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Elucidating the Anomalous Solubility Behavior of Small Molecules in Fluoropolymers
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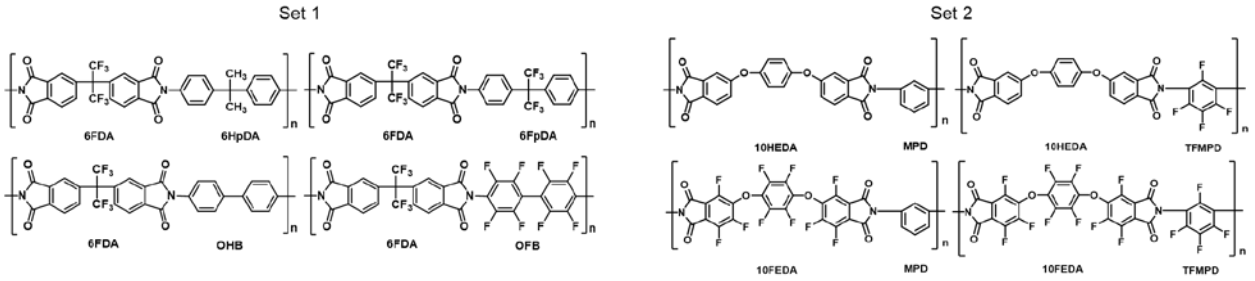
In the past year, we have made excellent progress on our ACS PRF project by investigating the anomalous solubility behavior through both an experimental and theoretical approach. Experimentally, we have been synthesizing structural analogues of high-performing polyimides that contain either C-H or C-F bonds. These modifications allow us to evaluated how varying degrees of fluorination influence transport of small molecules through these polymers, including an investigation of permeation, sorption, and mixed-gas studies. We have been comparing our findings to a variety of theoretical expectations and mathematical models, including (1) simplistic comparisons of trends expected for other high performance polymers of different structures, (2) thermodynamic sorption models such as the non-equilibrium lattice fluid (NELF) model, and (3) atomistic level calculations using molecular dynamics to evaluate sorption and diffusion.

Experimentally, we have succeeded in synthesizing 2 sets of 4 polyimides, each consisting of structural analogues with varying degrees of fluorination. The structures are shown below. We are currently finishing the transport characterization for set 1 and plan to move on to set 2 in the near future.



We have also made significant progress on the theoretical front, specifically with regard to the high-level performance trends and molecular dynamics simulations. Through an analysis comparing solubility trends of perfluorinated polymers to conventional hydrocarbon polymers, we were able to decouple the effects of sorption and diffusion on overall separation performance by accounting for differences in chemical composition. Extending this analysis to a large database of polymer separation performance, we were able to establish a new upper bound, the perfluoropolymer upper bound (see Publication below), which provides a more accurate description of the separation performance of perfluoropolymers. We have also started developing the initial framework for molecular dynamics simulations to obtain computational sorption isotherms in a timely manner. We are planning to continue our work in this direction to compare simulated versus experimental isotherms – in this way, we will be able to study the anomalous sorption effects of our fluorinated polymers at an atomistic level.

During the reporting period, we have published a paper in AIChE Journal (details below) and presented our findings at the North American Membrane Society Annual Conference in May 2019.

Publication: Wu, A.X., Drayton, J.D., Smith, Z.P., "The perfluoropolymer upper bound", AIChE Journal, 2019;e16700.