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Polymer Rigidity Improves Microporous Membranes

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One Sentence Summary:

Microporous membranes with rigid polymer chains have high gas permeability combined with the ability to distinguish between small differences in molecular dimensions of gases

Abstract:

Microporous materials, such as inorganic crystalline zeolites, have uniform interconnected microcavities or channels, imparting them with large surface areas. They are referred to as molecular sieves because their highly rigid pore channels of exact molecular width allow them to separate out molecules with slightly different molecular dimensions. Many fascinating synthetic microporous molecular scaffolds have been constructed from metal organic frameworks (MOFs) (1) and microporous organic polymers (MOPs) (2,3,4), extending the range from crystalline inorganic, to inorganic-organic hybrids to purely organic molecular building blocks. MOPs can be divided broadly into three-dimensional networks and solvent-processable polymers. Carta and McKeown now describe a soluble highly rigid microporous organic polymer, from which a fabricated membrane has the extraordinary ability to distinguish between slight differences in molecular dimensions of gases such as O₂ and N₂, having only a 5% difference in kinetic diameters, while simultaneously having very high gas throughput of the smaller O₂ gas molecule through the membrane (5).

Main Text:

Membrane separations have become an important part of modern life in contributing to processes spanning from obtaining drinking water by seawater desalination, production of ultrapure water for the electronics industry, wastewater treatment, and gas separations. Membrane gas separation has been commercialized for over thirty years for the production of nitrogen from air, hydrogen recovery from industrial processes, and removal of carbon dioxide from natural gas. Commercial membranes have been largely derived from polymers having relatively low gas permeability and moderate to high gas selectivity, with moderately rigid chains that pack closely. Gas transport through typical polymer membranes is described by the solution-diffusion mechanism. Gas

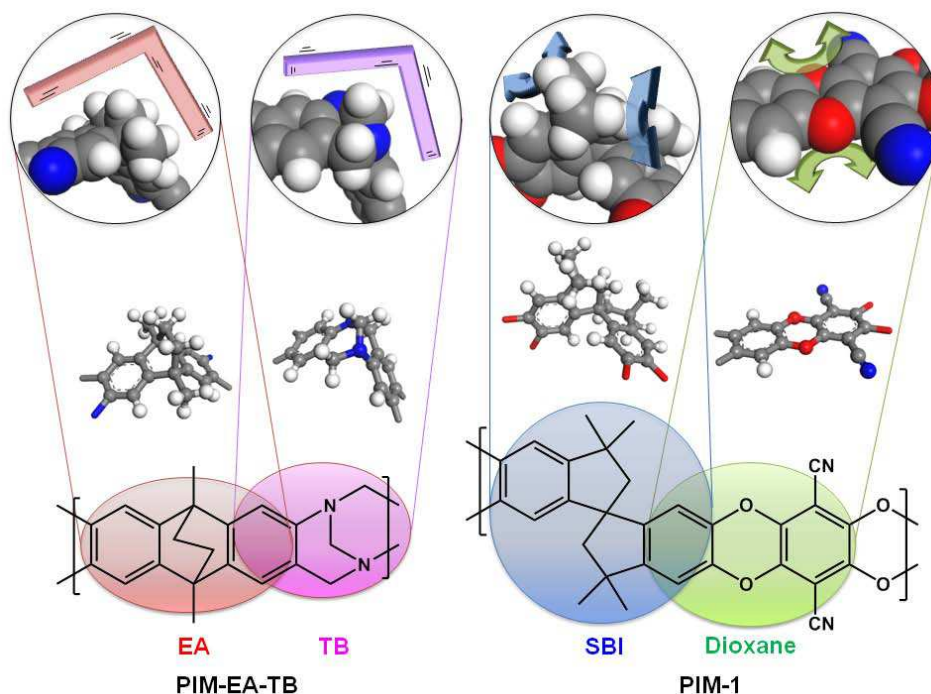
contacting the upstream side sorbs and diffuses through the membrane and desorbs on the downstream side, under a driving pressure. Gas permeability (P) through the membrane is given by $P = D \times S$, where D and S are the diffusion and solubility coefficients, respectively. From this, selectivity ($\alpha_{x/y}$) of a faster gas over a slower gas (e.g. P_{O_2} / P_{N_2}) is influenced by a combination of diffusivity selectivity (D_{O_2} / D_{N_2}) and solubility selectivity (S_{O_2} / S_{N_2}). Empirical performance limits, essentially plots of $\log \alpha_{x/y}$ versus P_x of various gas pairs, were proposed based on the selectivity-permeability trade-off upper-bound performance data up to 1991, and subsequently updated in 2008 (6). A theoretical basis for the upper-bounds was also established, which most importantly showed the path forward to achieve higher performance in polymeric membranes, by targeting D and/or S (7). Increasing solubility selectivity and increasing polymer chain rigidity are both viable approaches. However, chain rigidity must be coupled with higher inter-chain spacing to achieve both higher permeability from the gaps between the polymer chains, and higher selectivity derived from the rigid chain structure, exactly what Carta and McKeown demonstrate (5).

