A highly permeable polyimide with enhanced selectivity for membrane gas separations†

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A highly permeable polyimide with improved molecular sieving properties is produced by using a bisanhydride monomer based on the rigid ethanoanthracene unit. The polymer (PIM-PI-EA) demonstrates enhanced selectivity for gas separations so that its gas permeability data lie above the 2008 Robeson upper bounds for the important O2–N2, H2–N2, CO2–CH4 and CO2–N2 gas pairs.

Polymers that can be processed from solution to form microporous solids are of growing interest for use as highly permeable membranes for gas separations including O2 or N2 enrichment from air, natural gas upgrading (predominantly removing CO2 from CH4), and hydrogen recovery from ammonia manufacture (separating H2 from N2).1–3 Polymers currently used as membranes for commercial gas separation, such as the polyimide Matrimid,4 generally demonstrate high selectivity but low permeability thus limiting industrial membrane applications to small and medium-scale gas separations. In contrast, highly permeable polymers have potential for large-scale separations but only if selectivity can be enhanced.5 However, for the separation of two gases (x and y), there is a well-established empirical trade-off between permeability (P) and selectivity (αxy = Px/Py) that was quantified by Robeson initially in 1991 (ref. 5) and then updated in 2008.6 Based on the permeability data for a large number of polymers, Robeson identified an “upper bound” in plots of log P versus log αxy for each gas pair of interest. The position of a polymer’s gas permeability data relative to the relevant upper bound is used as the universal performance indicator for assessing its potential for the separation of two gases.

Robeson noted7 that each of the upper bounds are populated by data from glassy polymers with rigid chains that promote diffusivity selectivity i.e. the preferential transport of lighter gas molecules of smaller kinetic diameters (e.g. He = 2.65; H2 = 2.80; CO2 = 3.3; O2 = 3.45 Å) over that of larger molecules (e.g. N2 = 3.64; CH4 = 3.87 Å). Hence it was predicted that greater size selectivity could be obtained by increasing polymer chain rigidity whereas high gas permeability relies on large inter-chain separation.7 Polymers of Intrinsic Microporosity (PIMs), such as the archetypal PIM-1 (Fig. 1a), fulfil both of these design criteria by possessing a rigid chain structure within which motion is restricted and sites of contortion, often provided by spirobisindan (SBI) units, to prohibit space efficient packing and generate high free volume.8–10 Therefore, permeability data for PIMs generally lie over the 1991 upper bound for most gas pairs10,11 and some approach, or even exceed, the 2008 upper bounds (Fig. 2).12–13 Similarly, microporous polyimides based on the SBI unit also demonstrate high permeability with modest selectivity (e.g. PIM-PI-SBI; Fig. 1b).14,15

Fig. 1 The molecular structures of (a) PIM-1; (b) PIM-PI-SBI; (c) PIM-EA-TB and (d) PIM-PI-EA. Spirobisindan (SBI) is blue, ethanoanthracene (EA) is red.
Recently, we demonstrated that the polymerisation of 2,6(7)-diamino-9,10-dimethylanthracene by the formation of linking groups based on Tröger’s base (TB) provides a highly permeable polymer (PIM-EA-TB; Fig. 1c) with remarkably high gas selectivities so that its data lie well above the 2008 upper bounds for O$_2$–N$_2$ (Fig. 2a), H$_2$–N$_2$ (Fig. 2b), H$_2$–CH$_4$ and H$_2$–CO$_2$.

The exceptional performance of PIM-EA-TB was attributed to enhanced diffusivity selectivity as a result of its highly shape-persistent structure provided by the bridged bicyclic ethanoanthracene (EA) component as compared to the more flexible SBI unit.

Hence it is important to establish whether the exchange of SBI components for EA units in other types of PIMs may also result in enhanced size-selectivity for gas separations and provides a general concept for improving polymers for gas separations.

Here we validate this concept by the synthesis of an EA-based polyimide (PIM-PI-EA; Fig. 1d), which has a structure that allows the direct comparison of its performance with a recently reported highly permeable SBI-based polyimide (PIM-PI-SBI; Fig. 1b).

The required novel EA-based bisanhydride monomer 1 was prepared from 2,3,6,7,9,10-hexamethylethanoanthracene and reacted with commercially available 3,3’-dimethylnaphthalidine, a monomer of previous utility for preparing highly gas permeable polyimides (Scheme 1 and ESI†).

The resulting polymer, PIM-PI-EA, was obtained in 88% yield and proved freely soluble in chloroform and THF, which facilitated its characterisation by $^1$H NMR spectroscopy and Gel permeation chromatography (GPC). The latter indicated that PIM-PI-EA was of very high average molecular mass ($M_w = 340000; M_n = 110000$ g mol$^{-1}$) as calibrated against polystyrene standards. Consequently, cast films of PIM-PI-EA from chloroform solution proved robust and suitable for gas permeability measurements. Nitrogen adsorption...
isotherms for a powdered sample of PIM-PI-EA at 77 K showed significant uptake at low relative pressures indicative of intrinsic microporosity and provided an apparent BET surface area of 616 m$^2$ g$^{-1}$, which is lower than that of PIM-PI-SBI (699 m$^2$ g$^{-1}$).

