Separation and Purification Technology xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

In-situ crosslinking of anion exchange membrane bearing unsaturated moieties for electrodialysis

Yanbo Liu [a], Qi Pan [a], Yaoming Wang [a,b], Chunlei Zheng [b], Liang Wu [a,*], Tongwen Xu [a,*]

[a] CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, PR China
[b] Hefei Chemjoy Polymer Materials Co. Ltd., Hefei 230601, PR China

ARTICLE INFO

Article history:
Received 11 August 2015
Received in revised form 30 September 2015
Accepted 2 October 2015
Available online xxxx

Keywords:
Anion exchange membrane
In-situ crosslinking
Electrodialysis
Membrane area resistance
Desalination

ABSTRACT

This study reports the preparation of the *in-situ* crosslinked anion exchange membrane that does not require the use of crosslinkers or catalysts. A polyelectrolyte bearing flexible unsaturated side chains was synthesized via the Menshutkin reaction with poly(2,6-dimethyl-1,4-phenylene oxide) and N,N-Dimethylvinylbenzylamine. The crosslinked derivatives were then prepared by the thermal crosslinking of the unsaturated side chains during the membrane formation process. This approach incorporates crosslinks, bearing quaternary ammonium cations, between the polymer chains in order to mitigate against excessive water swelling, and to enable the high ion contents to provide favorable low resistance of ion transport. Additionally, the resultant dense crosslinked network has the additional advantage of improving anion selective permeability of membrane. When being applied in ED application, the crosslinked membranes exhibit much higher desalination efficiency than commercial Neosepta AMX membrane, suggesting its potential application in ED.

1. Introduction

Electrodialysis (ED) is today by far the state-of-the-art ion exchange membrane (IEM) processes for water desalination and deionization in the chemical process industry [1,2]. The conventional electrodialysis is composed of a series of cation- and anion exchange membranes (AEMs and CEMs) alternating arranged between two electrodes. The AEMs and CEMs are separated by the spacer gasket to form individual concentrate cells and dilute cells. When an electrical potential difference between the electrodes is established, salt ions (cations and anions) selectively permeate from dilute cells to concentrate cells through IEMs, separately. Apparently, the selective permeability and stability of IEMs in an electric field dominate the efficiency of ED. CEMs have successfully commercialized for the reliable manufacturing technique, however, AEMs still face technique challenges in facile preparation and further improving their performance, i.e. high ions selective permeability and stability [3,4].

AEMs are capable of conducting anions as they contain fixed positive charged ions, such as ammonium, phosphonium, [5–9] guanidinium ions [10–12]. Traditional preparation of AEMs usually employs the post-modification of pristine polymers. It was commonly carried out by chloromethylation or bromomethylation of the polymers so as to further cationize them with trimethylamine or other tertiary amines. A variety of polymers, such as polysulfone [13], poly(phthalazinone ether sulfone ketone) [14], poly(ether-imide) [15], poly(phenylene oxide) [16], poly(phenylene) [17], could act as scaffolds for preparing AEMs. Although these examples illustrate the remarkable progress in the area of AEMs, they still face scientific challenge in providing sufficiently high ions selective permeability for the heterogeneous post-quternarization technique in forming highly ordered ions transport morphology. To overcome this drawback, scientists have devoted their efforts into preparing AEMs by directly solution-casting of soluble quaternary ammonium based polymers or polymerization of ammonium-functionalized monomers. Hickner et al. have performed a comparing study on preparation of benzyl quaternary ammonium based polysulfone AEMs by post-modification of bromobenzylmethyl polysulfones films and directly solution-casting of quaternary ammonium salt, respectively. It is concluded that the latter favors the formation of continuous ionic aggregations, thus imparting higher ions selective permeability [18]. Our previous work has described the polyacylation of pre-quaternized monomers to endow the resultant AEMs with excellent hydroxide ion conductivity [19]. It should be noted that ion transport performance of the resultant AEMs depends on the content of fixed charge groups. Likewise, a lot of AEMs with high ionic contents, such as AEMs

* Corresponding authors.
E-mail addresses: liangwu8@ustc.edu.cn (L. Wu), twxu@ustc.edu.cn (T. Xu).

http://dx.doi.org/10.1016/j.seppur.2015.10.002
1383-5866/

Nomenclature

Symbol	Content
IEM	ion exchange membrane
AEM	anion exchange membrane
CEM	cation exchange membrane
CP	chemical pure
AR	analytical reagent
ED	electrodialysis
BPPO	bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide)
VBN	N,N-Dimethylvinylbenzylamine
TMA	trimethylamine
NMP	N-methyl
DMA	Dimethylamine
FTIR	Fourier transform infrared spectroscopy
IEC	ion exchange capacity

containing pendant bis(phenyltrimethylammonium) groups [20], AEMs with side chains that contain double quaternary ammonium cations [21] and quaternary ammonium-functionalized 4-vinylbenzyl chloride grafted polyelectrolyte AEMs [22,23], have been intensively developed by the pre-functionalization method. Although increasing the ionic content in the AAEM can help to reach a high ion conducting performance, it, in turn, causes undesirable mechanical stability loss during ED process, unless new strategies are introduced to mitigate against this effect.

