



## Editorial Note

## Polymeric Gas Separation Membranes: What Makes them Industrially more Attractive?

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Polymeric membrane-based gas separation has found many attractive applications in air separation (to obtain technical grade nitrogen or oxygen enriched air), hydrogen separation, natural gas sweetening, treatment of flue gas, etc. The main advantages of membranes over different competing gas separation technologies include their fabrication simplicity, low cost and environmental pollution, and general ease of the operation. However, there are a number of challenges that need to be overcome to unlock the full potential of the membranes in industrial gas separation processes. The most important challenge is the inherent trade-off between gas permeability and selectivity for a pair of gases that limits the large scale applications of gas separation membranes [1]. It has been demonstrated recently that although selectivity is paramount to the economic viability of a membrane process, for industrial gas separations, membranes with high permeability and moderate selectivity are more in demand, particularly in multistep membrane separation [2]. Therefore, designing polymeric membranes possessing significant gas permeability has become an important strategy in the field of membrane science and research. In recent years, different strategies have been pursued to cover the issue. Among them, the use of aromatic polyamides (PA), polymers of intrinsic microporosity (PIMs) and thermally rearranged (TR) polymers, as the membrane materials seems to be the most promising ones.

Aromatic polyamides, well known for their excellent chemical, thermal and mechanical stability, are able to be easily modified by introducing appropriate substituents to achieve other required properties for gas separation applications, such as solubility, processability and high gas permeability. The group of Banerjee at the Materials Science Center of Indian Institute of Technology, have started researches on preparation of different highly gas permeable aromatic polyamide membranes, since 2013, by systematic changes of diamines and diacids in the polymerization reactions of the polyamides [3-6]. The monomers were altered in such a way that they incorporated various bulky groups such as 2,5 t-butyl phenylene, trifluoromethyl, adamantyl and tri-tert-butylphenol in the polyamide main chain. The motivation for the incorporation of bulky groups in the main chain was to increase fractional free volume (FFV) and rigidity simultaneously, thereby improving the gas permeability and permselectivity of the resulted membranes. The designed PA membranes showed high gas permeability for CO<sub>2</sub> and O<sub>2</sub> with moderate gas separation efficiency for CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> gas pairs, touching or even surpassing the Robeson's upper bounds of 2008. Most recently, this research group reported high performance PA membranes with both high permeability and selectivity for CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> separations, fabricated by introducing a pendant triphenylmethyl (trityl)-substituted triphenylamine moiety in the PA backbone [7].

Furthermore, polymers of intrinsic microporosity (PIM), a group of novel polymers synthesized by English researchers in 2004, may be another highly promising class of materials providing unprecedented gas separation performance [8]. The ladder type structure of these polymers consisting of stiff main chains without any single bond in the backbone governs their physicochemical and transport properties. PIMs incorporate sites of contortion or spiro-center that force the formation of large and well interconnected free volume elements, making the polymer highly permeable but moderately selective for technically important gas pairs [9]. Various approaches are now being investigated by researchers around the world to make PIM membranes more permselective. For example, cross-linking and UV irradiation of archetypal PIM, referred to as PIM-1, have resulted in polymers with attractive membrane properties, locating them on Robeson diagrams above the upper bounds of 2008 [1]. Also, it has been demonstrated that the introduction of bridged-bicyclic contortion centers (i.e., ethanoanthracene, Troger's base, triptycene) into fully fused-ring ladder and semi ladder PIM-polyimides (PIM-PIs) would result in highly ultramicroporous (<7 Å) PIMs with high selectivities matching those of existing commercial membranes but with up to 3 orders of magnitude higher permeabilities, especially in the large-scale industrial applications of nitrogen production from air and hydrogen purification [10, 11]. Furthermore, the use of nanoparticles within PIM materials has shown to be promising in enhancing the selectivity of the resulted membranes, provided that optimal combinations of polymer matrices and nanoparticles are realized. For instance, silica nanoparticles dispersed in the polymer of intrinsic microporosity PIM-1, led to a typical trade-off between permeability of O<sub>2</sub> and selectivity of O<sub>2</sub>/N<sub>2</sub>, and the data points did not overcome the 2008 upper bound of performance for this gas pair [12]. On the other hand, utilizing metal organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIF-8s) as nano additives, turned the same polymer into a more permeable and permselective system, so the data points were located above the related upper bounds [1].

Finally, thermally rearranged (TR) polymers, first reported by Park et al. in 2007 [13], have shown outstanding properties for a number of gas separations such as CO<sub>2</sub>/CH<sub>4</sub>, O<sub>2</sub>/N<sub>2</sub>, and hydrogen separation [14, 15]. TR polymers are traditionally synthesized through the solid-state thermal rearrangement of hydroxyl-containing polyimides to polybenzoxazoles at 300 to 450 °C.

The thermal rearrangement process leads to microporous polybenzoxazoles showing extraordinarily fast molecular transport for small gas molecules [16]. It has been shown that the microporous structure and size distribution of TR polymers can be tuned easily by varying the chemical

structure of the precursor hydroxyl–polyimide and by applying different thermal treatment protocols [16]. It is believed that the excellent upper bound performance (i.e., both high permeability and selectivity) of currently available TR polymers is due to a combination of higher diffusion selectivity, high diffusion coefficients, and high solubility coefficients, relative to other glassy polymers [15].

Despite all the above-mentioned advantages, polymers with extra high gas permeability are relatively expensive and prone to physical aging, which can severely affect the performances of the glassy polymer membranes. Thus, research efforts still need to be directed toward decreasing the cost and increasing the aging resistance of highly permeable membranes making them commercially attractive and industrially reliable.

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