The gas permeability data for a 72 μm thick film of PIM-PI-EA are provided in Table 1 and the equivalent data for PIM-PI-SBI, PIM-1 and PIM-EA-TB are given in the ESL. Prior to analysis the film of PIM-PI-EA was treated by immersion in methanol as this is known to reverse the effects of physical ageing for glassy polymers and also removes the last residues of the casting solvent. Hence, this treatment allows a direct comparison between the gas permeabilities of different polymers.

The order of gas permeabilities for the freshly methanol treated film of PIM-PI-EA is CO$_2$ > H$_2$ > He > O$_2$ > CH$_4$ > N$_2$. This differs from most other PIMs including PIM-1 and PIM-SBI in that He is faster than O$_2$. It is notable that the value for N$_2$ permeability through PIM-PI-EA is very similar to that of PIM-SBI, whereas gases composed of smaller molecules (He, H$_2$, CO$_2$ and O$_2$) are transported faster and CH$_4$ composed of larger molecules, is transported significantly slower through PIM-PI-EA relative to PIM-SBI. These results validate the efficacy of the rigid ethanoanthracene unit as a component for inducing high gas selectivity via molecular sieving.

Importantly, the data points for PIM-PI-EA are above the Robeson upper bounds for O$_2$–N$_2$ (Fig. 2a), H$_2$–N$_2$ (Fig. 2b), CO$_2$–CH$_4$ (Fig. 2c), CO$_2$–N$_2$ (Fig. 2d) and H$_2$–CH$_4$ gas pairs, in contrast to those of PIM-PI-SBI, which fall below these upper bounds. The results for the CO$_2$–CH$_4$ and CO$_2$–N$_2$ gas pairs are particularly encouraging, as the equivalent data for the ethanoanthracene-containing PIM-PI-EA-TB are anomalously poor and fall below the relevant upper bounds.

Physical ageing (i.e. loss of free volume and gas permeability over time) is a general feature of glassy polymers and is observed for PIM-PI-EA (Table 1). However, the loss of permeability due to ageing is matched by a commensurate increase in selectivity so that the data points for the polymer aged for 273 days all lie above the upper bounds for O$_2$–N$_2$ (Fig. 2a), H$_2$–N$_2$ (Fig. 2b), CO$_2$–CH$_4$ (Fig. 2c), CO$_2$–N$_2$ (Fig. 2d) and H$_2$–CH$_4$ gas pairs. For the O$_2$–N$_2$ gas pair, the selectivity in favour of O$_2$ of 5.0 is the minimum limit.

Table 1: The gas permeabilities $P_x$, diffusivity $D_x$, solubility coefficient $S_x$ and ideal selectivities $\alpha(P_x/P_{N_2})$ for a methanol treated film of PIM-PI-EA of thickness = 72 μm with comparable data for a the same film obtained after 273 days given in parentheses

|       | N$_2$ | O$_2$ | CO$_2$ | CH$_4$ | H$_2$ | He     |
|-------|-------|-------|--------|--------|-------|--------|
| $P_x$ | 369 (131) | 1380 (659) | 7340 (3230) | 457 (156) | 4230 (2860) | 1580 (1130) |
| $\alpha$ | (—) | 3.7 (5.0) | 19.9 (24.6) | 1.2 (1.2) | 11.5 (21.8) | 4.3 (8.6) |
| $D_x$ | 84 (32) | 270 (144) | 95 (48) | 24 (8.4) | 40$^*$ (120) | 60$^*$ (191) |
| $D_x/D_{N_2}$ | — | 3.2 (4.8) | 1.1 (1.6) | 0.29 (0.28) | ≤0.09 (0.60) | ≤0.23 (0.15) |
| $S_x$ | 3.29 (3.3) | 3.83 (3.4) | 57.8 (50.1) | 14.2 (13.5) | 4.3 (4.1) | 0.29 (0.18) |
| $S_x/S_{N_2}$ | — | 1.2 (1.1) | 17.6 (15.2) | 4.3 (4.1) | 0.29 (0.18) | 0.07 (0.04) |

$^a$ Units = barrer. $^b$ $\alpha = (P_x/P_{N_2})$. $^c$ Units = 10$^{-12}$ m$^2$ s$^{-1}$. $^d$ Units = cm$^3$ cm$^{-2}$ bar$^{-1}$. $^e$ For He and H$_2$ the time lag is too short (<1 s) for determination of $D$ with error <10%, and the value of $D$ is the minimum limit.
addition, PIM-PI-EA has gas permeability data that lie well above the Robeson upper bounds for important gas pairs including CO\textsubscript{2}–CH\textsubscript{4}, of interest for natural gas upgrading, and CO\textsubscript{2}–N\textsubscript{2}, of interest for post-combustion carbon capture applications. This significant enhancement of gas selectivity for highly permeable polyimides is of particular importance as polyimides are the most studied class of polymer for membrane applications. Therefore, methodologies that have been developed for polyimide membrane technology (e.g. cross-linking strategies) can also be applied to PIM-PI-EA, thus making it a strong candidate for exploitation as a membrane material.

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