



Synthesis and characterization of polybenzimidazole membranes for gas separation with improved gas permeability: A grafting and blending approach



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ABSTRACT

Polybenzimidazoles (PBIs) are promising materials for gas separation membranes at elevated temperatures due to their excellent chemical and thermal stability and high T_g s. Their properties make them useful for gas separation of H_2 and CO_2 from pre-combustion syngas, which requires operating temperatures of 150–300 °C. PBIs have inherently low gas permeabilities, and thus the focus of this work was to improve permeability without sacrificing selectivity or mechanical properties of the membranes. Low molecular weight poly(ethylene oxide) (PEO) or poly(propylene carbonate) (PPC) were incorporated as thermally labile grafts and blends. It was believed that removing these low molecular weight sacrificial components via a controlled heat treatment would allow formation of “nanovoids” in the membrane that could increase the permeabilities. Gas transport for blends of PBI with 7 and 11 wt% of PPC and a PBI-g-PEO copolymer with 13 wt% of PEO were measured before and after heat treatment. Unlike other methods of increasing membrane permeability which results in a selectivity trade-off, heat treatment of these PBI blends and graft copolymers resulted in increases in both H_2 permeability and H_2/CO_2 selectivity. The PBI-PPC blend containing 7 wt% of PPC, after heating at 350 °C, maintained most of the toughness of the PBI homopolymer.

1. Introduction

In 2009, it was estimated that over 90% of gas separations were conducted by distillation [1]. However, distillation is an energy-intensive process, so alternative technologies that reduce energy consumption are greatly needed. One such alternative is membrane separation which has garnered much attention on the academic and industrial scale in the past three decades [2,3]. The benefits of membrane separation include low capital and operating cost, ease of operation, and low impact on the atmosphere relative to conventional gas separation technologies [1,4–6]. Separation of common gas pairs via membrane technology requires dense, non-porous membranes because of the similarity in the kinetic diameters of the gases to be separated. Some common gas pairs that are commercially separated via dense membranes include O_2/N_2 , CO_2/CH_4 , H_2/N_2 , He/air, H_2O/air and H_2/CH_4 [6].

Gas separation membrane performance is optimized by balancing the product purity of the separated gas and the throughput, or flux, of the membrane. These membrane characteristics are described using the ideal selectivity, α , and permeability, P (Barrer), of the membrane. In 1991 and 2008, Robeson published two papers denoting an empirical tradeoff relationship between gas permeability and selectivity [6–9]. It

was shown that if permeability and selectivity for a given gas pair are plotted on a log-log scale, there is an upper limit for most polymeric membranes [8]. These log-log plots have been termed “upper bound” plots. The goal for most researchers working in the field of membrane separations is to produce a membrane that has both a high selectivity and high permeability.

Most transport data reported for gas separation membranes have been measured at 25–35 °C. However, industrial operating conditions may be harsh, and the desirable membrane separation temperatures can exceed ambient conditions [4]. One example is the separation of H_2 from CO_2 in pre-combustion syngas where the ideal operating conditions could be between 150 and 300 °C [4,10,11]. If the membrane cannot withstand these elevated temperatures, then the combustion syngas must first be cooled to conduct the separation. The high temperatures and harsh conditions eliminate most polymers from consideration as viable membrane candidates. Alternatively, at the expense of energy efficiency, the syngas is cooled to commercial membrane operating temperatures, less than 100 °C, then reheated to process temperatures after the separation is performed [12].

