Triptycene Induced Enhancement of Membrane Gas Selectivity for Microporous Tröger's Base Polymers

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Polymer membranes are of increasing importance for a range of molecular separations due to their potential for enhanced energy-efficiency over competing technologies. For example, gas separation using polymer membranes is an established industrial technology that is applied to O₂ or N₂ enrichment of air, natural gas upgrading (i.e., predominantly removing CO₂ from CH₄), and hydrogen recovery from ammonia manufacture (separating H₂ from N₂). In addition, polymer membranes are also predicted to play an increasing role in hydrogen production (e.g., separating H₂ from CO₂) and post-combustion capture of CO₂ (separating CO₂ from N₂). For any gas separation membrane it is desirable to have good selectivity for one gas over another, combined with high permeability (i.e., flux or throughput). Generally, polymers used for commercial gas separation membranes demonstrate high selectivity but low permeability, however, to compete with other technologies for very large-scale applications, membrane materials with greatly enhanced gas permeabilities are desirable. Unfortunately, for the separation of a given gas pair (x and y), highly permeable polymers display inadequate selectivity due to the well-established trade-off between permeability (Pₓ) and selectivity (αₓᵧ = Pₓ/Pᵧ). For example, one of the most permeable polymers, poly(trimethylenylpropane), has very poor selectivity (e.g., PO₂ = 6000 Barrer; αO₂/N₂ = 1.8). The permeability-selectivity trade-off was quantified by Robeson in 1991, and revised in 2008, by plotting log Pₓ versus log αₓᵧ for a large number of polymers. For each gas pair, an “upper bound” was identified and the position of the gas permeability data relative to the upper bound is used as a universal performance indicator when assessing the potential of a new polymer as a membrane material for the separation of the two gases. The position of the Robeson upper bound for each gas pair is related to the difference in the kinetic diameter of the gas molecules and the size-sieving nature (i.e., diffusivity selectivity) of the rigid glassy polymers that define it. Theory suggests that greater selectivity can be obtained by suppressing polymer motion by increasing chain rigidity whereas high gas permeability relies on the generation of a large amount of free volume through large inter-chain separation. Conforming to these design criteria, Polymers of Intrinsic Microporosity (PIMs), such as the archetypical PIM-1, are a class of membrane-forming polymer that are designed to possess a wholly fused-ring structure to restrict chain motion and a contorted chain structure to prohibit space efficient packing. Hence, gas permeability data for PIMs generally lie over the 1991 upper bound for most important gas pairs and some approach, or even exceed, the 2008 upper bounds. Recently, we introduced a new class of PIM prepared using a polymerisation reaction based on the efficient formation of the bridged bicyclic diamine called Tröger’s base (TB; i.e., 6H,12H-5,11-methanodibenzo[b,f][1,5]diazocine). For example, the reaction of 2,6(7)-diamino-9,10-dimethylethanoanthracene yields the highly rigid ladder polymer (PIM-EA-TB) (Figure 1b). PIM-EA-TB demonstrates very fast gas permeability and good selectivity so that its data lie well above the 2008 upper bounds for O₂/N₂ (Figure 2a), H₂/N₂ (Figure 2b), H₂/CH₄ and H₂/CO₂ due to exceptional diffusivity selectivity that favours the transport of gas molecules of smaller kinetic diameters (e.g., H₂ = 2.8; CO₂ = 3.3; O₂ = 3.46 Å) over that of larger molecules (e.g., N₂ = 3.64; CH₄ = 3.87 Å). This enhanced molecular sieving performance of PIM-EA-TB was attributed to its highly rigid macromolecular structure, which does not contain the relatively flexible spiro-centres or dioxin linkages found in conventional PIMs such as PIM-1. Anomalously, the permeability data of PIM-EA-TB for the technologically important gas pairs of CO₂/CH₄ and CO₂/N₂ proved unremarkable relative to that of other PIMs and fall below the 2008 upper bounds (Figure 2b and c). Here we report the properties of a novel triptycene-based PIM prepared via Tröger’s base formation that demonstrates further enhancement of gas permeability data for O₂/N₂ and performance near the 2008 upper bounds for the CO₂/CH₄ and CO₂/N₂ gas pairs. PIM-EA-TB was designed to possess extreme rigidity being composed solely of benzene rings fused to alternating TB and ethanoanthracene bridged bicyclic units. Therefore, it is a challenge to reduce polymer chain mobility still further. However, one possible enhancement to the polymer design is the removal of the methyl substituents at the bridgehead of the ethanoanthracene unit as their turnstile-like rotary thermal motion may reduce the gas selectivity of PIM-EA-TB by facilitating transport of larger gas molecules through narrow elements of
free volume that would otherwise be inaccessible. These methyl
groups were originally envisioned to increase the distance
between polymer chains of PIM-EA-TB to ensure high perme-
bility. Instead, triptycene was considered as a desirable alter-
native bicyclic building unit as it has been used extensively to
generate free volume and intrinsic microporosity within poly-
mers.\textsuperscript{[15]} The use of triptycene, to give PIM-Trip-TB (Figure 1c),
was anticipated to maintain inter-chain distances, without the
need for bridgehead methyl substituents.

