

V.P.27 Porous and Glued Ultrathin Membranes

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Objectives:

The long-term goal of this program is to create materials and methods that can be used to fabricate ultrathin (< 10 nm) membranes for the separation of H₂ from CO₂. The immediate objectives of this research are to examine the feasibility of (i) creating thin films via the layer-by-layer (LbL) deposition method, which exhibit reverse size-selectivity, and (ii) introducing a molecular sieving mechanism into ionically cross-linked (i.e., “glued”) Langmuir-Blodgett (LB) bilayers.

Technical Barriers:

Of the three main methods that are currently available for separating gases (i.e., adsorption, cryogenic and membrane methods), it is membrane technology that holds the greatest opportunity for improvement. Based on current technologies, it has proven difficult to prepare membranes that are thinner than ca. 100 nm without introducing major defects and losing selectivity. Thus, the creation of defect-free membranes that are less than 10 nm in thickness, which afford high flux rates and permeation-selectivities that exceed the “upper-bound”, would significantly increase the competitiveness of membrane technology for gas separations. This program seeks to create such membranes for the separation of H₂ from CO₂.

Abstract.

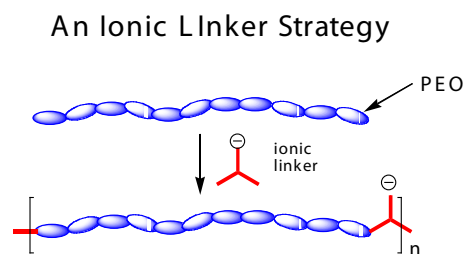
An ionic linker strategy has been developed for converting poly(ethylene oxide) into a polyanion that can form polyelectrolyte multilayers (PEMs) via the layer-by-layer deposition method. These polyanions have been combined with poly(allylamine hydrochloride) (PAH) to produce 7 nm-thick membranes having modest reverse He/CO₂ permeation selectivity favoring CO₂ by a factor of 1.3, and exceptional CO₂/N₂

size-selectivity, favoring CO₂ by a factor of >200. For these measurements, He has been used as a surrogate for hydrogen for safety reasons. In addition, a calix[5] arene-based surfactant has been synthesized that will be used to test the feasibility of introducing a molecular sieving mechanism into ionically cross-linked (i.e., “glued”) Langmuir-Blodgett (LB) bilayers.

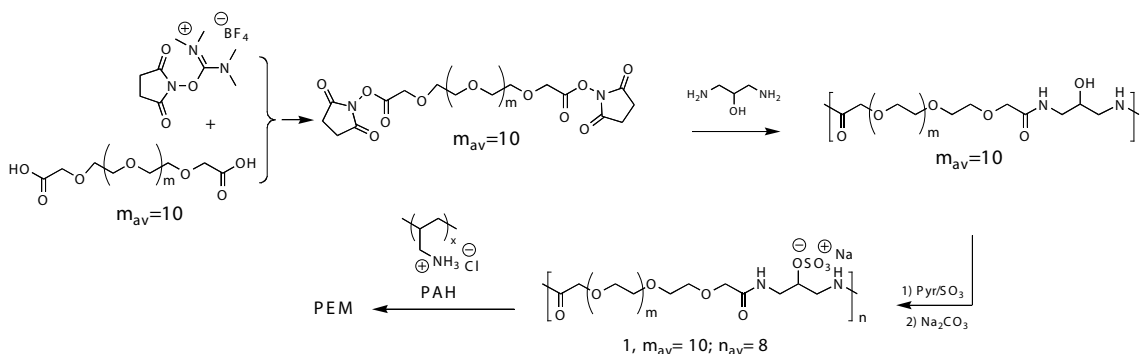
Progress Report

A. Reverse Selectivity of Layer-by-Layer Thin Films Derived From a Poly(ethylene oxide)-Based Polyelectrolyte. Polymers that contain poly(ethylene oxide) (PEO) are of considerable current interest as membrane materials for the separation of acid gases from light gases and hydrocarbons; e.g., the removal CO₂ from H₂/CO₂ and CO₂/N₂.¹⁻⁸ The main virtue of PEO for such separations is its affinity towards CO₂, which results in relatively high solubility and permeability.¹ In principle, the creation of ultrathin PEO-based films that combine high flux rates with such selectivity properties could lead the way to advanced materials and processes for the purification of hydrogen, as well as the removal of CO₂ from flue gases. While there have been several reports in the literature of gas permeation across polyelectrolyte multilayers (i.e., PEMs), to our knowledge, none have exhibited preferential CO₂ permeation over H₂ with film thicknesses below 10 nm.⁹

We have now shown how poly(ethylene oxide) (PEO) can be converted into a polyelectrolyte using an ionic linker strategy, and that this polymer is suitable for forming polyelectrolyte multilayers (PEMs) (Scheme 1). Specifically, we showed that **1** can combine with poly(allylamine hydrochloride) (PAH) to form (PEMs) via the layer-by-layer (LbL) deposition method (Scheme 2). We have also shown that such materials, in the form of 7 nm thin films, exhibit reverse size-selectivity favoring the permeation of CO₂ over He by a factor of 1.3. In the course of these studies, we also discovered that the permeation selectivity with respect to CO₂/N₂ (flue gas) has been found to be exceptional, favoring CO₂ over N₂ by a factor >200.¹⁰



SCHEME 1.