Microporous materials, which are defined as those having interconnected pores, channels or voids of less than 2 nm in diameter, are of great interest in catalysis, gas capture and storage, and improving separation efficiency. The first MOPs studied for membranes were polyacetylenes, exemplified by poly(trimethylsilyl-1-propyne) (PTMSP) (8). While their gas permeability is the highest among polymers, stemming from their high free volume, the contorted chain structure is not sufficiently rigid to ensure adequate size discrimination of small gas molecules. McKeown and Budd were the first to report a new class of soluble microporous polymer, coining the phrase ‘polymers of intrinsic microporosity’ (PIMs) (9,10). PIMs have very high permeabilities, though roughly an order of magnitude lower than PTMSP, with gas-pair selectivities in a higher and more useful range, giving them gas transport performance that defines the 2008 upper bound for some gas pairs. PIMs derive their microporosity and high free volume from rigid ladder-like polymer chains having sites of contortion, frustrating chain packing. The best-known PIM-1, an attractive soluble fluorescent yellow polymer, is prepared by polycondensation of a contorted spirobisindane (SBI) tetrafunctional monomer with an electron-withdrawing dinitrile monomer, resulting in dioxane chain-forming bridges. It would be reasonable to expect ladder polymers to be entirely rigid structures, since no bond rotation is possible, but both the SBI and dioxane bridge can flex to a greater extent than previously realized (11). This can be seen in Fig. 1D of (5), which models the relevant fragments of the polymer. SBI has a broad bimodal profile with two dihedral angles, indicating it is relatively flexible. The barrier between the two energy wells corresponds to adjacent indane methylene hydrogens on SBI interacting with each other as the rings wiggle past each other. The planar dioxane has a single dihedral angle with a broad distribution, also indicating bending flexibility like SBI.

In a radical departure from typical ladder-forming polymer reactions using tetrafunctional monomers, PIMs with extremely rigid bridged bicyclic amines were formed directly in high yield simply from diamine monomers linked through the formation of six covalent bonds. This

interesting bond-forming reaction was discovered accidentally by Tröger in 1887, and the correct bridged structure of the resulting Tröger's base (TB) was determined much later. Only now has it been exploited as a versatile polymer chain-forming reaction, and it seems likely that many new microporous systems will be constructed using this efficient TB bond-forming chemistry. Membrane performance gains from the PIM-SBI-TB polymer, which still retains the relatively flexible SBI unit but incorporates the highly rigid TB unit, are modest ((5) Fig. 2) compared with PIM-1, because there is insufficient overall chain rigidity. By replacing both the SBI and dioxane units in PIM-1 with more rigid ethanoanthracene (EA) and TB units shown in the Figure below, each with single narrowly distributed dihedral angles, and overall unit 'pincer' angles of $\sim 107^\circ$ and $\sim 112^\circ$ respectively, the chains are much more rigid and contorted and with higher microporosity and free volume. As a result, PIM-EA-TB exhibits dramatic performance increases in terms of permeability and selectivity, with data for the separation of some commercially-relevant gas pairs well above the upper bound.

The successful strategy of increasing chain rigidity in other microporous membrane materials having high inter-chain spacing to improve performance is also demonstrated in Thermally Rearranged (TR) polymers (12), and in spirobifluorene-containing (13) and tetrazole-substituted PIMs (TZ-PIMs) (14). Increased rigidity in TZ-PIM occurs through a hydrogen-bonded network, while it simultaneously incorporates CO_2 -sorbing tetrazole units for enhanced CO_2/N_2 selectivity. Highly permeable and selective membrane materials provide the opportunity to address difficult separation challenges, such as large gas-stream separations containing CO_2 (15).



‘Polymers of Intrinsic Microporosity’. Both contorted ladder polymers have rotational inflexibility in the chain. PIM-1 contains spirobisindane (SBI) and dioxane linkages, but both are

capable of bending and flexing to a considerable extent. PIM-EA-TB, with ethanoanthracene and Tröger's base units, has a more rigid architecture, allowing high gas permeability in tandem with size discrimination between gases having slight differences in molecular dimensions.

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