Designing Selective Membranes from the Ground-Up: A Polymer Scientist's Playground

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ABSTRACT

Controllable molecular transport through polymeric membranes constitutes an important consideration in the design of functional soft materials intended to remove undesirable component species from gas or liquid mixtures. Of particular interest here are membranes capable of selectively separating gases such as CO_2, an acid gas and combustion diluent largely responsible for global climate change, from other commercially relevant gases (e.g., N_2, O_2, H_2, or CH_4). While gas separation routinely relies on the use of glassy polymers (with relatively low intrinsic free volume) to sieve gases on the basis of molecular size, alternative approaches combine glassy polymer matrices with (non)porous nanoscale additives to achieve desired performance through the use of mixed matrix membranes (MMMs). Since permeation in the limit of Fickian diffusion is generally described by a solution-diffusion mechanism, gas permeation that is not limited by molecular transport (diffusivity) can likewise be controlled by thermodynamic means (solubility). Such membranes are referred to as "reverse-selective" since they can promote the permeation of larger molecules relative to smaller molecules due to chemical affinity with the polymer membrane. Examples of solubility-driven gas-separation membranes are discussed here with specific regard to CO_2 removal. Although most commercial membrane modules employ homopolymers or polymer blends, we likewise explore the possibility of using nanostructured polymers, such as block copolymers, for the purpose of controlling molecular transport during filtration. This consideration leads to the under-investigated use of polymer "mesoblends" and block ionomers. By combining the physical properties associated with diffusion through heterogeneous media and the chemical properties afforded by targeted synthesis/modification, next-generation polymer filtration membranes exhibiting high gas permeabilities and selectivities can yield new design paradigms for functional materials with superior properties from the ground-up.