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Layer-by-Layer Assembly of a Polymer of Intrinsic Microporosity: Targeting the CO₂/N₂ Separation Problem

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A polymer of intrinsic microporosity, **1**, has been incorporated into a series of polyelectrolyte multilayers *via* the Layer-by-Layer deposition method. One of these assemblies [a 6 nm multilayer derived from **1** plus poly(diallyldimethylammonium chloride)] showed exceptional permeation properties with respect to CO₂ and N₂. Specifically, this film exhibited a CO₂ permeance of 130 GPU and a CO₂/N₂ selectivity of 33.

The ability to separate mixtures of gases efficiently and economically can have a major environmental impact. A prime example of this relates to the fight against global warming where improved methods of separating post-combustion CO₂ from N₂ are now being sought.¹ While the selective absorption of CO₂ is one approach that is attracting broad attention, such methods tend to be costly in terms of their energy and capital requirements.^{2,3} For this reason, membrane-based alternatives that can have significantly reduced energy and capital costs are of special interest. A main goal, in this regard, is the design of new membranes having improved permeation properties.⁴⁻¹²

Gas transport across solid organic polymers generally follows the solution-diffusion model where the flux (*J*) of the gas is directly proportional to a permeability coefficient (*P*) and the pressure gradient (Δp) that is applied across the membrane. This flux is also inversely proportional to the thickness (*l*) of the membrane (eq. 1).⁷ Rearranging eq. 1 to eq. 2 expresses this relationship in terms of a normalized flux, *P/l*, which is commonly referred to as permeance. Thus, permeance is a measure of permeability that has been normalized to a

membrane's thickness. Typically, permeances are reported in gas permeation units (GPU) where 1 GPU = 1 × 10⁻⁶ cm³/cm²·s·cm Hg. The selectivity of a membrane, α , with respect to two permeants of interest (*i*, *j*), is then given by the ratio of their permeances (eq. 3)

$$J \text{ (cm}^3\text{/cm}^2 \cdot \text{sec)} = \frac{P \cdot \Delta p}{l} \quad (1)$$

$$\frac{P}{l} \text{ (cm}^3\text{/cm}^2 \cdot \text{sec} \cdot \text{cmHg)} = \frac{J}{\Delta p} \quad (2)$$

$$\alpha_{ij} = \frac{\left(\frac{P}{l}\right)_i}{\left(\frac{P}{l}\right)_j} \quad (3)$$

For a real-world membrane-based separation of CO₂ and N₂ from flue gas, cost estimates indicate that after a CO₂/N₂ selectivity of ca. 30 has been reached, further increases in membrane CO₂ permeance are more important than further increases in selectivity.⁴ Thus, *creating membranes having CO₂/N₂ selectivities that are ≥ 30 with CO₂ permeances as high as possible is the major scientific challenge.*

Virtually all organic polymer membranes that have been reported to date that do not involve facilitated transport either have CO₂/N₂ selectivities below 30 or CO₂ permeances less than ca. 50. One notable exception is a graphene oxide-based membrane where ca. 3-7 nm thick films were reported to have a CO₂ permeance of 120 and a CO₂/N₂ selectivity of 55.⁹

Our own efforts in the gas separation area have focused, sharply, on polyelectrolyte multilayers (PEMs) as membrane materials.^{13,14} The fact that such assemblies can be readily fabricated in hyperthin (<100 nm) form *via* the Layer-by-Layer (LbL) method and can be applied to hollow fiber supports makes them especially attractive.¹⁵⁻¹⁹ While flue gas contains a significant amount of water vapor that can adversely affect the permeability properties of a PEM, such water can be removed, effectively, using drying agents.⁶ It is also noteworthy that

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these drying agents can be regenerated without the need of an additional source of energy by taking advantage of the heat of combustion.

Recently, we found that a 6-bilayered (26 nm) PEM made from two common polyelectrolytes [i.e., poly(sodium 4-styrene sulfonate (PSS)) and poly(diallyldimethylammonium chloride (PDDA)), when deposited onto 30 μm poly[1-(trimethylsilyl)-1-propyne] (PTMSP) supports, exhibits a limiting CO_2/N_2 selectivity of 120 and a CO_2 permeance of 14 GPU.²⁰ By reducing the thickness of the PEM to 4 bilayers (15 nm), the CO_2 permeance was found to increase to 44 GPU as its CO_2/N_2 selectivity decreased to $\alpha=46$. Thinner PEMs that were made from these two polyelectrolytes led to CO_2/N_2 selectivities that fell well below the targeted threshold value of $\alpha=30$.

