Screening polymers of intrinsic microporosity: membrane performance predictions for diverse organic species

Dylan M. Anstine [a,b], Alexander G. Demidov [b,c], Coray M. Colina [a,b,c]

[a] Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611 United States of America
[b] George and Josephine Butler Polymer Research Laboratory, University of Florida, Gainesville, FL 32611 United States of America
[c] Department of Chemistry, University of Florida, Gainesville, FL 32611 United States of America

Considering the annual volume of industrially performed chemical separations, which accounts for approximately 10-15 % of global energy use, the development of high-performance polymeric membranes that enable sorption-based separation techniques is of essential importance. Among the most promising candidate polymers examined are polymers of intrinsic microporosity (PIMs), which are defined by a contorted ladder-like backbone that result in inefficient packing of chains that yields a naturally occurring microporous structure. We have shown that it is possible to generate model PIMs *in silico*, which display characteristics that compare well with experimental measurements (wide-angle x-ray scattering (WAXS), bulk density, transport properties, and elastic modulus). Upon validation of the modeling approach, the PIM samples have been used in Monte Carlo (MC) simulations of gas adsorption .

While predictions made from MC simulations are in excellent agreement with experimental measurements at low-pressures, values obtained at higher pressures display significant under prediction. This is commonly attributed to the use of fixed-framework MC simulations not accounting for sorption-induced plasticization/swelling, which is defined by polymer chain rearrangement in response to the adsorbate species and an associated volume expansion. To account for this phenomenon, this work utilized a combined MC and molecular dynamics (MD) approach to provide higher accuracy predictions of the full adsorption isotherm. Thousands of MC/MD simulations are performed to predict PIM membrane performance for diverse adsorbate species: common gases (*e.g.* CH_4, CO_2), paraffin/olefin (*e.g.* C_3H_6, C_3H_8), and polar molecules (*e.g.* C_3H_6O, CH_4S). The effectiveness of the method is demonstrated by comparing membrane performance predictions (*e.g.* gas loading or selectivity) for PIM systems from the MC/MD approach to those observed experimentally. This MC/MD approach is among the first of its kind applied to adsorption predictions in polymeric membranes and provides a marked increase in accuracy of simulations performed at relatively high pressures.