SCHEME 2.

Significance. This work has led to the introduction of a fundamentally new structural motif of polyelectrolytes that can be used for the construction of PEMs based on an ionic linker strategy. It has also demonstrated the feasibility of creating films that are 7 nm in thickness, which exhibit reverse size-selectivity, when poly(ethylene oxide) is converted into a polyanion. While the reverse He/CO₂ selectivity is only modest for such membranes (i.e., ca. 0.8), its size-selectivity for CO₂/N₂ (>200) is exceptional; the latter could be practical interest for membrane-based separations of flue gas.

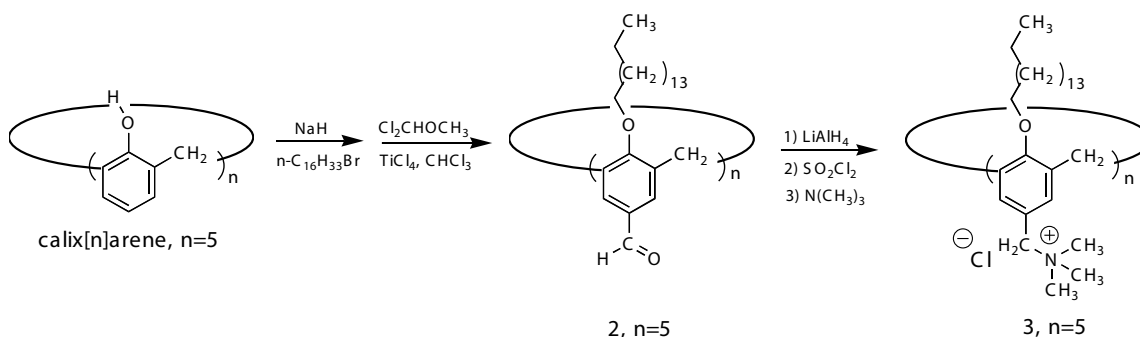
B. A Calix[5]arene for Glued Langmuir-Blodgett Membranes. During the course of the current grant period, a calix[5]arene-based surfactant, **3**, has been successfully synthesized and characterized using the sequence of reactions that are shown in Scheme 3.

Significance. The successful synthesis of **3** now provides us with an opportunity to determine whether a molecular sieving mechanism can be introduced into ionically cross-linked (i.e., “glued”) Langmuir-Blodgett (LB) bilayers. Specifically, since the *maximum* internal pore diameter of the calix[5]arene framework (0.36 nm) is closer to the kinetic diameter of CO₂ (0.33 nm), as compared to the calix[6]arene framework (0.48 nm), and since H₂ (0.28 nm) has a smaller kinetic diameter, one would expect that molecular sieving could make a

significant contribution to the permeation selectivity of calix[5]arene-based, glued bilayers.

Future Directions:

- Poly(ethylene oxide)-containing Polyelectrolyte Multilayers.** Our preliminary results with layer-by-layer thin films made from **1**/PAH are sufficiently encouraging that they warrant a detailed examination. Obvious extensions of this work, which will be explored, include a systematic study of the influence of (i) polyelectrolyte concentration, (ii) the size the poly(ethylene oxide) used to form the polyanion, (iii) the molecular weight of the polyanion that is used (iv) the formation of PEMs from polyanions and polycations that both contain poly(ethylene oxide).
- Introducing a molecular sieving mechanism into ionically cross-linked Langmuir-Blodgett (LB) bilayers.** Our expectation is that by decreasing the pore diameter of the calix[n]arene framework from n=6 to n=5, we will observe an intrinsic permeation behavior of this film that crosses the upper bound. Such behavior would lend strong support for a molecular sieving mechanism. To test this hypothesis, we will examine the barrier properties of two types of membranes: LB bilayers that have been glued together with (i) PSS, and (ii) poly(acrylic acid). It should be noted that in



SCHEME 3.

a previous study, we have shown that a calix[6]arene analog of **3**, formed glued LB bilayers with poly(acrylic acid) at pH 3.5 having exceptional He/CO₂ permeation selectivity; that is a selectivity of ca. 150, which lies close to the upper bound.¹¹ We think it's likely that the calix[5]arene analog (**3**) can “push” the barrier properties of such membranes across the upper bound, but this needs to be confirmed by experiment.

3. **A Change from He to H₂.** Until now, we have used He, extensively, as a surrogate for H₂ because it has a similar size, similar permeation behavior, and because it is non-combustible. However, we now intend to measure the permeation of H₂, directly, in a fume hood for laboratory safety.

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