Here, we report that a “polymer of intrinsic microporosity” (PIM) can be successfully incorporated into a PEM. Of particular significance is the fact that one such PEM exhibited a CO_2 permeance of 130 GPU and a CO_2/N_2 selectivity 33. Owing to the twisted geometry of their repeat units, dense films of PIMs have a relatively high free volume and high CO_2 permeabilities.²¹⁻²³ Recently it was reported that a 30 nm thick PIM that was deposited onto PTMSP *via* the Langmuir-Schaefer method showed a CO_2 permeance as high as 114 GPU but with a CO_2/N_2 selectivity of 13.5.²²

In this study we chose polymer **1** as a PIM-prototype for investigation (Fig. 1). In its carboxylic acid form, dense films of **1** exhibit a CO_2/N_2 selectivity of 53.6.²³ Based on the permeability coefficient for CO_2 that was reported for a 48 μm thick membrane ($P=96\times 10^{-10}$ $\text{cm}^3\text{-cm}/\text{cm}^2\text{-s-cm Hg}$), its CO_2 permeance corresponds to only 2 GPU. We have since found that the Na^+ salt form of **1** is soluble in water and that it can be combined with a variety of cationic polyelectrolytes to form PEMs. This report documents our principal findings.

Using PEMs made from PSS/PDDA as a frame of reference, we expected that substitution of PSS with **1** would lead to a higher internal free volume and higher CO_2 permeances. Polymers **2** and **3** were also selected as polycations to be combined with **1** based on the hypothesis that they would produce tighter PEMs due to increased hydrophobic interactions and pi stacking (Fig.1).²⁴ In principle, since **3** has two aromatic moieties per repeat unit, pi stacking could lead to especially tight assemblies. How sensitive the CO_2/N_2 selectivity would be towards such substitutions, however, was less predictable.

The methods that we used for synthesizing PIM-1 and its hydrolyzed product, **1**, were similar to those previously reported.²³ Polymers **2** and **3** were synthesized from poly(4-vinylbenzyl chloride) using established procedures.¹⁴

The film growth behavior that was observed for PEMs derived from $(1/\text{PDDA})_n$, $(1/2)_n$, and $(1/3)_n$ are shown in Fig. 2. The film growth behavior for PEMs made from

$(\text{PSS}/\text{PDDA})_n$ was essentially the same as that found for $(1/\text{PDDA})_n$ and $(1/2)_n$ (not shown).²⁰

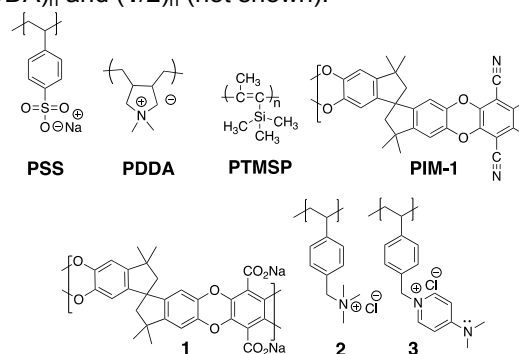


Fig. 1. Structures of PSS, PDDA, PTMSP, **1**, **2**, **3**, and PIM-1.

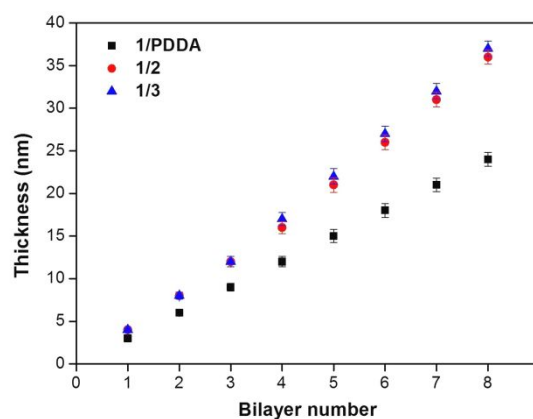


Fig. 2. Ellipsometric film thickness versus number of bilayers of $(1/\text{PDDA})_n$, $(1/2)_n$ and $(1/3)_n$ deposited from aqueous solutions containing 15 mM repeat units plus 100 mM NaCl.

To assess the permeability properties of these PEMs, the permeances for H_2 , CO_2 and N_2 were measured as a function of the number of bilayers using a constant volume-variable pressure apparatus, a pressure gradient of 40 psi, and 30 μm PTMSP as support material.¹⁴ All permeances shown in Fig. 3-5 are averages of two independently prepared membranes that generally varied by less than 10%.

