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One-pot solvent-free synthesis of cross-linked anion exchange membranes for electrodialysis

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ABSTRACT

Solvent-free strategy has attracted a broad interest in preparation of ion exchange membranes in recent years stemming from the no need of organic solvents and facilitated construction of highly crosslinking networks. However, post-functionalization is commonly required for further introducing ion-exchange groups. In this study, we report a one-pot solvent-free synthesis of cross-linked anion exchange membranes (AEMs) without the need for post-functionalization. We firstly dissolved brominated poly (2, 6-dimethyl-1, 4-phenylene oxide) (BPPO) in liquid monomers mixture of 4-vinylbenzyl chloride (VBC) and styrene without any organic solvent, then added appropriate amount of N-vinylimidazole and N-methylimidazole to introduce imidazolium groups into both of polyelectrolyte and solvents. The transparent, robust and crosslinked AEMs were obtained by the thermal crosslinking of the unsaturated moieties during the membrane forming process. This approach, distinct from the classical post-functionalization processes, performs crosslinking and functionalization simultaneously. Particularly, imidazolium cations locating on cross-links endow the resultant membrane a high concentration of charge carriers (ion-exchange capacity) for target low resistance, while maintain a high mechanical stability.

1. Introduction

Ion-exchange membranes (IEMs) are polymer electrolytes that conduct anions or cations, as they contain counter charged groups bound covalently to a polymer backbones [1]. Over the last decade or so, there is an increasing worldwide interest in the use of IEMs on a large industrial scale in processes such as electrodialysis, electrodeionization, diffusion dialysis, and energy conversion and storage systems [2–5]. Among them, electrodialysis (ED), in which a series of alternating anion- and cation-exchange membranes arranged between two electrodes, is today one of the most state-of-the-art ion-exchange membrane process. It has found industrial scale application in water desalination and recovery of useful substances from industrial waste water [3]. As the key component in ED devices, cation-exchange membranes (CEMs) have successfully been commercialized for the reliable manufacturing technique, however, anion-exchange membranes (AEMs) still face technique challenges in large-scale preparation and further improving their performance, *i. e.* high ions selective permeability and stability [6,7].

AEMs have a selective permeability for anions as they contain fixed positive charged ions, such as ammonium, phosphonium, guanidinium ions [8–15]. Traditional preparation of AEMs usually employs the post-modification of pristine polymers or direct polymerization of functionalized monomers. For post-modification method, the most common approach is to carry out a chloromethylation or bromomethylation on the polymer so as to further cationize them with trimethylamine. A variety of polymers, such as polysulfone [16], poly (phthalazinone ether sulfone ketone) [17], poly(ether-imide) [18], poly(phenylene oxide) [19], poly (phenylene) [20], could act as scaffolds for preparing AEMs. The direct polymerization is usually performed by polymerization of monomers with moieties bearing ammonium, halomethyl-containing or amine-containing groups, that can be conveniently converted into anionic exchange groups in organic solvent. Coates et al. reported their work on the facile synthesis and ring-opening metathesis polymerization of a tetraalkylammonium-functionalized norbornene with dicyclopentadiene as a cross-linkable monomer to yield strong AEMs [21,22]. Zhang et al. reported that

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partially fluorinated poly (arylene ether sulfone) with pendant ammonium groups were prepared by copolymerization of bisphenol monomers containing amine groups and partially fluorinated monomers, followed by quaternization [23]. We have reported preparation of high performance AEM by polyacylation of pre-quaternized monomers to endow the resultant AEMs with excellent hydroxide ion conductivity [24]. Although these strategies represent a promising progress in the development of AEMs in recent years, they all require excess reagents and long reaction time to obtain highly functionalized polymers. Particularly, the large amount of organic solvents in both reaction and membrane formation processes will carries toxic risk to the environment. Hence, to further industrial-scale manufacture, it is important to develop simple, rapid and environmental friendly methods for production of AEMs with excellent performances.

To overcome these obstacles, we previously developed a solvent-free strategy for AEMs by the in-situ polymerization [25]. Different from the above mentioned post-modification and direct polymerization, it starts from the dissolving of polymer electrolytes by liquid monomers, other than organic solvent, followed by in-situ polymerization to obtain un-charged membranes. It should be noted that post-quaternization was required to convert halomethyl groups to ammonium cations by immersing base membrane into trimethylamine (TMA) aqueous solution. The disadvantages of this strategy include: a) the reaction efficiency is very low due to the solid-liquid heterogeneous reaction. b) The quality of the membrane is hardly to be controlled for different production batch, and membranes usually exhibit a loose morphology due to the erosion of TMA.

