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Gas permeation properties of poly(sulfone-co-ethylene glycol) membranes containing bis(phenyl)fluorene moieties

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ABSTRACT

Copolymers based on glassy and rubbery units have been developed to take advantages of both domains to enhance solubility and diffusivity. Well-tuned microstructure in copolymers has provided high gas permeability and selectivity. In this study, we report on the syntheses and characterizations of copolymers using poly(ethylene glycol) and high free volume polysulfone. Bulky and flexible bis(phenyl)fluorene moiety is introduced in polysulfone domain. Comparison between conventional bisphenol-A based polysulfone and the polysulfone in this work is made in terms of fractional free volume and gas permeation properties. In the poly(sulfone-co-ethylene glycol), the composition of sulfone/ethylene glycol results in the improvement of thermal and physical properties. Copolymers are characterized using gel permeation chromatography, thermogravimetric analysis, differential scanning calorimetry, wide angle X-ray diffraction, and gas permeation measurements.

1. Introduction

Membrane-based gas separation has been rapidly developed with large industrial demands over the last several decades [1–3]. It has become one of the major gas separation processes due to the technical advantages such as compact configuration, simple operation, energy saving and low operation cost [2]. From hydrogen recovery and olefin/paraffin separation in petrochemical industries to air separation for nitrogen generation, gas separation membrane has been widely applied mostly using polymer membranes owing to the easy fabrication and scale-up and tailoring [2,4–6]. Potential application of this technology includes CO_2 capture to reduce the release of greenhouse gases in the atmosphere [7,8]. Pre-combustion and post-combustion of CO_2 captures involving H_2/CO_2 and CO_2/N_2 separation in major, respectively, are the key issue of environmental friendly and sustainable development for the next several decades [7,9]. The increasing demand to capture enormous amount of CO_2 from power plants requests highly permeable and selective membranes with long-term sustainability and economical feasibility [7].

Permselective properties of a membrane for efficient gas separation can be improved by the membrane material development. Gas permeation through a polymer membrane is governed by the 'solution-diffusion mechanism' where both sorption on the membrane surface and diffusion through the membrane decide the molecular transport [5]. Diffusivity and solubility are dependent on not only the penetrating molecules but also the structure of a polymer membrane; diffusivity, a kinetic factor, is decided by the diameter of gas molecules and the free volume of polymer while solubility, a thermodynamic factor, is by the chemical interaction between gas molecules and the polymer [10]. Therefore, selective permeation can be achieved by tuning of diffusivity and solubility for the targeted molecules in a gas mixture. It is generally accepted that high diffusivity-selectivity results from controlling molecular structures and properties of glassy polymers such as polysulfone (PSf), polycarbonate (PC), polyimide (PI) and poly(phenylene oxide) (PPO), etc. [11–16]. Polymer chain mobility, stiffness and chain packing affect the size, shape and distribution of the free volume elements which decide gas diffusion. On the other hand, solubility-selectivity can be improved by a specific affinity of a gas molecule mostly with rubbery polymers; it is generally known that poly(ethylene glycol) (PEG) has a good CO_2 solubility owing to the polar moiety like ether group, which is induced by dipole–quadruple interaction between CO_2 penetrant molecules and polymer chains [17,18].

PEG-based polymers have been developed to exploit CO_2 separation membranes by a number of researchers. Lin et al. reported that CO_2 permeability of unmodified PEO was 13 Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg), and CO_2/N_2 and CO_2/CH_4 selectivities were 55 and 21, respectively, at 35 °C under

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4.4 atm [17]. The CO_2 selectivities versus other gases were considerably feasible for the separation of flue gas or biogas due to the high CO_2 solubility, however, CO_2 permeability did not reach to a commercially available level due to the formation of partial crystalline phase of high molecular weight PEG where gas transport through crystalline regions was considerably restricted. Therefore, copolymerization of hard-segment with PEG as a soft-segment has been highlighted to take advantage of high CO_2 selective properties of PEG to control the polymer microstructure [8,18]. Those polymers have exhibited higher CO_2 permeabilities without significant loss of selectivities. Poly(ethylene oxide-b-amide) known commercially as PEBAX® was a block copolymer comprising of a polyether (PE) block as a soft segment and a polyamide (PA) block as a hard segment [19,20]. Bondar et al. has obtained CO_2/N_2 and CO_2/H_2 selectivities as high as 9.8 and 51, respectively, where CO_2 permeability was up to 120 Barrer depending on the segment length [20]. Yoshino et al. prepared the PEG-polyimides (PIs), -polyamides (PAs), and -polyurethanes (PUs) copolymer membranes with various molecular weight of PEG [21]. The PEG-PI membrane with 60 wt% of PEG loading exhibited a CO_2 permeability of 150 Barrer and a CO_2/N_2 selectivity of 53 at 35 °C. Kim et al. prepared polysulfone-PEG copolymers for diffusivity, solubility and permeability investigation [22]. CO_2 permeability varied from 4.5 to 1.8 Barrer while CO_2/N_2 was slightly improved in the overall range of 20–30 as increasing PEG content to 30 wt%.