For PEMs derived from $(1/\text{PDDA})_n$, a gradual decrease in the H_2 , CO_2 and N_2 permeances and a gradual increase in CO_2/N_2 and H_2/N_2 selectivities were observed on going from one to eight bilayers (Fig. 3). Optimal PEMs were found with only two bilayers (6 nm) where the CO_2/N_2 selectivity was 33 and the CO_2 permeance was 130. It is noteworthy, in this regard, that a similar 6 nm thick PEM made from PSS/PDDA showed a dramatically higher CO_2 permeance (1200 GPU) and a dramatically lower CO_2/N_2 selectivity ($\alpha=6$).²⁰ Thus, the main consequence of replacing PSS with **1** is not simply to increase the intrinsic permeability of the PEM but rather to tighten the membrane and make it more selective. Both of these changes are likely due to pi stacking. The exceptional CO_2 permeance at a selectivity of 33, we

believe, is the result of gaps between rigid sheets of 1 and PDDA.

Similar behavior was found for PEMs made from 1/2 and 1/3, except that maximum permeation selectivities were reached after depositing only two bilayers (Figures 4 and 5). The lower H_2 , CO_2 and N_2 permeances that were observed, on going from $(1/PDDA)_2$ to $(1/2)_2$, to $(1/3)_2$, is consistent with our hypothesis of increased membrane tightness due to hydrophobic interactions and pi stacking. Fig. 6 shows that this same trend can be correlated with surface roughness; i.e., as the membrane becomes tighter, its surface becomes smoother as evidenced by the root mean square surface roughness (RMS) values of 3.57, 2.10 and 1.47 nm, respectively.

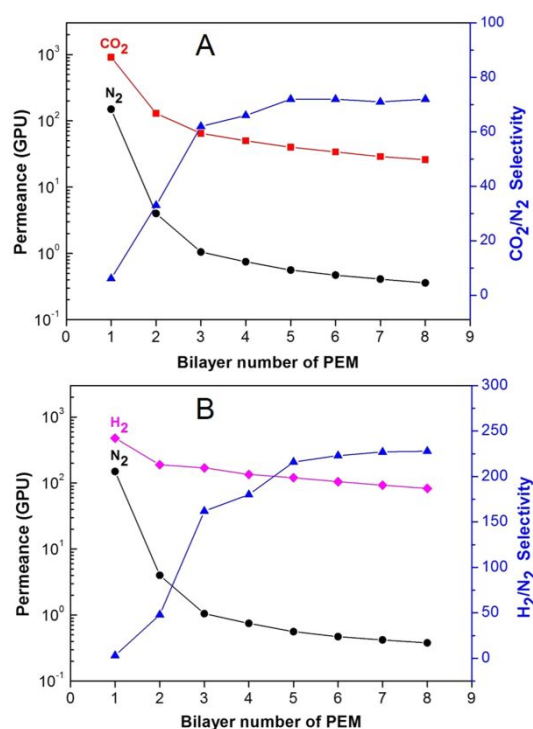


Fig.3 Permeances and selectivities as a function of number of bilayers of 1/PDDA for (A) CO_2/N_2 and (B) H_2/N_2 .

To place of the performance of these membranes into perspective, we compared the one PEM from each series having the highest CO_2 permeance and a CO_2/N_2 selectivity ≥ 30 with the graphene oxide-based membrane previously reported.⁹ Both the bilayer membrane derived from 1/PDDA and the graphene oxide-based membranes previously reported showed impressive CO_2 permeances with CO_2/N_2 selectivities in excess of 30. Those membranes derived from 1/2 and from 1/3 were less impressive.

To the best of our knowledge, the only membrane materials reported to date that have exceeded the performance of 1/PDDA, have required the presence of amine groups for facilitated transport or poly(ethylene glycol) units for enhanced CO_2 solubility.⁴

