

# Creating Hyperthin Membranes for Gas Separations

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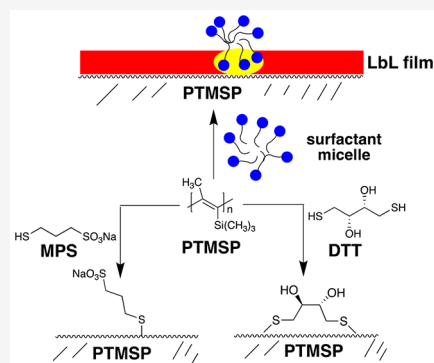
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**ABSTRACT:** Interest in creating membranes that can separate gases has intensified in recent years owing, in large part, to climate change. Specifically, the need for separating CO<sub>2</sub> and N<sub>2</sub> from flue gas in an economically viable fashion is now considered urgent. This Perspective highlights two recent developments from my laboratory—defect repair of polyelectrolyte multilayers (PEMs) using micellar solutions of sodium dodecyl sulfate (SDS) and the surface modification of a highly permeable polymer, poly[1-(trimethylsilyl) propyne] (PTMSP)—which I believe have significant implications not only for this CO<sub>2</sub>/N<sub>2</sub> problem but also for the ever-growing area of layer-by-layer (LbL) thin films. A brief mention is also made of past efforts that have been aimed at creating hyperthin membranes from porous surfactants and from PEMs with a view toward gas separations.



## INTRODUCTION

Considerable interest in the separation of gases using polymer membranes continues to grow.<sup>1</sup> Much of this interest stems from practical developments that have recently emerged. The membrane-based recovery of H<sub>2</sub> from H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CH<sub>4</sub>, and H<sub>2</sub>/CO mixtures is one such example where the market size now exceeds ca. \$200 million/year. Natural gas treatment applications that use polymer membranes to separate CH<sub>4</sub> from CH<sub>4</sub>/CO<sub>2</sub>, CH<sub>4</sub>/H<sub>2</sub>S, and CH<sub>4</sub>/He mixtures represent a market size that exceeds \$300 million/year. In principle, new polymer membranes should lead to significant advances in (i) the removal of CO<sub>2</sub> from natural gas, (ii) the separation of olefins from paraffins, and (iii) the separation of ethanol from water.<sup>1</sup>

One gas mixture that is currently attracting worldwide attention because of climate change is CO<sub>2</sub>/N<sub>2</sub>.<sup>2</sup> Specifically, flue gas that is emitted from power plants is now considered to be the major anthropogenic source of CO<sub>2</sub> and the major source of global warming.<sup>2</sup> A typical composition of flue gas that is produced from coal-fired boilers consists of 12 vol % CO<sub>2</sub>, 8 vol % H<sub>2</sub>O, 5 vol % O<sub>2</sub>, and 75 vol % N<sub>2</sub>. Although a practical method has been devised for removing H<sub>2</sub>O from flue gas, the major challenge has been to develop an economically viable means for separating CO<sub>2</sub> from N<sub>2</sub>.<sup>3,4</sup> Because membrane technology has relatively low energy and capital requirements, it has attracted broad attention.<sup>4</sup> It should be noted, however, that significant advances continue to be made with the creation of novel physisorbents and chemisorbents that can selectively capture CO<sub>2</sub>.<sup>5,6</sup>

In this Perspective, I will briefly highlight our own efforts in the gas separation area with a special emphasis on the CO<sub>2</sub>/N<sub>2</sub> problem. The common theme that runs throughout all of our studies in this area has been the design and synthesis of

“hyperthin” membranes, i.e., membranes that are much thinner than ca. 100 nm. My primary purpose in writing this Perspective is to draw attention to two recent advances that we have made, which I believe can serve as a starting point for future research not only in the gas separation area but also for the ever-growing area of layer-by-layer thin films.

## WHY HYPERTHIN MEMBRANES?

The reason that hyperthin membranes are important for gas separations is very simple. The answer comes, directly, from the solution-diffusion model for gas transport.<sup>1</sup> According to this model, the flux of a gas ( $J$ ) is directly proportional to an intrinsic permeability coefficient ( $P$ ) and the applied pressure gradient ( $\Delta p$ ) and inversely proportional to the membrane's thickness ( $l$ ) (eq 1). Thus, thin membranes are especially desirable because they maximize a permeant's flux across a membrane.<sup>7</sup> Although  $P$  values are often used to compare the permeability of polymers, it is also common to use permeance values ( $P/l$ ), which are permeabilities that have been normalized with respect to membrane thickness. Permeances are calculated by dividing the observed flux by the applied pressure gradient that is used. Most often, permeances are recorded as GPU values (gas permeation units) where 1 GPU =  $1 \times 10^{-6}$  (cm<sup>3</sup>/cm<sup>2</sup>·s·cm Hg) (eq 2)

