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Synthesis of PVA-*g*-POEM graft copolymers and their use in highly permeable thin film composite membranes

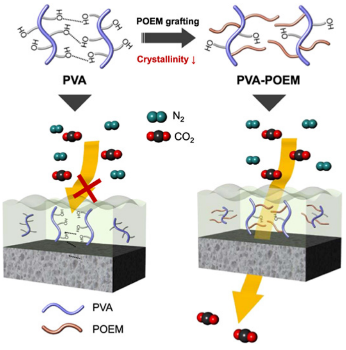
Do Hyun Kim[a], Min Su Park[a], Yeji Choi[b], Ki Bong Lee[b,*], Jong Hak Kim[a,*]

[a] *Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea*
[b] *Department of Chemical and Biological Engineering, Korea University, Anam-ro 145, Seongbuk-gu, Seoul 02841, Republic of Korea*

HIGHLIGHTS

- Graft copolymer consisting of PVA main chains and POEM side chains was synthesized.
- Crystallinity of PVA-*g*-POEM decreased gradually with POEM content.
- Composite membrane with PVA-*g*-POEM exhibited a high CO_2 permeance (347.3 GPU).
- This separation performance is close to the target area for commercialization.
- Improved performance results from the intermingled CO_2-philic POEM chains and the decrease in crystallinity.

GRAPHICAL ABSTRACT



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ABSTRACT

Polymeric gas separation membranes are a viable solution to mitigate greenhouse gas emissions directly linked to global warming due to their environment-friendly synthetic process and low cost. Poly(vinyl alcohol) (PVA) synthesized *via* non-petroleum routes is an eco-friendly material with several advantages for membrane applications such as good film-forming properties, good compatibility, and water solubility. Despite these benefits, the gas barrier property of PVA prevents its application in gas separation membranes. Therefore, we synthesized a graft copolymer consisting of PVA main chains and poly(oxyethylene methacrylate) (POEM) side chains *via* one-pot free radical polymerization and applied it to a highly CO_2 permeable thin film composite membrane. Synthesis of the PVA-*g*-POEM graft copolymer was confirmed by Fourier transform infrared and proton nuclear magnetic resonance spectroscopy. X-ray diffraction and differential scanning calorimetry analyses revealed that the crystallinity of PVA-*g*-POEM decreased gradually with increasing POEM content, with the PVA-*g*-POEM graft copolymer becoming amorphous at a POEM content of 64 wt%. The composite membrane prepared with PVA-*g*-POEM exhibited a high CO_2 permeance (347.3 GPU) and moderate selectivity (21.6 for CO_2/N_2). This performance is superior to other PVA-based membranes reported to date and is close to the target area for commercialization. The improved separation performance is due to the intermingled CO_2-philic POEM side chains and the decrease in crystallinity of PVA.

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* Corresponding authors.
E-mail addresses: kibonglee@korea.ac.kr (K.B. Lee), jonghak@yonsei.ac.kr (J.H. Kim).

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1. Introduction

Since the phenomenon of global warming became widely known in the late 20th century, a plethora of studies to reduce greenhouse gas emissions have emerged, with their number further accelerated by the 2015 Paris climate accord [1]. Among many viable solutions to reduce carbon dioxide (CO_2) emissions for the prevention of global warming, renewable energy sources for diminishing reliance on fossil fuels and gas separation technologies for reducing generated CO_2 predominate over other solutions [2–6]. As a key component of the above two fields, membrane system has drawn much attention, and it has been utilized in various fields. In the former case, membranes consisting of amorphous polymers with high ionic conductivity play a critical role in facilitating electrochemical reaction in renewable energy production and storage system such as supercapacitors [7], dye-sensitized solar cells [8] and secondary batteries [9]. In the latter case, membranes effectively separate greenhouse gas emissions from gas mixtures, mitigating global warming.

Membrane-based gas separation processes have great potential due to their simple and flexible operation, low energy consumption, and low capital cost [10–12]. In particular, polymeric membranes have attracted much attention because of their notable benefits such as low cost, versatile applications, and eco-friendly processes [13]. However, most polymer membranes suffer from distinct trade-offs involving permeability and selectivity; that is, selectivity diminishes at high permeability and vice versa, which clearly has an adverse effect on membrane performance [14]. Thus, it is imperative to address this drawback of polymer membranes by preparing highly permeable membranes with high selectivity.

Glassy polymers have been considered as a commercial source of membranes for gas separations because they have outstanding gas selectivity and excellent mechanical strength. In practice, some glassy polymers, including polysulfone, polyimides, and cellulose acetate, are used to separate gases in industrial membrane processes: polysulfone for H_2 separation [15], polyimide for CO_2/CH_4 separation [16], and cellulose acetate for CO_2 separation [17,18]. Poly(vinyl alcohol) (PVA), a representative glassy polymer, is beneficial for the preparation of polymer-based membranes due to its desirable benefits such as good film-forming properties, good compatibility with inorganic and organic compounds, environmental friendliness, non-toxicity, and its water-soluble nature [19]. However, despite these advantages, PVA has rarely been applied to gas separation technologies due to its intrinsic barrier properties in dry conditions [20]. This undesirable property is caused by its high crystallinity, which does not allow gases such as H_2, O_2, N_2, and CO_2 to penetrate through dry PVA films.