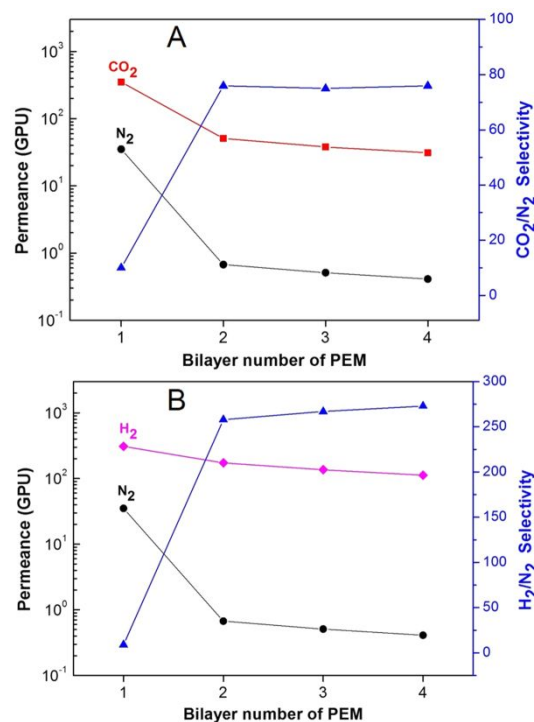


Fig.4 Permeances and selectivities as a function of number of bilayers of 1/2 for (A) CO_2/N_2 and (B) H_2/N_2 .

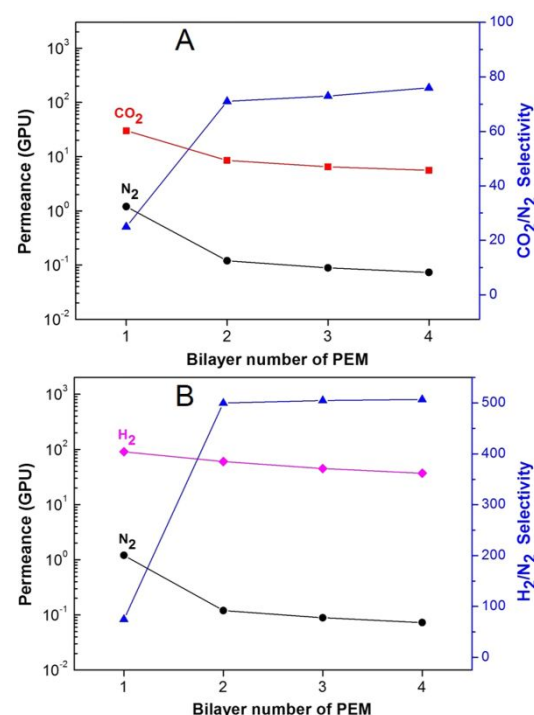


Fig.5 Permeances and selectivities as a function of number of bilayers of 1/3 for (A) CO_2/N_2 and (B) H_2/N_2 .

Because both such functionalities are sensitive towards autoxidation (as opposed to graphene oxide and 1/PDDA), and because such degradation is likely to limit their long-term use in the real-world separation of CO_2

and N₂ from flue gas, they have not been included in this comparison.

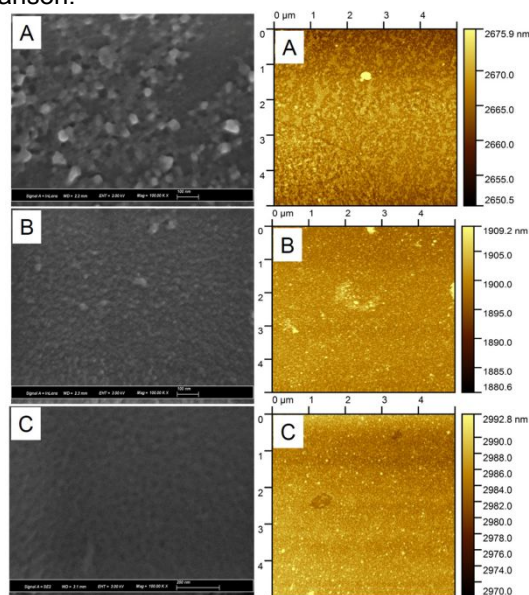


Fig. 6 SEM (left) and AFM (right) micrographs obtained for A: (1/PDDA)₂, B: (1/2)₂ and C: (1/3)₂ on PTMSP supports.

The experimental ease of the LbL method in assembling membranes based on **1** and PDDA, together with its applicability to hollow fiber supports (where surface areas can be an order of magnitude higher than those of flat membranes), highlights the potential of such assemblies as membranes for the capture of CO₂ from flue gas. Given the variability in the CO₂ permeances among (1/PDDA)₂, (1/2)₂ and (1/3)₂, it's reasonable to expect that even higher CO₂ permeances should be possible through systematic structural and compositional changes in such PIM-based PEMs.

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Conflicts of interest

There are no conflicts to declare.

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