Post-Synthetic Chemical and Morphological Modifications of Polymer Membranes for Gas Separations

by

Taigyu Joo

Abstract

Microporous polymers have rigid backbone structures or bulky monomer units that inhibit efficient packing of polymer segments, resulting in high free volume materials with good diffusion selectivity when processed into films. As a result of these characteristics, these materials have become potential candidates for developing next-generation gas separation membrane materials. Over the past two decades, this potential has sparked extensive membrane material development research, resulting in a library of microporous polymers. However, despite these significant advancements in developing novel polymer structures, gas separation membrane technology has yet to achieve the performance levels and operational stability required to replace traditional gas separation methods like cryogenic distillation and amine absorption processes. This gap underscores the need for continued research and development in microporous polymer membranes to fully realize their potential in gas separation applications.

Free volume manipulation (FVM) is an innovative post-synthetic modification approach designed to address the permeability–selectivity tradeoff of polymer membranes. This method involves protection/deprotection chemistries of labile functional groups, such as a tert-butoxycarbonyl group (tBOC), to modify the physical packing structures, and hence, transport properties of the modified membranes. This thesis combines rational design principles with synthetic chemistry and materials characterization to further develop FVM and incorporate *in situ* thermal oxidative crosslinks. The developed FVM approach is demonstrated through its application to amine-functionalized PIM-1 and microporous poly(aryl ether) (PAE) polymers. A comprehensive analysis of transport properties, using various permeation and sorption experiments, reveals that FVM is an effective strategy for enhancing gas separation performance and stability of microporous polymer membranes. Furthermore, the chemistries developed from the FVM approach are used to systematically understand and provide valuable insights into the role of free volume, chemical functionality, and crosslinking in physical aging behavior of microporous membranes. This thesis primarily focuses on developing structure–property–performance relationships of FVM-modified membranes, offering strategic directions for the future development of high-performing microporous membranes.

Thesis Supervisor:
Zachary P. Smith
Robert N. Noyce Career Development Chair and Professor of Chemical Engineering