

## FUNCTIONALIZED POLYMERS OF INTRINSIC MICROPOROSITY FOR HIGHLY ENERGY-INTENSIVE GAS SEPARATIONS

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Membrane-based gas separation is a rapidly emerging technology that has been established in the purification of air and hydrogen streams and is showing an increasingly larger role in natural gas sweetening and vapor/gas separations. One strategy actively pursued to generate polymers with combinations of high permeability and high selectivity is the introduction of microporosity (pores  $< 20 \text{ \AA}$ ) in the polymer matrix. It has been shown that rigid ladder-type chains comprising fused rings joined by sites of contortion pack inefficiently in the solid state to produce polymers of intrinsic microporosity (PIMs). Recently, a successful integration of monomers contorted by spirobisindane, ethanoanthracene, Tröger's base and triptycene moieties into polyimide structures has also generated highly permeable intrinsically microporous polyimides (PIM-PIs). Some of these PIM-PIs have shown significantly enhanced performance for  $\text{O}_2/\text{N}_2$ ,  $\text{H}_2/\text{N}_2$  and  $\text{H}_2/\text{CH}_4$  separations with properties defining the most recent 2015 permeability/selectivity upper bounds.

Here, we will discuss several series of novel PIM-PIs and ladder PIMs based on rigid and bicyclic moieties, which are solution processable to form mechanically robust films with high internal surface areas (up to  $1100 \text{ m}^2/\text{g}$ ). Gas permeation and physisorption data indicate the development of an ultramicroporous structure that is tunable for different gas separation applications. Specific emphasis will be placed on the potential use of hydroxyl- and carboxyl-functionalized PIMs for highly-energy demanding applications for natural gas treatment and olefin/paraffin separation.