Investigating Structure-Property Relationships of Fluorinated Polymer Membranes Concerning Plasticization Resistance

by

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Abstract

As the push for more sustainable industry processes carries onward, membranes have been identified as a promising technology for performing chemical separations cleanly and efficiently. The application space for membranes is constantly evolving, and contemporary innovations such as composite mixed-matrix membranes or highly-contorted backbone structures have pushed the upper bound of membrane performance. However, current membrane technology is not robust enough to serve industry ubiquitously, as there are fundamental material realities which limit their current capabilities. A major issue which causes much pain for industrial use is plasticization, in which polymer chains will become mobilized by the introduction of a condensable penetrant into the polymer matrix, becoming "lubricated." This phenomenon has had implications in polymer material science for many years; in the context of membrane separations, it causes a debilitating drop in selectivity of the separation because these mobilized polymer chains lose their size-sieving properties. Plasticization in membranes is a critical issue to address because high-profile contemporary separations involve condensable penetrants such as carbon dioxide, ethane, ethylene, propane, and propylene, all cornerstones of the energy and materials industries. Another important class of chemicals are refrigerants, highly common types of which being chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs). Recovery and reclamation of fluorinated gases is becoming increasingly urgent as the US moves to phase down high global warming potential refrigerants spurred on by the American Innovation and Manufacturing Act. Unfortunately, these separations are accomplished primarily via distillation today, and studies in the open literature on separating fluorinated gases are exceedingly rare. This thesis investigates the effect of polymer fluorination in two critical scenarios: first, by determining whether fluorine moieties can be leveraged to reduce the deleterious effects of plasticization by carbon dioxide; secondly, by investigating the influence of backbone fluorine on the mass transport properties of fluorinated refrigerant penetrants. Membrane transport properties were evaluated by a combination of in-depth permeability, sorption, and diffusion experiments. These tests were further supplemented by multi-temperature and multi-pressure studies in order to evaluate transport properties and membrane performance at a variety of testing conditions. By conducting a thorough

transport property analysis on a systematically designed fluoropolymer material set, this thesis serves to both provide insight into how the often little-understood phenomenon of plasticization affects glassy polymers, as well as to provide material design strategies in order to mitigate plasticization in future cutting-edge membrane materials so that they may be maximally effective in applications at risk of plasticizing conditions. This thesis then concludes by providing an outlook on the direction of plasticization research and by providing several avenues for future studies with good potential to be worthwhile research.

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