PIM-Trip-TB is prepared in three simple steps from commer-
cially available triptycene. The final step involves polymerisation
of 2,6(7)-diaminotriptycene\textsuperscript{[16]} by reaction with six equivalents
of dimethoxymethane in trifluoroacetic acid (TFA) at ambient
temperature. The resulting polymer is soluble in chloroform
allowing for analysis by Gel Permeation Chromatography
(GPC) which indicates that a reasonably high average molec-
ular mass was achieved ($M_n = 21\,000; M_w = 50\,000$; calibrated
relative to polystyrene standards). An apparent BET (Brunauer,
Emmett, Teller) surface area of 899 m$^2$ g$^{-1}$ could be calculated
from the $N_2$ isotherm for a powdered sample of PIM-Trip-TB at
77 K\textsuperscript{[17]} which is less that that obtained for the related polymer
PIM-EA-TB (1028 m$^2$ g$^{-1}$) but higher than the range quoted for
PIM-1 (720–820 m$^2$ g$^{-1}$) in the literature.\textsuperscript{[10b,18]} The fabrication
of optically clear films suitable for gas permeability studies
was achieved by casting from chloroform solution. Films of
PIM-Trip-TB proved robust with a Young’s modulus of 1206 ±
42 MPa and tensile strength of 44.6 ± 5.2 MPa, which are an
improvement on the equivalent values for PIM-EA-TB,\textsuperscript{[12a]} and
maximum deformation of 13.0 ± 8.2%.

The gas permeabilities of a film of PIM-Trip-TB of 132 μm
thickness are given in Table 1 together with the corresponding
values for a thicker film of PIM-EA-TB (182 μm), which are similar
to those recently reported.\textsuperscript{[12a]} Prior to analysis both films
were treated by immersion in methanol as this is known to reverse
the effects of physical ageing for glassy ultra-permeable polymers and
also removes the last residues of the casting solvent.\textsuperscript{[10d]} Hence,
this treatment allows a direct comparison between the gas perme-
abilities of the different polymers in an unaged state.

The order of gas permeabilities for the freshly methanol
treated film of PIM-Trip-TB is CO$_2$ > H$_2$ > O$_2$ > He > CH$_4$ > N$_2$, which
is different from that of PIM-EA-TB (H$_2$ > CO$_2$ > He > O$_2$ > CH$_4$ > N$_2$)
but similar to most other PIMs. Greater values of gas perme-
abilities are obtained for PIM-Trip-TB over PIM-EA-TB with the
exception of H$_2$ and H$_2$, which are similar. This enhancement
is particularly notable as the film of PIM-Trip-TB was thinner
than that of PIM-EA-TB and, generally for glassy polymers,
the gas permeabilities for thinner films are lower due to the
larger relative contribution of the more densely packed surface
regions of the film.\textsuperscript{[11a,19]} Of particular interest is the greater
CO$_2$ permeability for PIM-Trip-TB. In addition, ideal selec-
tivities for PIM-Trip-TB are significantly higher than those of
PIM-EA-TB for some important gas pairs (O$_2$/N$_2$, CO$_2$/CH$_4$
and CO$_2$/N$_2$) whilst similar for others (H$_2$/N$_2$, H$_2$/CO$_2$, and H$_2$/
CH$_4$). Hence, the permeability data for PIM-Trip-TB are well
above the Robeson upper bounds for O$_2$/N$_2$ (Figure 2a), H$_2$/
N$_2$ (Figure 2b), H$_2$/CH$_4$, and H$_2$/CO$_2$. In particular, the strong
enhancement in O$_2$/N$_2$ performance vindicates the choice of
triptycene as a structural unit to enhance diffusivity selectivity
as the separation of this gas pair relies almost exclusively on
size selectivity based on only a small difference in kinetic di-
ameter between the gas molecules. Importantly, the PIM-Trip-
TB data for CO$_2$/CH$_4$ (Figure 2c) and CO$_2$/N$_2$ (Figure 2d), both
lie very close to the respective 2008 upper bounds in contrast to
that of PIM-EA-TB, which fall well below.

