Hydrogen Purification Using Advanced Polymeric Membranes

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Objectives

Acid gases like CO_2 are major impurities in gas streams containing hydrogen, and membrane-based separation may be utilized to remove these acid gases. One strategy for acid gas removal from mixtures with light gases takes advantage of the affinity of acid gases for polar groups, such as ether oxygens incorporated within polymeric membranes. Our research on cross-linked poly(ethylene oxide) revealed good separation performance in removing CO_2 from CO_2/H_2 mixtures and indicated possible further performance improvement by engineering the molecular structure of such materials. To achieve this goal, we are pursuing a fundamental study of the effect of various structure modification strategies on the transport properties of cross-linked poly(ethylene oxide). In addition, we are exploring other materials with novel separation properties that may contribute to our understanding in this field, such as membranes containing nanoparticles.

Technical Barriers

Our initial research has shown the viability of cross-linked poly(ethylene oxide) for CO_2 removal from H_2 and suggests that fundamental understanding of the relationship between network structure, polymer chemical composition and transport properties may yield even better materials.

Abstract

Rubbery cross-linked poly(ethylene oxide) facilitates separation of CO_2 from mixtures with light gases and exhibits favorable CO_2/H_2 separation properties. Because the separation is largely due to an affinity between CO_2 and polar groups in the membrane, unlike conventional polymers, plasticization of the material by CO_2 improves separation properties, especially at lower temperatures and high partial pressures of CO_2. In addition, we have explored the separation of other polar and condensable gases from mixtures with lighter gases.

Progress Report

Our progress in cross-linked poly(ethylene oxide) (XLPEO) for CO_2/H_2 separation is summarized in a recent paper [1]. Harnessing CO_2's affinity for polar groups within the polymer membrane underlies CO_2 removal using rubbery XLPEO [2], which has higher gas permeability than conventional membranes and exhibits weak size-sieving ability [3]. In these materials, CO_2 is preferentially permeated over H_2. Additionally, plasticization actually improves CO_2/H_2 separation by further reducing size-sieving ability and increasing permeability [1].

XLPEO is formed by photopolymerization of poly(ethylene glycol) diacrylate (PEGDA) [4]. Cross-linking eliminates crystallization of EO units that otherwise occurs in high molecular weight poly(ethylene oxide) (PEO), leading to reduced permeability [3] and reduced CO_2/H_2 selectivity [1, 2, 5]. In addition, PEGDA can be copolymerized with mono-functionalized PEO-bearing acrylates, such as poly(ethylene glycol) acrylate (PEGA) [4] or poly(ethylene glycol) methyl ether acrylate (PEGMEA) [1, 4]. While gas solubility in the membrane does not change with copolymer composition [6], diffusivity through the membrane changes strongly with polymer composition [7]. For instance, increasing PEGMEA content in PEGDA copolymer increases the fractional free volume (FFV) [8, 9] and, in turn, the CO_2 permeability and CO_2/H_2 selectivity.

Plasticization effects are demonstrated through pure and mixed-gas studies of the PEGDA/PEGMEA copolymers, where CO_2 and H_2 permeability increases are observed with increasing CO_2 partial pressure [1]. This effect is more significant at lower temperatures due to increased CO_2 condensability, leading to higher CO_2 sorption in the polymer [1, 6]. At low temperature and high CO_2 partial pressure, the increase in CO_2/H_2 selectivity is accompanied by high CO_2 permeability [1], which takes the performance above the separation 'upper bound' [1]. Additional mixed-gas studies explored the removal of CO_2 from other gases (such as CH_4 [10] and C_2H_6 [11]) using XLPEO, with similarly favorable performance. Plasticization effects are also observed when other polar impurities, such as H_2O and H_2S, are introduced [1].

Similar separation behavior was observed in cross-linked poly(propylene oxide) (XLPPO) made from acrylate analogues of poly(propylene glycol) [12]. However, although XLPPO in general displays slightly higher CO_2 permeability than pure cross-linked PEGDA, it has lower CO_2/H_2 selectivity than the XLPEO series, despite having higher FFV [12].

Our work on the gas transport behavior of nanocomposites is based on polymers such as 1,2-polybutadiene (PB). Neutral TiO_2 nanoparticles and basic MgO nanoparticles have been used to increase light gas solubility and permeability in heterogeneous membranes [13-16]. For instance, PB containing 27 vol.% TiO_2 has CO_2 permeability roughly 3 times higher than that of the unfilled polymer, while its CO_2/H_2 selectivity remains approximately equivalent to the unfilled polymer [14]; similar behavior was observed when MgO nanoparticles were added to PB [15]. Both the permeability and selectivity behavior in nanocomposite PB are due partly to higher light gas solubility in the nanocomposites than in unfilled PB.

Poly(1-trimethylsilyl-1-propyne) (PTMSP) is exceptional among glassy polymers for its very high free volume and gas permeability. Although its outstanding vapor/gas selectivity favors the transport of higher hydrocarbons from mixtures with H_2 and CH_4 [17], PTMSP is easily dissolved by many organic solvents. To improve its chemical stability, PTMSP can be cross-linked using bis-azides, but this method reduces gas diffusivity and permeability [17]. Adding nanoparticles such as TiO_2 and fumed silica to PTMSP increases its gas permeability due to an increase in diffusivity [13].

Future Work

Our future studies on XLPEO will focus on the effects of further structural modifications on transport properties. Specifically, the monomer EO length can be varied to modify XLPEO's cross-link density (which affects chain dynamics [8]), polar content, or crystallinity. Given the significant difference in transport properties between PEGDA copolymerized with PEGA and with PEGMEA [7], another way to modify XLPEO structure is to change the terminal end-group of the monoacrylate copolymer.

We are also exploring incorporation of nanoparticles into XLPEO to further improve separation performance. As polymer-particle interaction is a significant determinant of the resulting membrane properties, it is important to understand this phenomenon to control the resulting properties.

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