Journal of Membrane Science 563 (2018) 371–379

Contents lists available at ScienceDirect

Journal of Membrane Science

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

In situ crosslinking and micro-cavity generation in fabrication of polymeric membranes for pervaporation dehydration on methanol aqueous solutions

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ARTICLE INFO

Keywords:
Pervaporation
Methanol dehydration
Poly(2,6-dimethyl-1,4-phenylene oxide)
Crosslinked membranes

ABSTRACT

Crosslinked membranes exhibiting in situ crosslinking and micro-cavity generation in membrane fabrication processes have been reported for pervaporation dehydration on methanol aqueous solutions. Meldrum's acid (MA) modified poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-MA) with various MA contents have been synthesized and well characterized with Fourier transform infrared spectroscopy and ^{1}H nuclear magnetic resonance spectroscopy. PPO-MA polymers could perform thermally-induced self-crosslinking reaction through cycloaddition reaction between ketene groups generated from MA thermolysis reaction. Meanwhile, MA thermolysis reaction evolves CO_2 and acetone molecules which contribute to generation of micro-cavities in the formed membranes. Consequently, compared to the pervaporative separation performance of pristine PPO membrane (permeation flux: 290 $g\,m^{-2}\,h^{-1}$; separation factor: 57) on a 90 wt% methanol solution at 25 °C, the crosslinked PPO-MA membrane shows a separation factor of 809 with a slight decrease in permeation flux to about 226 $g\,m^{-2}\,h^{-1}$. Based on the pervaporation separation index (PSI, the product of permeation flux and separation factor), an 11-times enhancement has been achieved.

1. Introduction

Membrane based pervaporation on liquid-liquid separation is a relatively cost- and energy-effective process and has attracted massive studies in both academics and industries [1–6]. For a binary feeding solution, the utilized membrane should demonstrate sufficient selectivity for one component (usually the minor one) and satisfied resistance (stability) to the other component (the major one). As dehydration on completely miscible water-solvent mixtures could be the mostly studied topic in pervaporation separation, stabilized hydrophilic membranes have been employed with advantages of high water sorption and selective permeation [7–11]. Membranes made with solvent-resistant and hydrophobic polymers have also been reported to exhibit relatively high membrane stability. Hydrophilic surface modification has been applied to this class of membranes to enhance their water permeation flux without seriously scarifying membrane stability and selectivity [12–15].

Based on the conventional sorption-diffusion model for membrane permeation, the membrane selectivity on the binary components in feeding solutions could be contributed from difference in molecular sizes and polarities of the individual component. This feature relates to that most membranes have been reported for separation on mixtures of water with water-miscible organic solvents in relatively large sizes, such as ethanol, isopropanol, tetrahydrofuran, and others. Due to the similar in molecular sizes and polarities, pervaporation separation of water from water-methanol mixtures is relatively difficult to be achieved and has not received as much research attention [16–27]. Most of the polymer-based membranes did not demonstrate high membrane selectivity between water and methanol. High separation factors were only recorded on some inorganic filler-stabilized membranes with feeding solutions having very low water contents. Although inorganic membranes have shown relatively high separation efficiency, they usually suffer with high cost (like reduced graphene based membrane) and complicated fabrication process [28].

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), as an aromatic glassy polymer possessing high free volume and high resistance to chemical agents, has been utilized for membranes based gas separation [29–31] and pervaporation [32–35]. PPO-based membranes exhibited methanol-selective characteristics for pervaporation separation on methanol-ethylene glycol mixtures [32–34], and showed water-selective behavior while being applied for pervaporation dehydration processes [35]. Although sufficient water selectivity has been reported to

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https://doi.org/10.1016/j.memsci.2018.06.011
Received 30 March 2018; Received in revised form 9 May 2018; Accepted 6 June 2018

water-ethanol mixtures, the separation performance of neat PPO membrane for dehydration on water-methanol solutions is not high enough [35]. PPO membrane showed a separation factor of about 32 recorded with a pervaporation dehydration test on a 90 wt% methanol aqueous solution, in which a 78 wt% of water fraction was found at the permeate side [35]. The poor water selectivity could be attributed to the high free volume of PPO and the similar molecular sizes of water and methanol. Although introduction of crosslinked structure to polymeric membranes could be an effective approach to enhance the pervaporation separation ability of the membranes [7–11], to our best knowledge no previous work has been reported on crosslinked PPO membranes exhibiting satisfied pervaporation separation ability on water/methanol mixtures. Consequently, conventional approaches for preparation of crosslinked PPO based membranes might not be effective enough for separation of water from methanol aqueous solutions. A major concern could be the crosslinked membranes, although possibly received some enhancements on membrane stability and selectivity, usually suffered with serious reduction of membrane permeability. A membrane stabilization approach which provides sufficient separation ability without seriously scarifying the permeation fluxes for the pervaporation dehydration on methanol aqueous solutions is critical.

