Functionalized Hollow Fibers Spun from Microporous Organic Polymers (MOPs) for Membrane-Based Separations and Carbon Capture

by

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Submitted to the Department of Chemical Engineering
on March 19th, 2026 in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Abstract

Separations are an essential part of the chemical industry and are dominated by energy-intensive techniques, which can account for up to 15% of global industrial energy consumption. Membranes have existed as a possible supplement or alternative to traditional thermal-based separations. Despite this, polymer membranes see limited use in gas separation applications because of their inherent permeability–selectivity trade-off. To overcome this performance limitation, new polymeric membrane materials have been developed that incorporate rigid and contorted ladder structures into their backbones, resulting in a high free volume. An early example of a polymer of intrinsic microporosity, PIM-1, has been heavily investigated since it was first reported in the literature in 2004. Due to the promising separation performance of PIMs, other microporous organic polymers (MOPs) have been developed. This inspired a general technique for designing membrane materials that instead use free-volume generating monomers such as triptycene and spirobifluorene (SBF) to create microporous poly(arylene ether) (PAEs). Typically, studies have involved fundamental characterization and performance testing on flat sheet membranes. Unfortunately, a major limitation of this configuration is its lack of scalability, which limits membrane deployment in industrial settings. Along these lines, polymer hollow fibers represent a desirable form factor for industrial gas separation membranes given their substantially higher surface-area-to-volume ratios. This thesis seeks to investigate the post-synthetic modification of PIM-1 hollow fibers via amine functionalization into PIM-NH_2. This serves as the first in-depth physical aging study on hollow fibers spun from PIM-1 and PIM-NH_2 by monitoring their gas permeation properties over 2150 hours and comparing their aging behavior to dense films and thin film composites. Furthermore, the spinning of the microporous PAE, SBF-TBTrip-I, into the hollow fiber membrane configuration was investigated, representing the first time this form factor has been reported on this class of SBF-based PAEs and among the first times a microporous polymer has been spun after PIM-1. Lastly, amine functional variants of PIM-1 were further investigated along with the addition of zeolites under high temperature activation to manufacture microporous hollow fiber sorbents for the removal of CO_2 from flue gas streams.

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