Elucidating the Role of Fluorine on Gas Transport Through Fluorinated Polymer Membranes

By Albert Wu

Research Advisor: Prof. Zachary P. Smith

Gas separations are essential to obtain high purity gases used for a variety of applications, such as pure oxygen for medical procedures or pure olefins and paraffins as building blocks for plastics. Within the United States, the separations industry consumes 16 quadrillion BTU of energy per year, nearly half of which comes from energy-intensive, thermally driven separations such as distillation. Development of non-thermal methods of separation, such as membrane-based separations, is estimated to reduce energy costs by 90%, eliminate 100 million tons of CO_2 emissions, and save $4 billion in energy costs per year in the United States alone. To date, polymer membranes occupy a significant market share for a variety of industrial separations, such as hydrogen recovery, nitrogen generation, natural gas treatment, and vapor recovery. Continued development of structure–property–performance relationships for gas transport through polymer membranes is necessary to expand into new industrial applications.

Fully fluorinated polymers (*i.e.*, perfluoropolymers) are a unique class of materials that have shown exceptional separation performance due to their anomalous thermodynamic partitioning compared to typical hydrocarbon polymers. However, the mechanism by which fluorine affects the gas sorption behavior in polymers is not well-understood and only a limited amount of structure–property–performance relationships have been established. Therefore, the goal of this dissertation is to elucidate the role of fluorine on gas transport, with a particular emphasis on gas sorption. The aims of this dissertation are to quantify the effect of fluorination on gas separation performance, develop relevant structure–property–performance relationships related to fluorine, and identify specific mechanisms by which fluorination affects gas sorption. Through the systematic synthesis of hydrocarbon, partially fluorinated, and fully fluorinated polymers, changes in separation performance and sorption behavior were analyzed in the context of various transport and sorption models, such as upper bound theory, the Brandt model, the dual-mode sorption model, and the non-equilibrium lattice fluid model. The final aim of this dissertation is to examine and update group contribution theory to accommodate modern polymer structures and provide an accessible procedural framework for consistent and accurate fractional free volume calculation.