In view of the above mentioned issues, we herein presents our current efforts toward developing upgradable solvent-free strategy for AEMs. This approach, distinct from the classical post-quaternization processes, performs crosslinking and quaternization simultaneously. We firstly dissolved brominated poly (2, 6-dimethyl-1, 4-phenylene oxide) (BPPO) in liquid monomers mixture of 4-vinylbenzyl chloride (VBC) and styrene without any organic solvent, then added appropriate amount of N-vinylimidazole and N-methylimidazole to introduce imidazolium cations into both of polyelectrolyte and solvents. The transparent, robust and crosslinked AEMs were obtained by the thermal crosslinking of the unsaturated moieties during the membrane forming process. Particularly, the imidazolium cations locating on cross-links endow the resultant membrane a high concentration of charge carriers for target high ions permeability, while maintain a high mechanical stability. Properties characterizations, such as ion exchange capacity (IEC), membrane area resistance (R_m), electrodialysis related performance, etc., are discussed extensively to show the advantages of the solvent-free strategy over the conventional post-modification method.

2. Experimental methods

2.1. Materials

Brominated poly (2, 6-dimethyl-1, 4-phenylene oxide) (BPPO) was kindly supplied by Tianwei Membrane Corporation Ltd. of Shandong (China). 4-Vinylbenzyl chloride (VBC), which was purchased from Changzhou Wujin Linchuan Chemical Co. Ltd. N-vinylimidazole (N-VI, 98%) and N-methylimidazole (N-MI, 99%) were purchased from Energy Chemical Co. Ltd. Styrene, sodium sulfate (Na_2SO_4), sodium chloride (NaCl), N-Methyl pyrrolidone (NMP, AR grade), N, N-dimethylformamide (DMF, AR grade), chlorobenzene (CB, AR grade), dimethyl sulfoxide (DMSO, AR grade) were purchased from Shanghai-Sinopham Chemical Reagent Co. Ltd. (China). Commercial anion exchange membrane Neosepta AMX (thickness 120–180 μm, IEC 1.4–1.7 meq g^{-1}, area resistance 2.0–3.5 Ω cm^2) and cation exchange membrane Neosepta CMX (thickness 220–260 μm, IEC 1.5–1.8 meq g^{-1}, area resistance 2.0–3.5 Ω cm^2) were purchased from ASTOM, Japan.

2.2. Membranes preparation

As shown in Scheme 1, BPPO (1 g/0.00298 mol –CH_2Br) was dissolved in a liquid monomers mixture; then appropriate amount of N-Vinylimidazole was added to convert all bromomethyle of BPPO and half amount of chloromethyl groups of VBC to imidazolium cations. The remaining chloromethyl groups were converted to imidazolium cations by adding N-Methylimidazole dropwise. The composition of reaction mixture was determined according to the solubility of polymer electrolytes (BPPO) in the liquid monomers. In this study, the content of BPPO (1 g) keeps constant for the preparation of all membranes. Styrene, which is employed as solvent, need a critical content (18 ml) to completely dissolve BPPO. Hence, the contents of BPPO and styrene are kept constant during the preparation. The content of VBC was varied to tune the amount of functional groups in membranes. Accordingly, the contents of N-VI and N-MI were varied with the change of VBC content to convert functional groups (–CH_3Br and –CH_3Cl) to imidazolium cations, also to keep the membrane with an appropriate crosslinking degree. Table 1 shows the components of the different reaction mixtures. The resulting membranes are designated as M-x, where x represents the amount of VBC (0.25 ml. 0.5 ml, 0.75 ml and 1.0 ml). Before characterization, all membranes were immersed in ether at room temperature for 4 h to remove unreacted monomers (styrene, VBC, N-VI and N-MI, which are all soluble in ether), followed by thorough washing with deionized water to remove imidazolium salts (possibly resulting from the reaction of unreacted VBC with N-VI and N-MI).

2.3. Membranes characterizations

2.3.1. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra were measured using a Vector 22 Fourier transform infrared spectrometer (Bruker).

2.3.2. Measurement of gel content

Gel content was measured by calculating the ratio of mass remaining after immersing the membrane in organic solvent for 7 days at room temperature, typical procedure is as follows:

a) Four pieces of membranes (2 × 4 cm, BPPO-0.25, BPPO-0.5, BPPO-0.75, BPPO-1.0)were dried at 60 °C for 24 h, then weighted (m_0).
b) The dried membranes were soaked in NMP, DMSO, DMF and $CHCl_3$ at room temperature for 7 days, respectively. After that, they were washed and immersed in distilled water for 1 day.
c) Finally, they were dried at 60 °C for 24 h, and weighed (m_t).

The gel content was calculated according to the following equation:

$$D_C = \frac{m_t}{m_0} \times 100\% \quad (1)$$

2.3.3. Thermal analysis

TGA and DTG thermograms were recorded using a TGA Q5000 V3.15 analyzer at a heating rate of 10 °C min^{-1} under a N_2 atmosphere in order to evaluate the short-term thermal stability of membrane.