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Gas Separation by Polymer Membranes: Beyond the Border

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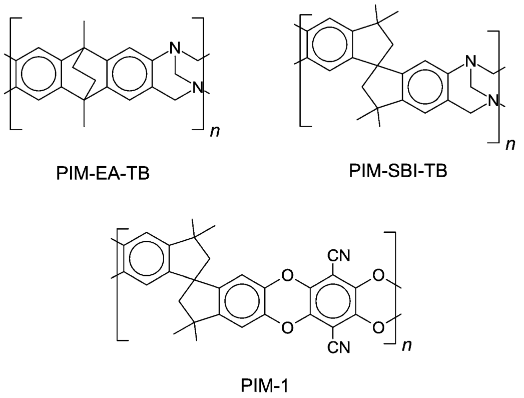
All polymers are permeable for all gases, at least to a certain extent. This permeability is different for each gas and each polymer, and the permeability coefficients are specific materials properties. Thus, the permeation of a gas mixture through a polymer membrane can be used to separate the gases. This effect is being employed in technical applications, for example for the separation of air into pure nitrogen (purity $\geq 99.5\,\%$) and oxygen-enriched air, and for the removal of CO_2 from natural gas.[1] In the case of dense, macroscopically pore-free membranes, the permeation proceeds by the solution-diffusion mechanism based on chain-segment mobility,[2] with the permeability coefficients depending on the solubilities as well as on the diffusivity coefficients of the gases in the polymer. The ratio of the permeability coefficients of two gases in the same polymer represents the ideal selectivity of this polymer for that gas pair.

Recently, McKeown et al.[3] published gas permeabilities and selectivities of a ladder or double-stranded polymer far beyond the well-known "upper bound"[4] in the so-called Robeson plot (see Figure 1). This upper bound represents an empirical upper limit for the combined selectivity and permeability. It was described first by Robeson,[5] and later Freeman[6] provided a theoretical explanation for its existence. The permeability coefficients of McKeown's new ladder polymer (PIM-EA-TB in Scheme 1) for certain industrially relevant gas pairs, such as O_2/N_2, H_2/N_2 and H_2/CH_4, are three to four times higher at the same selectivity[3] than the present limit described by the upper bound. For a comparison, this represents an improvement that is the same or greater than the improvement that had been made in the time between Robeson's first comprehensive data analysis in 1991[5] and the continuation of that analysis in 2008[4] (Figure 1 A, red squares vs. black triangles).

Polymers containing similar structural elements (PIM-SBI-TB, Scheme 1), but also spiro structures that interrupt the strict ladder or double-stranded architecture of PIM-EA-TB, exhibit significantly lower values for the gas pair O_2/N_2 (blue vs. red squares in Figure 1 A). Furthermore, the values of the true ladder polymer PIM-EA-TB for the gas pair CO_2/N_2 are considerably inferior (Figure 1 B) to those for O_2/N_2, H_2/N_2, and H_2/CH_4. This observation deserves an attempt at an explanation. According to the data from the paper by McKeown et al.,[3] the solubility of CO_2 in the ladder polymer PIM-EA-TB is 12 times higher than that of N_2, but the diffusion coefficients for CO_2 und N_2 are practically identical, resulting in the relatively low selectivity. This raises the question of the cause for the similarity of the diffusion coefficients.



Scheme 1. Ladder polymer PIM-EA-TB and spiro polymers PIM-SBI-TB and PIM-1 described by McKeown et al.[3]

Although the gas permeability of a large number of polymers has been studied,[4,5] the relationship between their chemical structures and the permeabilities and selectivities is not known in enough detail to provide practical "design rules" for the synthesis of polymers with optimal separation properties. However, it has become relatively clear that microporous materials based on rigid chain polymers, which are capable of gas separation by molecular sieving, possess considerable potential.[4] This was proposed already in the 1990s by Koros et al.,[7,8] who blended inorganic molecular sieves (zeolites) with soluble polymers in order to combine the mechanical properties of flexible polymer films with the separation properties of molecular sieves (mixed-matrix materials). Besides, some carbonized membranes also operate by the molecular-sieving mechanism, showing excellent combinations of selectivity and permeability. Unfortunately, these membranes tend to be very brittle and hard to handle and at present they are expensive and difficult to produce in large