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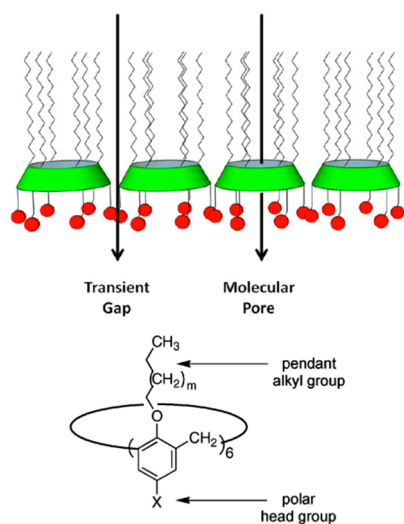
$$J = \frac{P \times \Delta p}{l} \quad (1)$$

$$\frac{P}{l} = \frac{J}{\Delta p} \quad (2)$$

From a basic science standpoint, the goal is to create not only membranes having high permeances but also ones that exhibit significant permeation selectivity. The latter is defined by the ratio of the permeances for two gases of interest, i.e.,  $(P_x/l)/(P_y/l)$ . Also, according to the solution-diffusion model, a permeability coefficient is the product of a diffusion coefficient ( $D$ ) and a solubility coefficient ( $S$ ), i.e.,  $P = D \times S$ . In other words, both solubility and diffusivity control the permeation properties of a polymer membrane. The main challenge in fabricating hyperthin membranes is to minimize the formation of defects (gaps in the membrane), which can reduce or eliminate permeation selectivity.<sup>7</sup>

### ■ FROM PERFORATED MONOLAYERS TO LAYER-BY-LAYER THIN FILMS

Our own efforts in the gas separation area began in 1988 with a seductively simple concept, i.e., the creation of “perforated monolayers from porous surfactants”.<sup>8</sup> Specifically, we hypothesized that a tightly packed monolayer or multilayer of porous surfactants would function like molecular sieves in which only those permeants that have kinetic diameters smaller than the pore diameter of the individual molecules would readily cross the membrane (Figure 1). On the basis of this concept, we made



**Figure 1.** (Top) Stylized illustration of a perforated monolayer from a porous surfactant. (Bottom) General structure of a porous surfactant derived from a calix[6]arene framework.

extensive use of Langmuir monolayers and Langmuir–Blodgett multilayers derived from calix[6]arene-based surfactants. An examination of space-filling models indicates that the calix[6]arene framework has a maximum pore diameter of ca. 0.48 nm. The real breakthrough for us in this area came shortly after Mark Conner joined my research group as a Ph.D. candidate. I do not remember if it was Mark or one of his co-workers at Air Products and Chemicals (possibly Lloyd Robeson) who suggested that we consider poly[1-(trimethylsilyl) propyne] (PTMSP) as a support material for our perforated monolayers.<sup>9</sup> In any event, this suggestion proved to be a godsend for us, and PTMSP has

since been our mainstay in this area. Our most important findings involving perforated monolayers have previously been reviewed and will not be discussed here.<sup>10</sup>

Because of its experimental simplicity and versatility, the layer-by-layer (LbL) method, which involves the alternate deposition of polyanions and polycations onto a suitable support, has become a popular alternative to Langmuir–Blodgett films.<sup>11–13</sup> For this reason, we have also examined hyperthin polyelectrolyte multilayers as potential membranes for gas separations. Because our most important findings have recently been reviewed, they will not be discussed in this Perspective.<sup>14</sup>

### ■ TWO RECENT DEVELOPMENTS

As is now widely recognized, the major challenge in stabilizing the earth’s atmosphere is to capture the CO<sub>2</sub> that is emitted by power plants from the combustion of fossil fuels.<sup>2</sup> A cost analysis for separating CO<sub>2</sub> from N<sub>2</sub> in flue gas via the use of polymer membranes led to two conclusions regarding the economics of this separation: (i) a CO<sub>2</sub>/N<sub>2</sub> selectivity that is much greater than 30 would have a negligible impact and (ii) the highest CO<sub>2</sub> permeance possible is very beneficial.<sup>15</sup> To date, the most promising polymers for this separation appear to be ones that are based on poly(ethylene glycol)s, where CO<sub>2</sub>/N<sub>2</sub> selectivities of ca. 50 and CO<sub>2</sub> permeances of ca. 1000–2000 GPU have been reported.<sup>15</sup>

In this section, I will discuss two recent developments from my laboratories that I believe could aid in the creation of new hyperthin polymer membranes for gas separations. One of these developments was based on rational design (defect repair). The other development came in the form of a serendipitous discovery that we made (polymer surface modification).