To overcome the impermeability of neat PVA, PVA membranes with high humidity have been fabricated and their properties have been measured under humidified conditions [21–23]. On the condition that the relative humidity is above 50%, the barrier properties of PVA declined and the gas permeability, especially for CO_2 and O_2, increased abruptly [20]. Saeed et al. controlled the swelling degree of PVA membranes by adjusting the solution pH and by using carbon nanotubes [21]. This membrane showed a CO_2 permeance of 0.44 GPU with a CO_2/N_2 selectivity of 60 at 1.2 bar. Additionally, various methods such as blending, cross-linking, and use of additives have been applied to fabricate PVA-based gas separation membranes. Deng et al. reported a polyvinyl amine (PVAm)/polyvinyl alcohol (PVA) blended membrane with a CO_2 permeance of 210 GPU and a CO_2/N_2 selectivity of 174 at 2 bar [24]. Francisco et al. fabricated PVA-based membranes with various amine carriers for CO_2/N_2 separation; in this case, a PVA/diethanolamine (DEA) membrane showed a high selectivity of 92 with a CO_2 permeance of 6 GPU [25]. Duan et al. prepared cross-linked PVA membranes containing poly(amidoamine) (PAMAM) dendrimers for CO_2/H_2 separation. The selectivity and CO_2 permeance of the free-standing PVA membrane with 63.3 wt% of PAMAM was 42 and 1.6 GPU, respectively, at a CO_2 partial pressure of 560 kPa [26]. Mondal et al. also studied a CO_2/N_2 separation membrane using cross-linked PVA/polyvinylpyrrolidone (PVP) blended membranes doped with a pentaethylenehexamine (PEHA) amine carrier. The membrane showed a high selectivity of 362 with a CO_2 permeance of 26.3 GPU at 2.8 atm [23]. Notwithstanding these efforts, most PVA-based membranes have showed a low CO_2 permeance and the studies were performed under humidified conditions.

Poly(ethylene oxide) (PEO) is a representative rubbery polymer that possesses polar ether groups, which are advantageous to increase CO_2 solubility due to their high affinity for CO_2 [27]. However, pristine PEO is difficult to apply to gas separation membranes because of its high crystallinity. This crystalline nature limits overall chain mobility, leading to low separation performance, and also often results in the formation of structural defects through which all gases pass easily without selectivity [28]. Moreover, the weak mechanical properties of PEO impede industrial applications; thus, modification of PEO is required. To this end, poly(oxyethylene methacrylate) (POEM), which is analogous to PEO with amorphous nature, has been suggested [29,30]. Although its lack of crystallinity is beneficial to CO_2 permeability and separation performance, POEM has poor liquid-like mechanical properties, which has hitherto hampered its application to gas separation membranes.

Here, we report the synthesis of graft copolymers consisting of PVA and POEM and their use in highly CO_2 permeable thin film composite membranes. To address the aforementioned drawbacks of PVA and POEM, the PVA-*g*-POEM graft copolymers were synthesized *via* free radical polymerization. The CO_2-philic PVA-*g*-POEM graft copolymers were characterized by Fourier transform infrared (FT-IR) spectroscopy, proton nuclear magnetic resonance (^1H NMR) spectroscopy, and thermogravimetric analysis (TGA). The crystalline behavior of the PVA-*g*-POEM graft copolymers was characterized by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Additionally, a series of PVA-*g*-POEM graft copolymers were coated on a microporous polysulfone (PSf) support to prepare thin film composite membranes. The gas permeation properties of the resultant membranes were tested at 25 °C to investigate the change in CO_2 permeation with POEM content.

2. Experimental

2.1. Materials

PVA (M_w = 85,000–124,000 g/mol, 99+ % hydrolyzed), POEM (M_n = 500 g/mol, containing 900 ppm monomethyl ether hydroquinone as an inhibitor), and ceric ammonium nitrate (CAN, ≥98.5%) were purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO, 99.9%) as a polymerization solvent was obtained from Duksan, Korea. Poly[1-(trimethylsilyl)-1-propyne] (PTMSP) was purchased from Gelest, Inc. The sponge-like PSf substrate was obtained from Toray. All materials were used as received without any purification or treatment.

2.2. Synthesis of the PVA-*g*-POEM graft copolymers

The PVA-*g*-POEM graft copolymer was synthesized *via* free radical polymerization initiated by ceric ammonium nitrate (CAN). Briefly, PVA (3 g) was dissolved in DMSO (95 mL) in a 250-mL round bottom flask equipped with a magnetic bar. The solution was heated at 60 °C with mild stirring until homogeneous. After cooling to room temperature, various POEM contents (1.3, 3, and 7 mL) were added to the solution in order to investigate the effect of the POEM content on the gas separation performance of the resultant graft copolymers. The weight ratios of PVA to POEM were approximately 7:3, 5:5, and 3:7, which are designated as PVA-POEM1, PVA-POEM2, and PVA-POEM3, respectively. The CAN solution (0.25 g) dissolved in DMSO was then added and the flask was sealed with a rubber septum. After purging with nitrogen for 30 min, the reaction was allowed to proceed at 60 °C for 20 h. The mixture was precipitated into an IPA/hexane solvent mixture (50/