To address the above-discussed problem, in this work a new reaction route for chemically crosslinking PPO has been explored with in situ generation of micro-cavities in the crosslinked PPO membranes, where the micro-cavities provide additional spaces for molecular permeation through the membrane so as to increase the membrane permeation fluxes. First, Meldrum's acid (MA) moieties were chemically incorporated to PPO chains, to provide thermally-induced self-crosslinking ability to PPO chains [36,37]. The crosslinking reaction was carried out with (i) thermolysis reaction of MA with generation of ketene groups and (ii) [2 + 2] cycloaddition reaction of ketene groups. MA thermolysis reaction produces acetone and CO_2 molecules as byproducts [33]. Evolves of the CO_2 and acetone molecules would generate additional micro-cavities [38] in the crosslinked PPO membranes. The micro-cavities might serve as permeation channels for molecules transporting through the membranes so as to increase the membrane permeation in separation processes. This effect has been demonstrated in our previous work on MA-modified polyimide based membranes for gas separation [39]. Consequently, in this work the structural design and preparation concept is further performed with crosslinked PPO membranes to avoid serious decreases in permeation fluxes while enhancing the membrane selectivity at high levels. While being applied to pervaporation dehydration on a 90 wt% methanol aqueous solution, neat PPO membrane shows a permeation flux of about 290 $g\,m^{-2}\,h^{-1}$ and a separation factor of about 57. The MA-modified PPO based crosslinked membrane exhibits a relatively high separation factor of about 740 with a slight decrease in permeation flux to about 240 $g\,m^{-2}\,h^{-1}$. A 10.7-times enhancement on pervaporation separation index (PSI, the product of permeation flux and separation factor) has been reported.

2. Experimental

2.1. Materials

PPO (molecular weight: about 15,000 Da) is a commercial product from Sigma-Aldrich Chemical Co. N-bromosuccinimide (NBS), 2,2′-azobis(2-methylpropionitrile) (AIBN), and 2,2,5-trimethyl-1,3-dioxane-4,6-dione (methyl Meldrum's acid, MA-M, 97%) were purchased from Sigma-Aldrich Chemical Co. and used as received. Potassium carbonate (K_2CO_3) and hydrochloride acid were products from Showa Chemical Co. Reagent grade solvents were dried with general methods prior to use.

2.2. Instrumental characterization

Fourier transform infrared (FTIR) spectra were recorded with an FTIR instrument from Perkin Elmer (Model: Spectrum Two). Powder samples were mixed with KBr powder and pelleted for measurements. Crosslinked membranes in a thickness of about 10 μm were directly applied to FTIR analysis. ^1H nuclear magnetic resonance (^1H NMR) measurements were carried out on a 500 MHz NMR instrument of VARIAN Uniytinova-500 NMR using $CDCl_3$ as a solvent. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) experiments were performed at heating rates of 10 °C min^{-1} under a nitrogen atmosphere with a DSC-Q20 and TGA-Q50 instrument from Thermal Analysis (TA) Company, respectively. Dynamic mechanical analysis (DMA) thermograms were recorded on a TA DMA-Q800 instrument at a heating rate of 5 °C min^{-1} using a tension film sample holder. The applied force and frequency was 0.0025 N and 1 Hz, respectively.

A positron annihilation lifetime spectroscopy (PALS) was utilized for measurements of the free volume pore sizes and distribution of the prepared membranes. ^{22}Na and BaF_2 were used as a positron source and a lifetime detector, respectively. A PATFIT program (purchased from Riso National Laboratory, Denmark) is utilized for data analysis and determination of the mean positron lifetime. The positron lifetime distribution was obtained with a MELT software employing a finite-term lifetime analysis and the maximum entropy method.

2.3. Preparation of brominated PPO (PPO-Br)

Bromination of PPO was carried out with a convention method using NBS as an agent [40]. A solution of PPO (4.0 g) in chlorobenzene (40 mL) was charged into a round-bottom flask. After being purged with an argon stream for 30 min, NBS (2.96 g, 16.6 mmol) and AIBN (0.166 g, 1.0 mmol) were added into the solution. The mixture was then reacted at 135 °C for 4 h under stirring. After being cooled to room temperature, the crude product was precipitated from excess methanol. The collected product was purified twice by being dissolved in tetrahydrofuran and precipitated from excess methanol. A product yield of about 92% is obtained. The degree of bromination (the ratio of $-CH_2Br/(-CH_2Br + CH_3)$ of the brominated PPO) has been adjusted with changing the feeding ratios of PPO and NBS.

2.4. Preparation of Meldrum's acid-modified PPO (PPO-MA)

PPO-Br, MA-M, and K_2CO_3 were dissolved in 200 mL of N-methyl-2-pyrrolidone (NMP). The amount of MA-M was 10 mol% excess of the $-CH_2Br$ groups of PPO-Br. MA-M and K_2CO_3 were charged in stoichiometric ratio. After being reacted at room temperature (about 25 °C) for 24 h, the solution was added to excess methanol dropwise. The precipitation was collected with filtration and purified with a dissolution-precipitation process twice using tetrahydrofuran as a solvent and methanol as a nonsolvent. A product yield of about 85% is obtained.

2.5. Preparation of crosslinked PPO membrane (CR-PPO)

A solution of PPO-MA (15 wt%) in NMP was manually coated on a glass plate using a blade with a gap of 300 μm. The sample was thermally treated in an oven at 80 °C for 1 h, 120 °C for 0.5 h, 150 °C for 0.5 h, 180 °C for 0.5 h, 210 °C for 0.5 h., and 240 °C for 1 h for removal of solvent and thermally-induced crosslinking reactions. The membrane thicknesses are of about 45–50 μm.

2.6. Pervaporation dehydration on 90 wt% methanol aqueous solution

Pervaporation dehydration on a 90 wt% methanol aqueous solution was carried out using a conventional pervaporation apparatus [41] with an effective membrane area of 7.3 cm^2 and a downstream pressure