**Defect Repair of Layer-by-Layer Thin Films.** An intrinsic problem of hyperthin films that are fabricated via the LbL method is that they contain defects. These defects result from incomplete pairing of the ionic groups of the polyanions and/or the polycations, which is necessary for successful deposition. A consequence of such defects can be seen from the permeation properties of hyperthin PEMs that have been made from two of the most commonly used polyelectrolytes, i.e., poly(sodium 4-styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDDA).<sup>16</sup>

When one bilayer of PSS/PDDA is deposited onto 30- $\mu$ m-thick PTMSP that has been surface treated with branched poly(ethylenimine), the permeances of H<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub> are only slightly lower than those measured in the absence of this bilayer (Table 1).<sup>16</sup> While a slight increase in the H<sub>2</sub>/N<sub>2</sub> selectivity is apparent, the CO<sub>2</sub>/N<sub>2</sub> selectivity is essentially unchanged. The incremental addition of PSS/PDDA bilayers then leads to a steady decrease in permeance and a corresponding increase in permeation selectivity. Although a CO<sub>2</sub>/N<sub>2</sub> selectivity of >40 is achieved with four bilayers, this comes at the expense of the CO<sub>2</sub> permeance, which is now reduced to a value that is slightly greater than 40 GPU. If one considers the kinetic diameters for H<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub>, (0.289, 0.330, and 0.364 nm, respectively), then the higher permeances of CO<sub>2</sub> relative to those of the smaller H<sub>2</sub> molecule, across PTMSP and the composite membranes containing fewer than four bilayers of PSS/PDDA, indicate that solubility is playing a major role. However, when four bilayers of PSS/PDDA are present, the order of the H<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub> permeances reflects their relative size. This implies that diffusion now plays a major role and that film defects have been repaired. Such a repair can

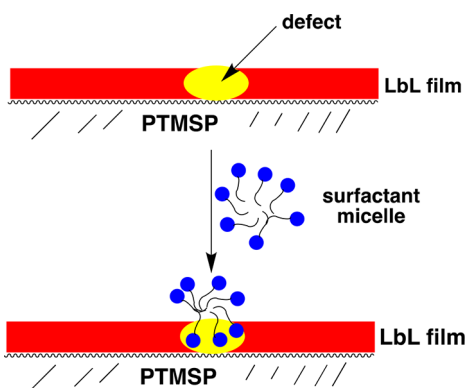
**Table 1. Permeances and Permeation Selectivities for PEMs Made from PSS/PDDA<sup>a</sup>**

bilayers (number) <sup>b</sup>	<i>l</i> (nm) <sup>b</sup>	H <sub>2</sub>	CO <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>
1	3	940	1900	420	2.2	4.5
1	3	850	1300	300	2.8	4.3
		840	1300	280	3.0	4.6
2	6	760	1200	220	3.5	5.5
		740	1200	210	3.5	5.7
3	10	370	670	65	5.7	10
		400	720	77	5.2	9.4
4	15	140	44	0.95	150	46
		140	40	0.94	150	43

<sup>a</sup>All permeances (GPU) and selectivities are from single gas measurements. <sup>b</sup>Film thicknesses were measured by ellipsometry.

best be thought of as a “self-patching” phenomenon. Specifically, because defects within a single polyelectrolyte bilayer will rarely overlap perfectly with defects in an adjoining bilayer, the resulting misalignment is expected to result in a patching of the defects in both bilayers.

