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Physical Aging and Mixed-Gas Transport Properties of Microporous Polymers for Gas Separation Applications

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Membrane-based gas separation has been practiced as an economically viable separation technology during the past 30 years. Progress in this field resulted from significant improvements in materials science, development of high-performance membranes, and optimization in process design. Important applications include: a) nitrogen production from air, b) hydrogen recovery in petrochemical operations, c) removal of acid gases from natural gas, and d) recovery of condensable, high-value organic vapors from a variety of waste-gas streams. This presentation will focus on novel, intrinsically microporous glassy polymers, which may find applications in a wide variety of commercially important applications. The first generation of microporous glassy polymers was based on ultra-high free-volume glassy polyacetylene-based polymers, which exhibit the highest organic vapor/permanent gas selectivties coupled with the highest organic vapor permeabilities of all known polymers. However, a significant disadvantage of this class of materials is their inherent poor physical and chemical instability when operated under industrial conditions. Recently, Budd et al. reported that a new class of rigid, glassy ladder polymers, so called 'polymers with intrinsic microporosity' (PIM) may offer advantages over microporous polyacetylene-based polymers for membrane separations. This presentation will compare the transport properties of these two classes of microporous polymers for membrane separations. This study includes, for the first time, long-term gas permeability data of PIM-based materials. We studied the pure-gas permeation properties of PIM for over one year and the polymer's properties are exceptional. The initial oxygen permeability dropped from 1,535 Barrer to 700 Barrer after one year of operation. On the other hand, the initial oxygen/nitrogen selectivity increased from 3.7 to 5.2. These are unmatched permeation properties for air separation, which lie far beyond the typical Robeson permeability/selectivity trade-off. In addition, PIM is stable in hydrocarbon environment with very high mixed-gas selectivity and permeability. For example, PIM-1 has a mixed- gas n-butane/hydrogen selectivity of 30-50 depending on the feed composition. In summary, microporous glassy polymers exhibit properties, which are unmatched

by conventional polymers and provide a window to broaden possible applications for membranes used for gas separations.