Polybenzimidazoles (PBIs), first developed by Vogel and Marvel in 1961, are a promising class of polymers for gas separation membranes because of their excellent physical, thermal, and chemical stability

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[4,13–16]. Many PBIs have glass transition temperatures well above 400 °C and excellent thermal and mechanical stability, which makes them one of the few polymeric material candidates for elevated temperature separations (150–300 °C) [4,13,15]. To date, Celazole® (also referred to as *m*-PBI) is the only known commercial PBI used to fabricate membranes for gas separation [4,14]. However, *m*-PBI and others that are prepared from the 3,3'-diaminobenzidine monomer are poorly soluble in common organic solvents [4,14]. This creates a challenge for membrane fabrication since membranes must be processed from solution. Previous work from our group investigated the effect of incorporating a kinked sulfone linkage group into the tetraamino-functional monomer [4]. Borjigin et al. demonstrated that PBIs synthesized from 3,3'-4,4'-tetraaminodiphenylsulfone (TADPS) had better solubility in dipolar aprotic solvents than 3,3'-diaminobenzidine-based PBIs [4]. Additionally, it was shown that the polymers investigated in that work all had high glass transition temperatures (> 400 °C) with comparable gas transport properties to *m*-PBI [4].

Because PBIs have inherently low gas permeability [17], the current work focuses on improving the gas permeability of the TADPS based PBIs. We have focused on TADPS-OBA PBI that is prepared from 3,3'-4,4'-tetraaminodiphenylsulfone and 4,4'-oxybis(benzoic acid). Two methods have been investigated, a grafting and a blending approach, wherein a low molecular weight sacrificial component was introduced that could later be removed via a controlled heat treatment to create “nanovoids” in the polymer membrane. An anionic “grafting onto” method was used to graft short chain ($M_n \sim 351$ Da) poly(ethylene oxide) (PEO) onto the PBI backbone. Alternatively, low molecular weight ($M_n \sim 1,000$ Da) poly(propylene carbonate) (PPC) was blended with the PBI. The motivation for studying PBI/PPC blends was due to the established clean thermal degradation of PPC that occurs at relatively low temperatures [18].

The hypothesis of selectively degrading and evolving a portion of the polymer to improve permeability was based on previous work that included thermally degrading polyimide-poly(propylene oxide) multiphase block copolymers to achieve voids leading to low dielectric constant foams [19–24], thermal rearrangement of polyhydroxyimides to polybenzoxazole membranes with elimination of CO₂ to enhance gas permeability and selectivity [25–29], and a method for preparing a gas separation membrane with enhanced porosity by degrading and evolving the byproducts of a porogen [30]. The thermally rearranged polybenzoxazoles were originally developed to improve membrane resistance to plasticization by CO₂ during gas separation processes [25,29]. Heterocyclic polymers like polybenzoxazole membranes have shown high resistance to CO₂ plasticization; however, these polymers tend to have low solubilities in organic solvents because of their highly rigid glassy structure [25–29]. This problem was addressed by synthesizing polyimides with *ortho*-positioned functional groups (i.e. hydroxyl, acetate, pivalate groups) and then treating them at high temperatures (350–450 °C) under an inert atmosphere to convert them to the polybenzoxazoles in membrane form [25–29,31]. The linear polyhydroxyimide membranes undergo intra- and inter-molecular thermal reactions to form crosslinked polybenzoxazoles [25]. Post-rearrangement, the permeability increased substantially with only a modest decrease in selectivity depending on the gas pair [26]. The rearrangement altered the topology of the polymer, and the size of the pores and distribution could be somewhat tailored via heat treatment and the choice of functional group on the polyimide precursor [29]. However, the thermal rearrangement process had to be conducted at high temperatures, and major problems with these thermally rearranged polybenzoxazoles that have inhibited market success are their poor mechanical properties post thermal rearrangement [32–34]. Thus, we have tried to develop alternative systems that rely on thermally eliminating sacrificial components in the membranes to improve permeability without detracting from the desired mechanical properties.

