## A Single Langmuir−Blodgett Monolayer for Gas Separations
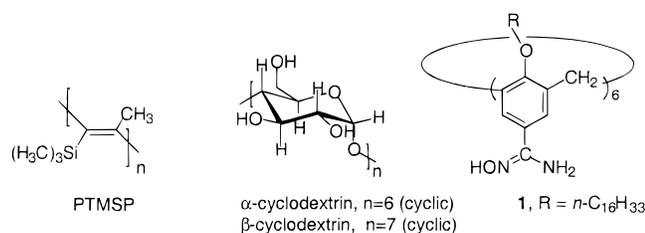
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In this paper we report the synthesis of novel composite membranes that use a single Langmuir−Blodgett (LB) monolayer as a separating layer. These membranes have been fabricated by using poly[1-(trimethylsilyl)-1-propyne] (PTMSP) as support material, α-cyclodextrin/sodium phenoxide or β-cyclodextrin/sodium phenoxide as a gutter layer, and a *single monolayer* of a calix[6]arene **1** as the primary barrier for transport.[1]



In an effort to create single monolayer composites, we have recently turned our attention to the surface modification of PTMSP. Specifically, we sought PTMSP film having a hydrophilic surface so that a single LB up-trip (water into air) would be possible. On the basis of the affinity of cyclodextrins toward hydrophobic pendant groups of polymers, we reasoned that a driving force should exist for their adsorption from water onto a PTMSP surface.[3] Thus, we hypothesized that the open microporous structure of PTMSP film would permit partial penetra-

A long-range goal that we have been trying to reach for the past decade has been to use *single* Langmuir−Blodgett (LB) monolayers as barriers for gas transport.[2] Our motivation for such work stems from the inverse relationship that exists between the flux of a gas across a membrane (*F*) and the thickness of that membrane (*l*), i.e., eq 1, where *A* is the area of the membrane,

$$F = P \cdot A \cdot \Delta p / l \tag{1}$$

$\Delta p$ is the pressure gradient that is used, and *P* is the permeability coefficient that characterizes the membrane/permeant combination. Thus, thin membranes are more productive than thick ones, provided that defects can be minimized and that permeation selectivity is maintained. To date, our ability to fabricate relatively defect-free composites has been strictly limited to LB *multilayers* of calix[n]arenes on cast films of PTMSP.[2]

tion into the surface of the polymer so that hydrophobic contact between the cyclodextrin interior and the pendant trimethylsilyl and/or methyl groups would be possible. Because of the large diameters of the cyclodextrins (i.e., 13.7, 15.3, and 16.9 Å for α-, β-, and γ-cyclodextrins, respectively) relative to ca. 10 Å pores that have been estimated within cast films of PTMSP, absorption into the bulk polymer was viewed as highly improbable.[4] Thus, significant coverage by cyclodextrins was expected to lead to a hydrophilic surface as a result of the cyclodextrin's hydroxylic exterior.

With the above rationale in mind, surface modification experiments were carried out as follows: Thin films (ca. 15 μm) of PTMSP were cast onto clean glass plates and immersed into 80 mM aqueous solutions of α-, β-, and γ-cyclodextrin. Due to the limited water-solubility of β-cyclodextrin, an elevated temperature (60 °C) was used in this case. Films were then removed as a function of time, rinsed with water, and allowed to dry in air. The minimal advancing contact angle for water that was reached in all cases was ca. 70°. As a point of reference, untreated PTMSP is strongly hydrophobic, having an advancing contact angle of ca. 112°. In related experiments, we were unable to modify the surface of cast films of poly(dimethylsiloxane), 1,2-poly(butadiene), polystyrene, polyethylene, and an octadecyltrichlorosilane-modified silicon wafer using an aqueous solution of α-cyclodextrin and identical procedures; i.e., advancing contact angles remained at ca. 112°, 94°, 90°, 105°, and 112°, respectively. These results support our hypothesis that an "open" hydrophobic film structure plays an important role in surface modification by cyclodextrins. For membrane fabrication studies, α- and β-cyclodextrin were deemed adequate as surface modifying agents.