Physical ageing (i.e., loss of free volume over time) is a gen-
eral feature of glassy polymers\textsuperscript{[20]} and is observed for both PIM-
Trip-TB and PIM-EA-TB (Table 1). The rate of ageing is more
rapid in thinner films and therefore, to allow direct compar-
ison, the values quoted are for a 60% reduction of the original
value of PO$_2$, which occurs after 100 days following methanol
treatment for the thinner film of PIM-Trip-TB (132 μm) and
470 days for that of PIM-EA-TB (180 μm). PIM-Trip-TB ages
gracefully with a corresponding enhancement of selectivity
for the reduction in permeability so that lines joining the non-
aged and aged data points on all the Robeson plots are approxi-
mately parallel to the upper bound for all important gas pairs
(Figure 2). For the O$_2$/N$_2$ gas pair, the selectivity in favour of O$_2$
of 5.7 for a value of PO$_2$ greater than 1000 Barrer is exceptional.
In addition, the data for the aged film of PIM-EA-TB crosses the
2008 upper bound for CO$_2$/CH$_4$ (Figure 2c) and is comparable
with the data of the best performing PIMs for this commer-
cially important gas pair.\textsuperscript{[11a]}

According to the solution-diffusion model the permeability
of a gas through a dense polymer is dependent on both its
Figure 2. Robeson plots for a) O₂/N₂; b) H₂/N₂; c) CO₂/CH₄ and d) CO₂/N₂ gas pairs showing the data for methanol treated PIM-Trip-TB with data points ■ for a 132 μm film and ♦ for PIM-EA-TB for a 180 μm film. Data at lower permeability, joined by a line, are for the same films but aged 100 and 470 days, respectively. The gray and black lines represent the 1991 [10] and 2008 [11] upper bounds, respectively. Also shown, as crosses, are data points of other PIMs reported since the upper bound was updated in 2008.

Table 1. The gas permeabilities Pₓ, diffusivity Dₓ, solubility coefficient Sₓ and ideal selectivities α (Pₓ/PN₂) for a methanol treated film of PIM-Trip-TB of thickness = 132 μm with comparable data for a the same film obtained after 100 days given in parentheses. To allow a direct comparison, data from a film of PIM-EA-TB (180 μm) (and aged for 470 day in parentheses), following an identical pre-treatment, is provided. Pₓ and Dₓ values were determined by time lag analysis, Sₓ was determined by gravimetric sorption measurements.