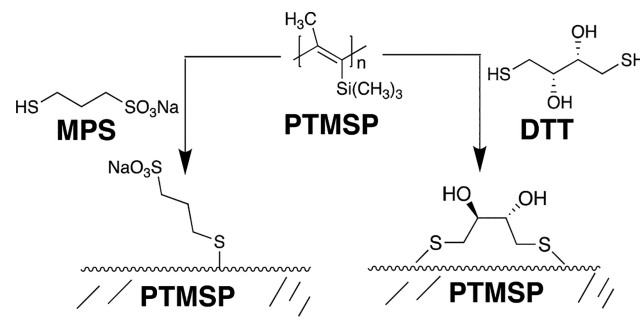
To improve the permeation properties of the hyperthin LbL film, we hypothesized that micellar solutions of an ionic surfactant would repair, i.e., “plug” defects. Specifically, we envisioned that the combination of micelles, micellar fragments, and monomers would fill in void space by binding to available sites through ionic as well as attractive van der Waals interactions (Figure 2). In a proof-of-principle study, we



**Figure 2.** Stylized illustration showing a surfactant micelle “plugging” a defect within an LbL thin film.

demonstrated that simple exposure of a single bilayer of PSS/PDDA to a micellar solution of sodium dodecyl sulfate (SDS) significantly improved its selectivity. Thus, a CO<sub>2</sub>/N<sub>2</sub> selectivity of 30 along with a CO<sub>2</sub> permeance of 200 GPU was observed.<sup>17</sup> We also showed that monomers, by themselves, were far less effective at repairing these defects.

**Polymer Surface Modification.** Recently, we sought to test the feasibility of replacing branched poly(ethylenimine) as an anchor layer for PTMSP by introducing sulfate groups along the surface of PTMSP. Specifically, we hypothesized that treating PTMSP with an aqueous solution of sodium 2-mercaptoethanesulfonate (MPS) under thiol–ene click reaction conditions would produce a surface that would readily bind PDDA (Scheme 1). What we soon discovered was that this surface-modified PTMSP, by itself, exhibited impressive permeation properties with a CO<sub>2</sub> permeance of 530 GPU and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 21.<sup>18</sup> A follow-up study that we carried out to test

**Scheme 1**

the influence of surface cross-linking using dithiothreitol as a cross-linking agent resulted in a CO<sub>2</sub>/N<sub>2</sub> selectivity of 37 and a CO<sub>2</sub> permeance of 410 GPU (Scheme 1).<sup>19</sup> Significantly, this trade-off of increased CO<sub>2</sub>/N<sub>2</sub> selectivity at the expense of a reduction in the CO<sub>2</sub> permeance raised the CO<sub>2</sub>/N<sub>2</sub> selectivity beyond the threshold value of 30, which is considered to be essential for practical exploitation. In preliminary studies, the storage of such membranes in a desiccator for 30 days at ambient temperature resulted in a decrease in their CO<sub>2</sub> permeance to 320 GPU along with an increase in the CO<sub>2</sub>/N<sub>2</sub> selectivity to 40.<sup>19</sup>

## MOVING FORWARD

I believe that the defect repair strategy that we have introduced and also the surface modification of PTMSP that we have serendipitously discovered will open new and important avenues for future research. I also believe that virtually all applications involving polyelectrolyte multilayers that are fabricated via the LbL method could benefit from such defect repair. Although we have explored SDS only as a repair agent, one could imagine a wide variety of other surfactants being used, e.g., porous surfactants for enhancing molecular sieving, gas-sensitive molecules for chemical sensing, and surfactant molecules of varying size and shape to enhance the barrier properties of a thin film for protective coating applications. Our serendipitous discovery that the selectivity of PTMSP can be significantly enhanced by simple surface modification should encourage related studies not just with PTMSP but with highly permeable polymers in general.

The question of whether LbL films that are repaired with micellar solutions and whether highly permeable polymers that are surface modified in ways that are similar to those that I have described can be considered for practical applications awaits appropriate testing under real-world operating conditions. For gas separations, the main issues that must be considered are aging, the influence of water vapor, the presence of other gases, and the physical and chemical stability of the membrane.<sup>19</sup> Finally, I point out that all of our work in this area has been based on the use of flat membranes. In principle, hollow fiber analogs that have surface areas that are 5 to 10 times greater per unit volume could be of even greater interest from a technology standpoint.<sup>20</sup> Thus, the footprint of a filtration system that employs hollow fibers made from a membrane material having a CO<sub>2</sub> permeance of 320 GPU could be compared with those based on flat membranes having a CO<sub>2</sub> permeance of 3200 GPU.

## AUTHOR INFORMATION

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### Notes

The author declares no competing financial interest.

### Biography



Steven L. Regen was born in Brooklyn, New York. He received a B.S. degree in chemistry from Rutgers University in 1968 and a Ph.D. degree from the Massachusetts Institute of Technology in 1972. He immediately began his academic career at Marquette University and subsequently joined Lehigh University in 1985, where he has served as a University Distinguished Professor since 1999. His research interests have mainly centered around gas separations, polymer chemistry, the lipid raft hypothesis, cholesterol's condensing effect, drug design, and drug delivery.

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