In this study, we have synthesized and characterized copolymer membranes comprising PEG and polysulfone (PSf) with a bulky and spacious moiety. Copolymerization of glassy and rubbery domain can have a synergetic effect to tune the microstructure of the free volume elements and to enhance sorption selectivity [19,23]. To overcome the low gas permeability, a cardo bis(phenyl)fluorene domain have been introduced in PSf domain. Bulky 3-dimensional domains such as bis(phenyl)fluorene, norbornene, triptycene and adamantane can disturb packing of linear aromatic chains, and expand the intra- and intermolecular spaces, thus provide the gas diffusive pathway through the internal microcavities, the interfacial boundary of the domain or the vacant space provided by rotation of the sp^3 carbon [24–28]. Here, bis(hydroxyphenyl)fluorene was polymerized with difluorodiphenyl sulfone to yield a high free volume polysulfone, which was compared to a common polysulfone using bisphenol-A in terms of diffusion and permeation characteristics. These packing-disruptive groups can inhibit close chain packing and increase the fractional free volume (*FFV*). Also, the bulky monomer was substituted for the different length and composition of hydroxyl-terminated PEG to investigate the effect of PEG segment on the solubility-selectivity and diffusivity-selectivity of polysulfone membrane.

2. Experimental

2.1. Materials

9, 9-bis(4-hydroxyphenyl)fluorene (HPF) was purchased from TCI Co. Ltd. (Japan) and recrystallized using benzene/ethanol co-solvents (Samchun Co. Ltd., Korea). Bisphenol-A (BPA), 4, 4′-difluoro diphenylsulfone (DFDPS), potassium carbonate (PC) and anhydrous dimethylacetamide (DMAc) were purchased from Sigma-Aldrich Co. (USA). BPA and DFDPS were recrystallized using ethanol before use. Hydroxyl-terminated oligomeric poly(ethylene glycol) (M_n=400, 2000 and 6000 g/mol) were purchased from Sigma-Aldrich Co. and Merck (Germany) and used without a further treatment.

2.2. Syntheses of PSf–PEG random copolymers

Poly(sulfone-co-ethylene glycol) (PSf–PEG) random copolymers were synthesized following the conventional polycondensation reaction of difluoro diphenylsulfone and dihydroxide monomers. 10 mmol of DFDPS were reacted with equimolar BPA to prepare a conventional polysulfone for a comparison, or with the different ratio of HPF and hydroxyl-terminated PEG as depicted in Fig. 1. The monomers were dropped into a four-neck round flask filled with DMAc, which was equipped with mechanical stirrer and Dean–Stark trap. Toluene (1/2 v/v % toluene/DMAc) was used as an azeotropic agent to accelerate polymerization by removing water as a by-product during the further reaction under nitrogen purge. The flask was heated to 110 °C to dissolve the monomers, further heated to 150 °C for 4 h [29]. It was slowly heated to 160 °C to remove toluene/water azeotrope, and finally maintained at 175 °C for 6–36 h. The reaction time was extended as increasing the molar ratio of PEG domain. The solution was cooled down to room

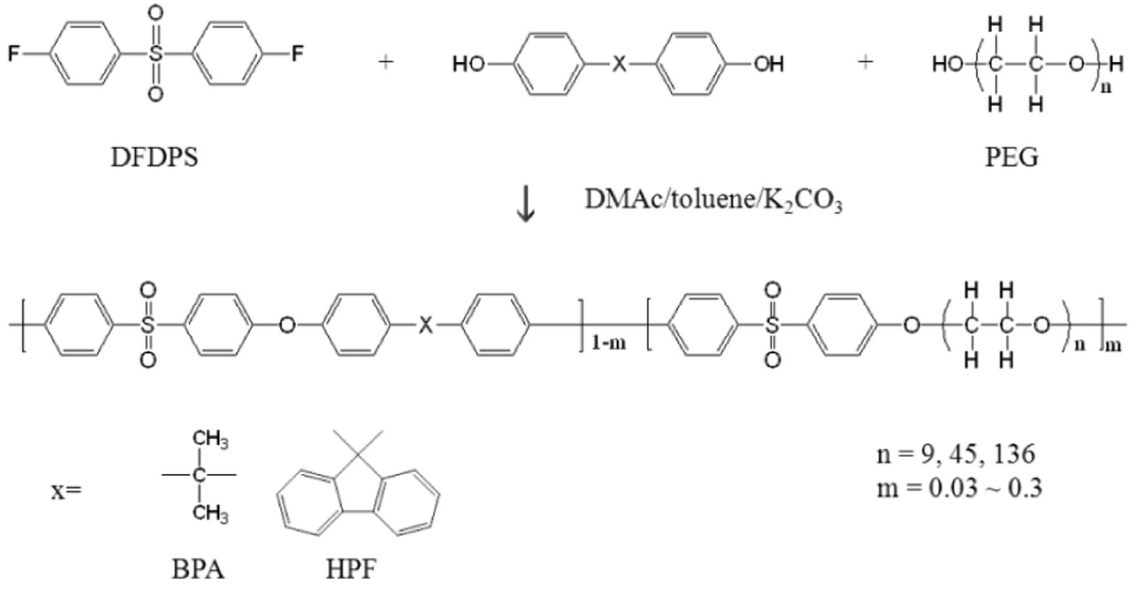

Fig. 1. Schematic diagram of copolymer preparation.