethylated polymers during the solvent evaporation in the membrane formation. The crosslinked quaternized membranes have higher IEC and hydroxide conductivity than that of the membranes quaternized by TMA in the conventional method. In addition, the chemical stability of crosslinked quaternized membranes is significantly enhanced simultaneously.

2. Experimental

2.1. Chloromethylation

In this paper we utilized three commercially available polymers, i.e., poly (ether ether ketone) (PEEK, Victrex, medium melt viscosity grade 450PF), poly (ether sulfone) (PES, reduced viscosity = 0.36 dL g⁻¹ in N, N-Dimethylformamide (DMF) at 25 °C, Changchun Jilin University Special Plastic Engineering Research) and poly (phthalazinone ether sulfone ketone) (PPESK, molar ratio of sulfone/ketone = 1:1, Dalian Polymer New Material Company, its reduced viscosity in Dimethylacetamide (DMAc) at 25 °C is measured to be 0.42 dL g⁻¹ in our laboratory), to demonstrate the new chloromethylation method.

Typically, 1 g polymer was dissolved into 30 mL (for PES and PPESK) or 60 mL (for PEEK) ice-cold 98% concentrated H₂SO₄ followed by addition of a given volume of 1, 4-bis (chloromethoxy) butane (BCMB) (≥95%, Xi'an Langene Bioscience Co. Ltd, China). Subsequently, the reaction was kept in the ice-water bath (for PES and PPESK) or ice-salt bath (for PEEK) for some time and the product was separated by precipitation the mixture in ice water, followed by thorough washing with de-ionized water, and then drying at 50 °C in air. Then the chloromethylated polymers (CMPES, CMPPEK and CMPEEK) were obtained.

2.2. Membrane preparation

For preparing the crosslinked membranes, 0.4 g CMPPEK was dissolved in 1-methyl-2-pyrrolidone (NMP) to make a 3 wt.% solution, followed by addition of a given volume of N, N, N', N'-tetramethyl-1,6-hexanediamine (TMHDA) (99%, Xi Ya Reagents, China). The mixture was stirred for 60–90 s and then poured onto a glass plate to cast the membrane and dried in oven at 70 °C for 24 h. This quaternization method is called homogeneous quaternization method (Scheme 1). The membranes obtained were denoted as C-QAPPEK/Cl-n, where n was the ratio of the actual added amount of TMHDA to the theoretical amount. Subsequently, the C-QAPPEK/Cl membranes were immersed in a 1 M KOH solution for 24 h, converting the membranes from the Cl⁻ form into the OH⁻ form (C-QAPPEK/OH), followed by washing with de-ionized water several times and storing in de-ionized water

for another 48 h to completely remove the residual KOH prior to further experiments.

In comparison, the CMPPEK was quaternized by the conventional method using trimethylamine (TMA). Briefly, 0.4 g CMPPEK was dissolved in 1-methyl-2-pyrrolidone (NMP) to make a 3 wt.% solution, followed by pouring the solution onto a glass plate to cast the membrane and drying in oven at 70 °C for 24 h. Then the CMPPEK membrane was soaked into 125 mL 33 wt.% trimethylamine aqueous solution at 50 °C for 12 h to prepare the quaternized PPESK membranes (QAPPEK/Cl). This quaternization method is called conventional quaternization method (Scheme 2). Subsequently, the QAPPEK/Cl membranes were immersed in a 1 M KOH solution for 24 h, converting the membranes from the Cl⁻ form into the OH⁻ form (QAPPEK/OH), followed by washing with de-ionized water several times and storing in de-ionized water for another 48 h to completely remove the residual KOH prior to further experiments.

2.3. Characterization

The degree of chloromethylation (DCM) for the chloromethylated polymer was determined by ¹H NMR spectroscopy on a Bruker Avance II 400 NMR spectrometer at a resonance frequency of 400.13 MHz, using tetramethylsilane (TMS) as an internal standard. The Fourier transform infrared (FT-IR) absorption spectra of membranes after drying at 60 °C under vacuum overnight were recorded by using a Bruker Tensor 27 spectrophotometer.

For the measurements of ion exchange capacity (IEC), water uptake (WU) and swelling ratio (SR) of membranes, the OH⁻ form membranes were dried at 60 °C under vacuum overnight.

The IEC of membranes was determined by the back titration method. Briefly, the dried OH⁻ form membranes were immersed in 30 mL 0.01 M HCl aqueous solutions for 24 h, followed by back titration of 0.01 M NaOH solution with phenolphthalein as the indicator. The 30 mL 0.01 M HCl solution was used as the blank sample for the control experiment. The measured IEC (mmol g⁻¹) of the membrane was calculated as follows:

$$IEC = \frac{(V_b - V_a)c_{HCl}}{m_{dry}} \quad (1)$$

where V_b and V_a were the consumed volumes (mL) of the NaOH solution for the blank sample and the membrane sample, respectively, c_{HCl} was the concentration of HCl solutions (mol L⁻¹), m_{dry} was the mass of dry membrane.

The water uptake of the OH⁻ form membranes were measured by the following equation:

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad (2)$$

where m_{wet} and m_{dry} were the mass of wet and dry membranes, respectively.

The swelling ratio of the OH⁻ form membranes in plane (SR_p) and in thickness (SR_t) direction were measured by the following equations:

$$SR_p = \frac{l_{wet} - l_{dry}}{l_{dry}} \quad (3)$$

$$SR_t = \frac{t_{wet} - t_{dry}}{t_{dry}} \quad (4)$$

where l_{wet} and l_{dry} were the average length [l_{wet} = (a_{wet} · b_{wet})^{1/2}, l_{dry} = (a_{dry} · b_{dry})^{1/2}] of wet and dry membrane samples, respectively, in which, a_{wet}, b_{wet} and a_{dry}, b_{dry} were the lengths and widths of wet and dry membrane samples, respectively. t_{wet} and t_{dry} were the thickness of wet and dry membranes, respectively.

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