

Free Volume Manipulation Techniques of Polymer Membranes for Gas Separations

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Gas separations are ubiquitous in today's industries and society, playing a role in many key applications such as oxygen generation for medical procedures and natural gas separations for power generation and petrochemicals. In the United States, separation processes consume about 16 quadrillion BTU of energy per year, with nearly half of that energy consumption coming from energy-intensive and thermally-driven processes such as distillation. Using non-thermally driven processes, such as polymer membranes, for gas separations could reduce energy costs by up to 90% and save the United States over 4 billion USD per year.

Recently, polymers of intrinsic microporosity (PIMs) have shown promise as a platform for energy-efficient gas separations due to their rigid and contorted chemical structures, which increase the amount of free volume and gas throughput. The combination of high permeability and good selectivity exhibited by many PIMs have placed them near or above the Robeson upper bound, a standard metric used to compare polymer membrane performance. However, free volume that is generated from PIMs is done in a "bottom-up" manner where the rigid and contorted chains cause free volume formation. The size and distribution of free volume elements, therefore, are not selectively controlled.

In this thesis, alternative methods to free volume generation are explored. The first method involves a "top-down" approach, where thermally labile functional groups are attached to a polymer backbone. After film formation, the functional groups are thermally removed well below the glass transition temperature to systematically template free volume elements of a desired size and distribution within the polymer matrix. The effect of various thermal treatments on both the packing structure and gas transport properties was analyzed, and the results suggest that polymer chain mobility occurring below glass transition temperatures can disrupt the templated free volumes. Therefore, more robust polymer systems that can preserve the free volume architecture after thermal treatment from this approach are needed.

The second method is a "bottom-up" approach similar to that used by PIMs, but with a new chemical structure consisting of a flexible polymer backbone and rigid side chains that form a "bottlebrush"-like structure. The polymers were generated via ring-opening metathesis polymerization (ROMP), and their gas transport properties were examined in ideal and realistic industrial conditions. These polymers, referred to as ROMP polymers, showed excellent gas transport properties, as well as unprecedented plasticization and physical aging resistance. The excellent stability exhibited by ROMP polymers was attributed to the rigid side chains. The effect of side-chain length on the gas transport properties of a methoxy-functionalized ROMP (OMe-ROMP) was also studied. In this case, increasing side-chain length led to increased free volume and plasticization resistance. Lastly, to further probe their plasticization resistance, sorption measurements and mixed-gas tests using realistic industrial conditions were conducted on OMe-ROMP samples with different side-chain lengths. Overall, this thesis focuses on alternative methods to free volume generation in polymer membranes that can be used for energy-efficient gas separations.