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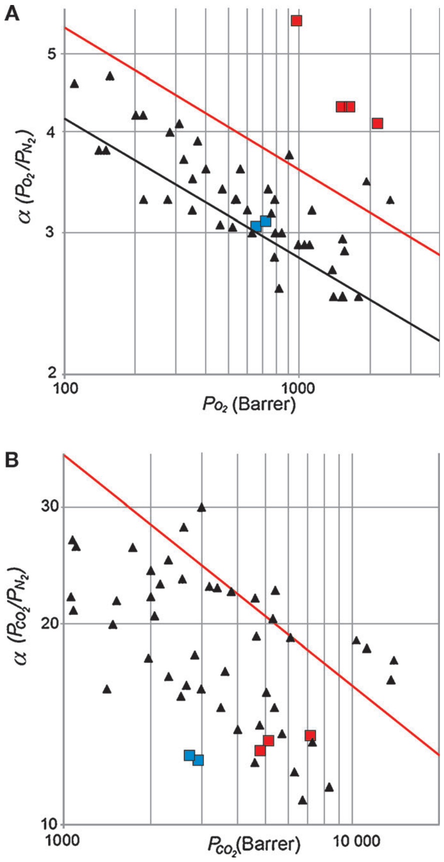

Figure 1. Robeson plot for O_2/N_2 (A) and CO_2/N_2 (B); red squares: PIM-EA-TB, blue squares: PIM-SBI-TB, black triangles: data of polymers close to or beyond the upper bounds of 1991[5] and/or 2008;[4] black line: upper bound of 1991, red line: upper bound of 2008 (from N. B. McKeown et al., Ref. [3]; reprinted with permission from AAAS).

quantities. Reference [9] provides a good overview on such materials.

All polymers with data near or beyond Robeson's present upper bound are composed of rigid chains, but they are strictly speaking single-chain polymers, not ladder polymers. The formation of an intrinsically microporous morphology due to stiff chains (PIM, polymers of intrinsic microporosity) alone does not appear to be sufficient for high selectivity. Apparently, the pore size distribution, and especially the mobility of short chain segments also play an important role. Segment mobility, which governs the gas transport through non-microporous glassy polymers,[10] would thwart the whole concept of molecular sieving in intrinsically microporous materials. The selectivity would no longer be governed by the size distribution of the micropores alone, but, as in conventional polymers, also by the segment mobility.

In comparison to single-stranded polymers (e.g. PIM-1 and PIM-SBI-TB; Scheme 1) with similar structures, the ladder polymer PIM-EA-TB exhibits a more narrow distribution of dihedral angles at characteristical "pivot points" (potentially flexible groups in the repeat units).[3] The difference in the kinetic sieving diameters of the molecules of O_2 and N_2 is considerably smaller than that of CO_2 and N_2 (H_2: 0.289 nm, CO_2: 0.33 nm, O_2: 0.346 nm, N_2: 0.364 nm). Therefore, it could be possible that gas transport in PIM-EA-TB membranes is not controlled exclusively by the micorpores, but also at least in part by the solution-diffusion mechanism, with segment mobility at an extent that is too large to discriminate between N_2 and CO_2. In that case, the smaller molecule would permeate faster.[10] However, this appears unlikely, considering the narrow distribution of the dihedral angles at potentially flexible groups, and the chain stiffness implied by that.

On the other hand, the molar mass of N_2 is significantly smaller than that of CO_2. If gas transport were governed by Knudsen diffusion[11] in pores with a diameter in the range of the mean free pathlength of the respective gases, the selectivity for the gas pair CO_2/N_2 would be reversed, since in that case, the lighter N_2 molecules would permeate faster than the heavier CO_2 molecules. While this is also the case for the pair O_2/N_2, the difference in molar mass between O_2 and N_2 is much smaller, and hence Knudsen diffusion would have a much smaller effect than for CO_2/N_2. Thus, the assumption appears justified that some of the gas transport takes place through a small fraction of micropores which are slightly too large.

Nevertheless, the high selectivities and permeabilities of PIM-EA-TB for some industrially relevant gas pairs showthe potential of polymers with ladder structures for membranes with improved properties. The micropore size and pore size distribution of this polymer are obviously already within the right size regime to a large extent, and the chain stiffness is sufficient to prevent transport through the bulk. At the same time, the inferior values of the spiro-group-containing polymers PIM-1 and PIM-SBI-TB show that the introduction of bulky, kinked groups is not necessarily helpful. Since these polymers do not only exhibit lower selectivities, but also lower permeability coefficients, the problem is likely the more strongly coiled structure of the spiro(bisindane) group, which results in a lower porosity, not necessarily larger pores.

McKeown's present results with ladder polymers show a promising approach to achieve the goal of flexible membranes from molecular-sieving microporous glassy polymers.

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