To quantify the amount of adsorbed α- and β-cyclodextrins, modified films were rinsed with $CH_3OH$ until the contact angle of the surface returned to its original value of 112°. The combined methanol rinse from each sample was then concentrated by solvent evaporation under a stream of nitrogen, and the cyclodextrins were subjected to digestion (resorcinol/$H_2SO_4$).[5] Subsequent analysis (UV−Vis), using calibration curves that were made from known concentrations of the cyclodextrins, indicated surface loadings of 0.27 and 0.21 nmol/cm$^2$ of geometric area for α- and β-cyclodextrin, respectively.[5,6] These loadings correspond to ca. 2.6 monolayers, if it is assumed that the central axis of each cyclodextrin lies perpendicular to the surface of the film in a tightly packed array; a parallel alignment would correspond to ca. 1.6 monolayers. It should be noted that these estimates of surface coverage assume a surface area for the support that is equivalent to its geometrical area. Since surface roughness will tend to increase the film's true surface area, we interpret these loadings as approaching monolayer coverage. Analysis of α-cyclodextrin that was removed from a film by methanol rinsing, via electronic imaging of a TLC spot (silica gel, charred with $H_2SO_4$/heating), indicated a surface loading of 0.31 nmol/cm$^2$.[7]

Helium and nitrogen permeances (*P/l*) were then measured across bare PTMSP, cyclodextrin-modified PTMSP, and composites derived from cyclodextrin-modified PTMSP plus a single monolayer of **1** (Figure 1).[8] For each of these experiments, the

(1) For recent reviews of organic membranes for gas separations, see: (a) Stern, S. A. *J. Membr. Sci.* **1994**, *94*, 1. (b) Koros, W. J.; Fleming, G. K. *J. Membr. Sci*. **1993**, *83*, 1. (c) Koros, W. J. *Chem. Eng. Prog*. **1995**, *91*, 68. (d) Robeson, L. M.; Burgoyne, W. F.; Langsam, M.; Savoca, A. C.; Tien, C. F. *Polymer* **1994**, *35*, 4970. (e) Polymers For Gas Separations; Toshima, N., Ed.; VCH Publishers: New York, 1992. (f) Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165. (g) Maier, G. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2960.
(2) (a) Markowitz, M. A.; Bielski, R.; Regen, S. L. *J. Am. Chem. Soc.* **1988**, *110*, 7545. (b) Lee, W.; Hendel, R. A.; Dedek, P.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1995**, *117*, 6793. (c) Conner, M.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 1178. (d) Markowitz, M. A.; Janout, V.; Castner, D. G.; Regen, S. L. *J. Am. Chem. Soc.* **1989**, *111*, 8192. (e) Hendel, R. A.; Nomura, E.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6909.

(3) (a) Harada, A.; Adachi, H.; Kawaguchi, Y.; Kamachi, M. *Macromolecules* **1997**, *30*, 5181. (b) Gonzalez, B.; Casado, C. M.; Alonso, B.; Cuadrado, I.; Moran, M.; Wang, Y.; Kaifer, A. E. *Chem. Commun*. **1998**, 2569.
(4) Yampol'ski, Y. P.; Shantorovich, V. P.; Cherrynyakovski, F. P.; Kornilov, A. I.; Plate, N. A. *J. Appl. Polym. Sci.* **1993**, *47*, 85.
(5) Monsigny, M.; Petit, C.; Roche, A.-C. *Anal. Biochem.* **1988**, *175*, 525.
(6) Analysis of additional methanol rinses (beyond that which was needed to return the advancing contact angle to 112°) showed negligible cyclodextrins. In addition, analysis of methanol rinses of unmodified PTMSP showed no evidence of a neutral sugar. Finally, analysis of known quantities of α-cyclodextrin (deposited onto PTMSP via evaporation of a methanolic solution) showed that recovery by methanol rinsing was quantitative.
(7) Foto/Analyst Image Analysis System, Fotodyne, Inc., Hartland, WI.

**Table 1.** Normalized Fluxes of He and $N_2$ through Surface-Modified PTMSP[a]

| surface modification | $10^6 P/l$ (cm$^3$/cm$^2$·s·cm Hg) | | $\alpha_{He/N_2}$ |
|---|---|---|---|
| | He | $N_2$ | |
| none | 593 | 672 | 0.9 |
| α-cyclodextrin | 570 | 612 | 0.9 |
| β-cyclodextrin | 651 | 719 | 0.9 |
| | 667 | 737 | 0.9 |
| α-cyclodextrin/**1** | 668 | 697 | 1.0 |
| β-cyclodextrin/**1** | 439 | 110 | 4.0 |
| | 444 | 142 | 3.1 |
| α-cyclodextrin/NaOPh | 580 | 611 | 0.9 |
| β-cyclodextrin/NaOPh | 596 | 639 | 0.9 |
| α-cyclodextrin/NaOPh/**1** | 147 | 2.2 | 70 |
| β-cyclodextrin/NaOPh/**1** | 313 | 7.2 | 43 |
| | 238 | 6.0 | 40 |