2. Experimental

2.1. Materials

Monomethoxypoly(ethylene oxide) ($M_n \sim 350$ Da), anhydrous dimethylsulfoxide (DMSO), and 4,4'-oxybis(benzoic acid) were purchased from Sigma-Aldrich and used as received. *p*-Toluenesulfonyl chloride, 98%, and Eaton's reagent were purchased from Alfa Aesar and used as received. Poly(propylene carbonate) (Novomer polyol 212, $M_n \sim 1,000$ Da) was purchased from Novomer. *N,N*-Dimethylacetamide (DMAc, anhydrous, $\geq 99.8\%$), was purchased from Chem-Impex International, Inc. and used as received. Anhydrous ethyl ether was purchased from Fisher Chemical and used as received. Sodium sulfate (granular) was purchased from Mallinckrodt Pharmaceuticals and used as received. Sodium bicarbonate (powder), sodium hydroxide, hydrochloric acid (37.1%), chloroform, and tetrahydrofuran were all purchased from Spectrum Chemical and used as received.

2.2. Synthesis of Poly(ethylene oxide) Tosylate (PEO-Tos)

The synthesis of monomethoxypoly(ethylene oxide) tosylate, PEO-Tos, was adapted from Hua and Ruckenstein [28]. Monomethoxypoly(ethylene oxide) (PEO-350, 32.768 g, 93.6 mmol) and 25 mL of THF were added to a 500-mL, one-neck, round bottom flask equipped with a magnetic stirrer. NaOH (5.5988 g, 139.8 mmol) was dissolved in 30 mL of DI water in a 50-mL beaker and added to the reaction flask. The flask was placed in a salt-ice bath, and the emulsion was stirred for several min at -5 °C. Toluenesulfonyl chloride (TosCl) was added in two parts. First, TosCl (5.5029 g, 28.85 mmol) was dissolved in 30 mL of THF and added dropwise to the reaction flask via an addition funnel over 1 h. Second, TosCl (12.7501 g, 66.88 mmol) was dissolved in 25 mL of THF and added dropwise to the reaction flask over another h. Throughout the TosCl addition, the reaction solution was held below 0 °C with stirring. After complete addition of the TosCl, the reaction temperature was held for an additional 2 h below 0 °C and then allowed to warm to room temperature and proceed for 18 h. The reaction was stopped by adding 100 mL of diethyl ether to the flask to form two layers. The water layer was extracted 3X with 30 mL of diethyl ether each time. The diethyl ether layer was washed with water until the pH was neutral (pH = 7). The diethyl ether layer was passed through a column containing anhydrous Na₂SO₄ (30 g) until a clear solution was obtained. The excess diethyl ether was removed by rotavap, and a clear liquid was obtained. The yield was 70%. ¹H NMR was used to quantify tosylation and confirm the molecular weight of the PEO segment.

2.3. Synthesis of tetraaminodiphenylsulfone-oxybis(benzoic acid) polybenzimidazole (TADPS-OBA)

The synthesis of tetraaminodiphenylsulfone, TADPS, monomer was previously reported by Borjigin and co-workers [4]. The TADPS-OBA polymer was synthesized by step-growth polymerization of TADPS with 4,4'-oxybis(benzoic acid), OBA, in Eaton's reagent which acted as both the condensing agent and solvent. The polymerization procedure was adapted from the work of Borjigin [4]. TADPS (13.191 g, 44.2 mmol), OBA (11.288 g, 43.7 mmol), and Eaton's reagent (122 mL) were added to a 500-mL, three-neck, round bottom flask equipped with a nitrogen inlet, mechanical stirrer, and condenser that was placed in a thermocouple-regulated oil bath. The oil bath was set to 145 °C, and the reaction solution was refluxed and stirred under nitrogen for at least 24 h. The hot, viscous solution was precipitated by pouring it directly into a beaker containing 3 L of deionized (DI) water. Solid NaHCO₃ was added slowly to neutralize the polymer-water mixture to pH = 7. The polymer was filtered and added to fresh DI water and boiled for 2 h to remove any residual Eaton's reagent. The polymer was filtered, boiled, and then filtered one more time. The polymer was dried at 150 °C in the vacuum oven for 24 h. Yield was 90%. ¹H NMR was used to confirm the TADPS-

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