<table>
<thead>
<tr>
<th></th>
<th>N₂</th>
<th>O₂</th>
<th>CO₂</th>
<th>CH₄</th>
<th>H₂</th>
<th>He</th>
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<tr>
<td>Pₓ (PIM-Trip-TB) [Barrer]</td>
<td>629</td>
<td>2718</td>
<td>9709</td>
<td>905</td>
<td>8039</td>
<td>2500</td>
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<tr>
<td>α (Pₓ/PN₂) (PIM-Trip-TB)</td>
<td>–</td>
<td>4.3</td>
<td>15.9</td>
<td>1.4</td>
<td>12.8</td>
<td>4.0</td>
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<tr>
<td>Dₓ (PIM-Trip-TB) [10⁻¹² m²/s]</td>
<td>135</td>
<td>462</td>
<td>111</td>
<td>48.9</td>
<td>&gt;7800</td>
<td>&gt;10000</td>
</tr>
<tr>
<td>Dₓ/ΔN₂ (PIM-Trip-TB)</td>
<td>–</td>
<td>3.4</td>
<td>0.82</td>
<td>0.36</td>
<td>58</td>
<td>74</td>
</tr>
<tr>
<td>Sₓ (PIM-Trip-TB) [cm³ cm⁻³ bar⁻¹]</td>
<td>5.3</td>
<td>–</td>
<td>51.0</td>
<td>21.5</td>
<td>–</td>
<td>–</td>
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<table>
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<th></th>
<th>N₂</th>
<th>O₂</th>
<th>CO₂</th>
<th>CH₄</th>
<th>H₂</th>
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</tr>
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<tr>
<td>Pₓ (PIM-EA-TB) [Barrer]</td>
<td>580</td>
<td>2294</td>
<td>7696</td>
<td>774</td>
<td>8114</td>
<td>2685</td>
</tr>
<tr>
<td>α (Pₓ/PN₂) (PIM-EA-TB)</td>
<td>–</td>
<td>3.95</td>
<td>13.3</td>
<td>1.3</td>
<td>14.0</td>
<td>4.6</td>
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<tr>
<td>Dₓ (PIM-EA-TB) [10⁻¹² m²/s]</td>
<td>89</td>
<td>310</td>
<td>76.4</td>
<td>31.9</td>
<td>&gt;7200</td>
<td>&gt;10000</td>
</tr>
<tr>
<td>Dₓ/ΔN₂ (PIM-EA-TB)</td>
<td>–</td>
<td>3.48</td>
<td>0.82</td>
<td>0.36</td>
<td>81</td>
<td>113</td>
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<tr>
<td>Sₓ (PIM-EA-TB) [cm³ cm⁻³ bar⁻¹]</td>
<td>4.4</td>
<td>–</td>
<td>47.0</td>
<td>17.2</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

For He and H₂ the time lag is too short (<1 s) for absolute determination of D and the indicated value of D is the minimum limit.

a) For He and H₂ the time lag is too short (<1 s) for absolute determination of D and the indicated value of D is the minimum limit.
diffusivity \((D)\) and its solubility \((S)\) (i.e., \(P = D_S S)\).[21] Generally, the observed enhancement in performance for PIM-Trip-TB as compared to PIM-EA-TB appears to be due to greater diffusivity selectivity as determined by analysis of the data obtained by the time-lag method for measuring gas permeabilities. This is consistent with the higher chain stiffness as expressed in a higher Young’s modulus. In order to investigate the mechanism of transport in these two polymers further, CO2, CH4 and N2 sorption isotherms were obtained at 25 °C (Figure 3a). The uptake of ∼20% (∼4 mmol g−1) by mass of CO2 at 0.7 MPa for these TB-based polymers is impressive as compared to other microporous polymers examined for CO2 adsorption.[17,22] Interestingly, the sorption of CO2, CH4 and N2 within PIM-Trip-TB is higher at relatively low pressures (0.1–0.3 MPa) as compared to PIM-EA-TB, thus contributing to their higher solubility coefficients and, hence, gas permeabilities at the feed pressure of 0.1 MPa (Table 1). In contrast, the sorption of CO2 and CH4 is greater at higher pressures (>0.3 MPa) for PIM-EA-TB relative to PIM-Trip-TB (Figure 3b). This difference in sorption behaviour indicates that PIM-Trip-TB has a higher proportion of smaller free volume elements that are capable of binding to gas molecules at lower pressures than does PIM-EA-TB, which is consistent with its enhanced size-sieving properties. Despite the clear enhancement noted for Trip-PIM-TB, the performance of both TB polymers appears anomalous for gas pairs involving CO2 with the expected benefits of enhanced diffusivity selectivity, which are obvious for other gas pairs, not being fully realised for CO2/CH4 or CO2/N2. In particular, the apparent diffusivity selectivity in favour of N2 over CO2 within unaged films of both Trip-PIM-TB and PIM-EA-TB (Table 1) is unusual and suggests that some of the free volume of PIM-EA-TB is blocked for CO2 transport but available for N2 and other gases. It is known that adsorbed water adversely affects the gas permeability of PIM-1[8] and therefore, to determine whether its presence may be influencing the performance of the TB polymers, IR spectroscopic analysis was carried out on films of PIM-EA-TB and PIM-Trip-TB following methanol treatment. Characteristic absorption bands of H2O at 3200–3600 cm−1 and 1630 cm−1 were observed in the spectrum of both films (Figure S1). In addition, a relatively strong and sharp band at 3650 cm−1 can be assigned to the presence of hydroxide anion, consistent with the basic nature of the TB units within the polymers.[19,24] Prior to the gas permeability measurements, the polymer films were subjected to reduced pressure (10−3 mbar) and hence, the IR spectra of films following a similar protocol were also collected. A distinct difference between the spectra of the resulting two films was observed with that of PIM-Trip-TB showing a large reduction (∼95%) in the intensity of the broad water peak centred at 3400 cm−1 whereas the intensity of the same peak for PIM-EA-TB is reduced by only ∼35%. Similarly, after exposure to reduced pressure, the intensity of the peak attributed to the hydroxide anion at ∼3650 cm−1 is reduced to 20% of its original intensity for PIM-Trip-TB but it is unchanged for PIM-EA-TB. Hence, the anomalously low permeability of CO2 relative to that of other gases may be due to its specific interaction with adsorbed water and associated hydroxide anions to form bicarbonate anions that will occupy free volume and reduce diffusivity. This behaviour is similar to that noted for another recently reported amine-containing PIM.[25] However, PIM-Trip-TB appears to offer an additional advantage over PIM-EA-TB in that it is less hydrosopic and therefore water does not have such a significant effect on its CO2 permeability.