[a] Permeance values ($P/l$) were calculated by dividing the observed flux ($F$) by the area of the membrane (1.19 or 9.36 cm$^2$) and the pressure gradient that was used (0.7 or 1.4 atm). Permeation selectivities are based on single-component permeances. All measurements were made at ambient temperatures. Values were obtained from 5–10 measurements; the error in each case was <5%. All LB transfers were made by using a subphase temperature of 25 °C, a constant surface pressure of 30 dyn/cm, and a dipping speed of 4 mm/min; the spreading solution was CHCl$_3$/CH$_3$OH (5/1, v/v), which contained ca. 1 mg of **1** per mL. Cast films of PTMSP were 15 μm in thickness.

PTMSP film was supported on a metal frame such that >60% of the film's surface was exposed on both sides.[2e] While no changes in permeation properties were observed after surface modification with α- or β-cyclodextrin, subsequent introduction of a single monolayer of **1** resulted in a slight increase in permeation selectivity (Table 1).[8] In an effort to reduce void space along the PTMSP/cyclodextrin surface, analogous films were prepared with 80 mM sodium phenoxide as an additive in the aqueous cyclodextrin solution (cyclodextrin/sodium phenoxide, 1/1), prior to LB transfer. Our presumption was that the adsorption of inclusion complexes on PTMSP, if possible, would provide a more contiguous hydrophilic surface that would help to minimize defects within the LB layer.[9,10] Whereas surface modification with α-cyclodextrin/sodium phenoxide did not alter the permeation properties of PTMSP, subsequent deposition of a single monolayer



**Figure 1.** Surface pressure−area isotherm for **1** over a pure water subphase at 25 °C, exhibiting hysteresis: (1) first compression; (2 and 4) second and third expansions, respectively; (3 and 5) second and third compressions, respectively.[2e] After two compression/expansion cycles the isotherm remained constant.

of **1** resulted in a dramatic increase in permeation selectivity (Table 1). Similar results were obtained using β-cyclodextrin/sodium phenoxide as an intermediate (gutter) layer.

The high permeation selectivity and extreme thinness of the membranes described herein are extraordinary. Given the recent emergence of methods that permit the continuous deposition of monolayers onto substrates, it would appear that the present findings may be translatable into practical membrane devices.[11]

(8) Specific procedures that were used for LB transfer and gas permeation measurements were similar to those previously reported.[2e] All transfers were made using a *single up-trip* (water into air); transfer ratios (defined as the decrease in monolayer area at the air−water interface divided by the geometrical area of the support that passes, vertically, through the interface) were 1.00 ± 0.05 in all cases. All transfers involved two films that were held "back-to-back" such that the LB monolayer was transferred to only one side of each PTMSP membrane.
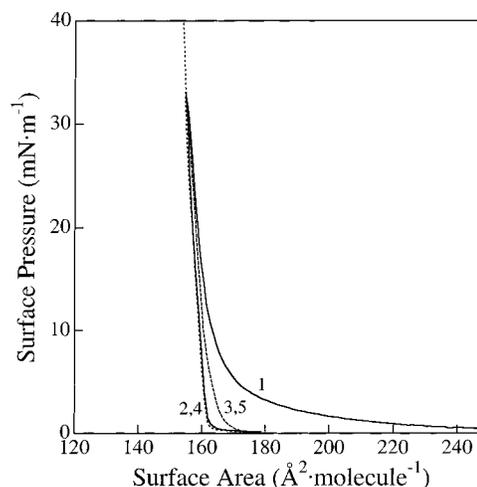
(9) The stability constant (log $K$) for complexes formed from phenol and α-cyclodextrin in water at 25 °C is 4.2; for β-cyclodextrin, it is 3.4: Rekharsky, M. V.; Inoue, Y. *Chem. Rev.* **1998**, *98*, 1875. On the basis of the observed differences in permeation behavior, we infer that a significant fraction of the adsorbed cyclodextrins is in a complexed form. We do not presently understand, however, how these complexes are held to the polymer surface.

(10) The advancing contact angle for PTMSP after modification by 80 mM α-cyclodextrin plus 80 mM sodium phenoxide was ca. 68°. The same contact angle was observed in the absence of sodium phenoxide.

(11) (a) Albrecht, O.; Matsuda, H. Apparatus and Process for Producing Organic Monomolecular or Multilayer Films. U.S. Patent No. 5,599,589, Feb. 4, 1997. (b) Picard, G.; Nevernov, I.; Alliata, D.; Pazdernik, L. *Langmuir* **1997**, *13*, 264.