To date, typical *in-situ* crosslinking via Friedel–Crafts electrophilic substitutions [7,24] or olefin metathesis techniques [25–27], has been considered as a promising technique to improve the mechanical stability of quaternary ammonium based AEMs. This strategy allows crosslinking during solution casting to yield AEMs with homogeneous morphologies, and endows enhanced mechanical stability without sacrificing ions transport performance relative to AEMs formed via post-crosslinking techniques involving additional crosslinkers. Moreover, crosslinks bearing ionic groups lead to increased ion incorporation, which in turn support high ion selective permeability. 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 comonomer to yield strong AEMs [25]. Li and Hickner reported a crosslinked "comb-sharped" AEMs with favorable hydroxide conductivity and much low water swelling [26].

Inspired by the *in-situ* crosslinking strategy, we report a new facile route for self-crosslinked AEMs for ED purpose that does not require the use of crosslinkers or catalysts. Unsaturated side chains were attached onto aromatic backbones via the Menshutkin reaction and then *in-situ* crosslinked during the membrane formation step via a thermal-only treatment. This approach incorporates ionic crosslinks between the polymer chains to enable the high ion contents required to provide favorable low resistance of ion transport. The effect of crosslinking on properties such as swelling ratio, membrane resistance, mechanical stability and desalination performance is presented and discussed.

2. Experimental

2.1. Materials

Bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) with a bromomethylation degree of 57.8% per repeat unit was kindly supplied by Shandong Tianwei Membrane Technology Co. Ltd. (China). Commercial Neosepta AMX and CMX membranes were purchased from ASTOM Corporation (Japan) (Neosepta AMX: thickness = 0.14 mm, membrane area resistance = 2.5 Ω cm^2, IEC = 1.4 mmol g^{-1}; Neosepta CMX: thickness = 0.17 mm, membrane area resistance = 3.5 Ω cm^2, IEC = 1.2 mmol g^{-1}, these data were measured using the procedure described below), 4-Vinylbenzyl chloride (VBC) was purchased from Beijing Bailingwei Co. Ltd. (China). N-methyl pyrrolidone (NMP, AR grade), Dimethylamine solution 33% (DMA, CP grade), magnesium sulfate ($MgSO_4$, CP grade) were obtained commercially and used without further purification. Deionized water was used in all experiments.

2.2. Synthesis of N,N-Dimethylvinylbenzylamine (VBN)

DMA solution (33%, 50 ml) was transferred to a 250 ml conical flask equipped with a magnetic stir bar. VBC (50 ml) was added dropwise to the DMA solution (33%) via a dropping funnel over a period of 3 h under vigorous stirring at room temperature. The oil phase was filtrated by a separating funnel to obtain N,N-Dimethylvinylbenzylamine (VBN). After washed 3 times using deionized water, VBN was dried by anhydrous magnesium sulfate for 1 day at room temperature.

2.3. Preparation of crosslinked membranes

BPPO-VBN copolymers were synthesized using the Menshutkin reaction. Typically, BPPO (1.0 g) was dissolved in NMP (6 mL) at 25 °C in a dry 25 mL three-neck round bottom flask equipped with a magnetic stirring bar. After the BPPO had dissolved completely, different amounts of VBN (0.25 ml, 0.375 ml, 0.5 ml, 0.625 ml, 0.75 ml, the corresponding mole ratios with bromomethyl groups of BPPO were 0.5:1, 0.75:1, 1:1, 1.25:1, 1.5:1) were added dropwise under stirring for 2 h at room temperature, respectively. The casting solutions were cast onto 5 separate glass plates, and heated at 70 °C (one temperature per glass plate) for the simultaneous removal of solvent and to perform crosslinking. Evaporation of NMP (with a high boiling point) takes a long time but has the advantage of ensuring complete crosslinking. After this drying-curing process, flexible, transparent, and yellow-tinged AEMs were obtained: these are designated as BPPO-VBN-*x*-*y* (x = 0.5, 0.75, 1, 1.25 and 1.5, y = 70 – where x represents the mole ratios of VBN to bromomethyl groups of BPPO, and y represents the drying temperature used). Additionally, to investigate the effect of curing temperature, another five membranes were prepared by casting the reaction mixture (mole ratio of VBN to bromomethyl groups of BPPO = 1:1) onto 5 separate glass plates and evaporating the solution at different temperature (30 °C, 40 °C, 50 °C, 60 °C, 70 °C) for 48 h, respectively. These membranes are designated as BPPO-VBN-*x*-*y* (x = 1, y = 30, 40, 50, 60, 70 – where x represents the mole ratios of VBN to bromomethyl groups of BPPO, and y represents the drying temperature used), respectively. All membranes were fully converted to the Cl^- anion form via immersion in aqueous NaCl (1 mol L^{-1}) solution at room temperature for 24 h, followed by thorough washing with deionized water to remove residual ions from the ion-exchange solution.

Please cite this article in press as: Y. Liu et al., *In-situ* crosslinking of anion exchange membrane bearing unsaturated moieties for electrodialysis, Separ. Purif. Technol. (2015), http://dx.doi.org/10.1016/j.seppur.2015.10.002