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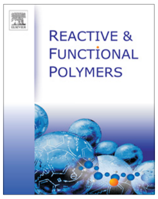

Review

Targeted gas separations through polymer membrane functionalization

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ABSTRACT

Gas separation membranes have been studied for several decades and are starting to find commercial acceptance. This review will focus on polymer functionalization to improve gas separation performance, namely, permeability, permselectivity, or both. The review will cover both "diffusivity controlled" and "solubility controlled" functionalization strategies; each strategy refers to the different mode of gas transport through the membrane. Diffusivity controlled functionalization strategies mainly involve control over free volume elements in amorphous polymers via promotion or inhibition of chain packing through functional groups. As such, the effects of this functionalization are typically confined to the well-known selectivity/permeability tradeoff. Solubility controlled modification strategies utilize functional groups that have strong chemical interactions with some of the penetrant molecules and offers an enhanced solution-diffusion or a non-solution-diffusion permeation pathway. This functionalization can potentially exceed the Robeson upper bound, but is often challenged by impurities and deactivation of the chemical functionality.

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1. Introduction

A combination of the increased prevalence of natural gas, rising CO_2 emissions, and a focus on environmentally-responsible industrial growth has created a growing demand for new, sustainable, energy-efficient technologies. Gas separation membranes are receiving increased attention due to the immense amount of energy and concomitant CO_2 emissions associated with current industrial gas separation technologies. In fact, these status-quo, thermal-based separations consume approximately 5–10% of the United States' primary energy supply [1]. One of the main advantages of gas separation membranes relative to current thermal separations lies in the membrane's ability to perform the separation near the thermodynamic limit of demixing. Another key advantage of membrane technology is the ability to package functional surface area into compact devices, which minimizes the chemical potential driving force necessary to provide the desired gas productivity [2]. The low cost of processing polymers into membranes and assembling them into high surface area to volume modules has made polymeric membranes a promising candidate for industrial gas separation applications.

Polymeric gas separation membranes have already found some use in industrial processes, primarily for small nitrogen generation requirements, hydrogen purification, and offshore natural gas purification. A handful of polymers have been used commercially including: cellulose acetate, polysulfone, polyimides, polyaramides, tetrabromo polycarbonate, polydimethlysiloxane, and polyphenylene oxide [3]. While effective, many of the commercially deployed membranes suffer from low selectivities, low flux, and other issues such as plasticization. There is a significant research effort underway to design and develop new polymeric membranes that can push the limits of productivity and efficiency while maintaining stability in aggressive feed conditions.

This article provides an overview of the state-of-the-art functionalized polymeric membranes for gas separations. We broadly define functionalized polymers as any base polymer with additional chemical groups that impart a change in either the physical or chemical characteristics, with an emphasis on improving the performance for a targeted gas separation application. Functionalization of polymers overcomes some of the inherent limitations of the base polymer while opening up the possibility to combine different desired properties to engineer high performance materials. We have split our definition of functionalization into two groups that seek to manipulate gas permeation by contrasting means: (i) "diffusivity controlled" functionalization that mainly seeks to control chain packing in glassy polymers and (ii) "solubility controlled" functionalization that seeks to enhance the desired gas solubility. We limit our discussion to the scheme shown in Fig. 1 for glassy polymers while excluding other more exotic classes of gas separation membranes fabricated from stimuli responsive, conducting, interpenetrating, and blended polymers. Finally, we will provide some perspectives and future directions for gas separation membranes.

2. Background

Membranes utilized for gas separations differ from other ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membranes for a variety of reasons. In these latter separations, the species being separated have size differences on the order of nanometers or larger. Moreover, the fast species in UF, NF, and RO are often substantially smaller—more than three times—than the rejected or slow species. Gas separations are much more difficult to achieve due to less pronounced size differences between penetrating molecules—several tenths of an Ångstrom difference are common. Table 1 lists the kinetic diameters of several commonly separated light gases. For instance, the separation of O_2 and N_2 from air is based on a size difference of 0.18 Å between the two molecules. Such a narrow size separation is challenging, especially from a materials development standpoint; even nanometer sized defects could compromise a membrane's performance. Defect-free membranes are essential to enable effective separation units.

Membrane performance is described in terms of specific gas permeability and selectivity and these metrics are commonly used to compare different membranes. The flux through dense polymers follows Fick's first law of diffusion where penetrant gases move through the membrane down a chemical potential gradient that

Table 1
Kinetic diameters and boiling points of industrially relevant gases.

Gas	He	H_2	O_2	N_2	CO_2	CH_4
Kinetic Diameter (Å)	2.60	2.89	3.46	3.64	3.30	3.80
Boiling point (K)	4.23	20.37	90.25	77.36	216.6	111.66

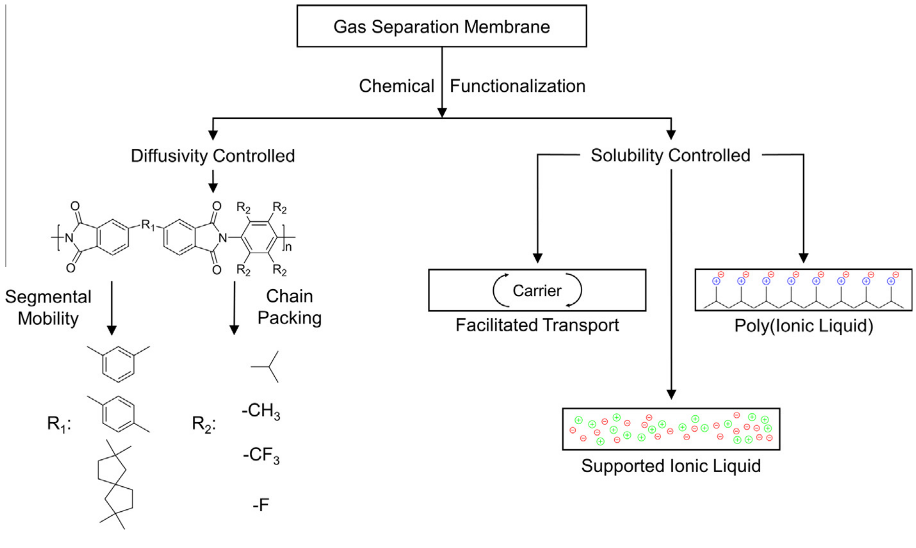

Fig. 1. The primary dichotomy of polymer functionalization discussed in this review.

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