To conclude, PIM-Trip-TB provides highly impressive data for a number of commercially relevant gas pairs including O2/N2, H2/N2 and CO2/CH4 in terms of permeability, selectivity and position relative to the Robeson upper bound. This performance is based on exceptional diffusivity selectivity of gas transport. The lack of methyl groups in PIM-Trip-TB may enhance performance as compared to PIM-EA-TB, within which methyl rotary motion may reduce diffusivity selectivity. Indeed, as PIM-Trip-TB is a ladder polymer that is composed of only benzene rings fused together by rigid bridged bicyclic units and contains no groups that can act as rotors, its performance as a molecular sieve is likely to be approaching the optimum achievable for gas separation for a solution processable polymer. Any further improvement in fundamental gas permeability data may require the additional enhancement of solubility selectivity for one gas over another.
Experimental Section

Preparation of PIM-Trip-TB: A mixture of 2,6(7)-diaminotriptycene (1.43 g, 5.0 mmol), dimethylosiloxane (2.60 g, 34.2 mmol) and dichloromethane (1.5 mL) was added dropwise to trifluoroacetic acid (15 mL) over 2 hours. The clear red solution was left stirring for 168 hours and the reaction quenched with water (100 mL). Aqueous ammonia (35%, 100 mL) was added and the mixture stirred vigorously for 2 hours before the precipitate was collected by filtration. The solid was washed with water (100 mL) and acetone (100 mL), dried and ground to a fine powder. The polymer was dissolved in chloroform (150 mL), precipitated with hexane (150 mL) and collected by filtration. This process was repeated twice. The solid was then refluxed in acetone and twice in methanol, each time for 16 hours. Filtration gave the polymer as a cream powder (1.28 g, 79%). Apparent BET surface area of powder = 899 m² g⁻¹; total pore volume = 0.55 ml g⁻¹ at p/p₀ = 0.98; TGA (nitrogen): weight loss due to thermal degradation started at 400 °C and totalled 30.5%; GPC (from chloroform solution and calibrated against polystyrene standards) M₅ = 21,200, M₈ = 50,700 g mol⁻¹; ¹H NMR (400 MHz, CDCl₃) δ ppm 3.89 (br s, 2H), 4.41 (br s, 2H), 4.80 (br s, 2H), 5.07 (br s, 2H), 6.97 (br m, 8H). Procedures: Film formation was achieved by preparing a solution of PIM-Trip-TB (0.50 g) in chloroform (20 mL) which was poured into a 9 cm circular Teflon mould. The film was allowed to form by slow solvent evaporation for 96 h. Prior to permeability measurements the films were soaked in methanol for 8 h to remove residual casting solvent and then dried in air. The density of the 132 µm film measured by simple geometric means, was found to be 1.14 g cm⁻³ after vacuum pump fitted with a trap to remove oil. The gases were tested in a calibrated against polystyrene standards)

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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