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A Polymerized Calix[6]arene Monolayer Having Gas Permeation Selectivity that Exceeds Knudsen Diffusion

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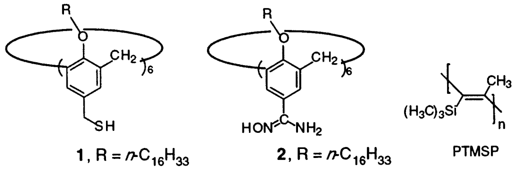
In this paper, we report the synthesis of a polymerized monolayer of 5,11,17,23,29,35-hexamercaptomethyl-37,38,39,40,41,42-hexakis-(1-*n*-hexadecyloxy)calix[6]arene (**1**) on the surface of an ca. 15 μm-thick film of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) (Chart 1). This monolayer represents the thinnest membrane (ca. 2.6 nm) reported to date, having a gas permeation selectivity that exceeds Knudsen diffusion. An analogous membrane derived from a nonpolymerizable calix[6]arene bearing amidoxime headgroups (i.e., **2**) showed typical Knudsen diffusion characteristics.

The design and synthesis of novel organic polymers, for use in gas separations, continue to attract considerable interest.[1] In particular, the creation of ultrathin, defect-free membranes that maximize gaseous flux and permeation selectivity has been a primary focus of attention. As shown in eq 1, gaseous flux (F) is inversely proportional to the thickness of a membrane (l) and directly proportional to its surface area (A), the applied pressure gradient (Δp), and the permeability coefficient that characterizes the membrane/permeant combination (P). Here, we show that *a single polymerized surfactant monolayer*, which is ca. 2.6 nm in thickness, exhibits gas permeation selectivity that exceeds Knudsen diffusion.[2]

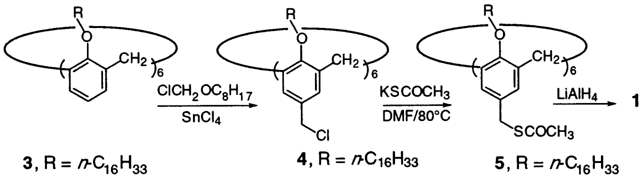
$$F = \frac{P \cdot A \cdot \Delta p}{l} \tag{1}$$

Calix[6]arene **1** was chosen as a target for this study for three reasons. First, thiol-based headgroups should allow **1** to be assembled at the air−water interface.[3] Second, intermolecular oxidative coupling to produce disulfide bonds would yield a cross-linked assembly. Third, changes in monolayer packing upon polymerization should be minimal, which would minimize the chances of forming defects. With these thoughts in mind, calix[6]arene **1** was synthesized by chloromethylation of 37,38,39,40,41,42-hexa-*n*-hexadecyloxycalix[6]arene (**3**) to give **4**, followed by thioester formation (**5**) and reduction with $LiAlH_4$ (Scheme 1).[4]

Chart 1



Scheme 1



As expected, **1** formed stable monolayers on the surface of water (Figure 1A). When a monolayer of **1** was compressed to 20 mN/m at 25 °C under an argon atmosphere, subsequent exposure to a 6.5 mm slit opening of a canal viscometer resulted in a steady decrease in surface pressure that was temperature-dependent (Figure 1B). A plot of the initial rate of the surface pressure decrease, $-(d\pi/dt)_o$, versus temperature is shown in Figure 1C. On the basis of the inflection point (and also the maximum of a second derivative plot), a solid-analogous to liquid-analogous phase transition is estimated to occur at ca. 32 °C; monolayers of **2** have shown such a transition at 31 °C.[5] When a monolayer of **1** was exposed to air for 60 min *before* exposure to the 6.5 mm opening, its surface pressure was fully retained after 40 min (Figure 1B). As discussed elsewhere, such a finding represents strong inferential evidence that the monolayer has undergone cross-linking.[4]

To characterize the gas permeability of a polymerized monolayer of **1**, PTMSP was chosen as support material due to its unique microporous structure.[6] In addition, two different methods of membrane fabrication were tested on the basis of the Langmuir−Schaefer (LS) horizontal lifting technique.[7,8] In method A, a monolayer of **1** was first compressed to 20 mN/m under an argon atmosphere. A PTMSP support was then placed, *horizontally*, on top of this monolayer. After exposure to air for 60 min, the support was removed, vertically, from the air−water interface at a rate of 1 cm/s. Recompression to 20 mN/m showed a transfer ratio (TR = decrease in monolayer area divided by the geometric surface area of the support) of 0.9 ± 0.1. A second method that was tested (method B) was similar to method A, except the monolayer was exposed to air *after* the transfer. For comparison, a monolayer of **2** was also transferred to PTMSP by the LS method (TR = 1.0 ± 0.1). All transferred films were maintained under an ambient atmosphere for 20 h prior to permeability measurements. Experimental procedures that were used to measure the flux of He and SF_6 were similar to those previously described.[6]

Our principal findings are reported in Table 1. In brief, polymerized monolayers that were prepared by methods A and B showed He/SF_6 selectivities (expressed as the ratio of individual permeances, P/l) that were signficantly *greater* than the theoretical value for Knudsen diffusion, that is, where $(P/l)_{He}/(P/l)_{SF6} = 6.04$ based on Graham's law. This finding indicates that the pores within the assembly are comparable in size to the permeants. Because He has a kinetic diameter of 0.26 nm, and the calix[6]arene has a *maximal* internal pore diameter of a ca. 0.48 nm (CPK models), He may diffuse through as well as between individual surfactants.[9−11] For the larger SF_6 molecule (kinetic diameter = 0.55 nm), however, diffusion is possible only between the calilx[6]arenes.[11] The

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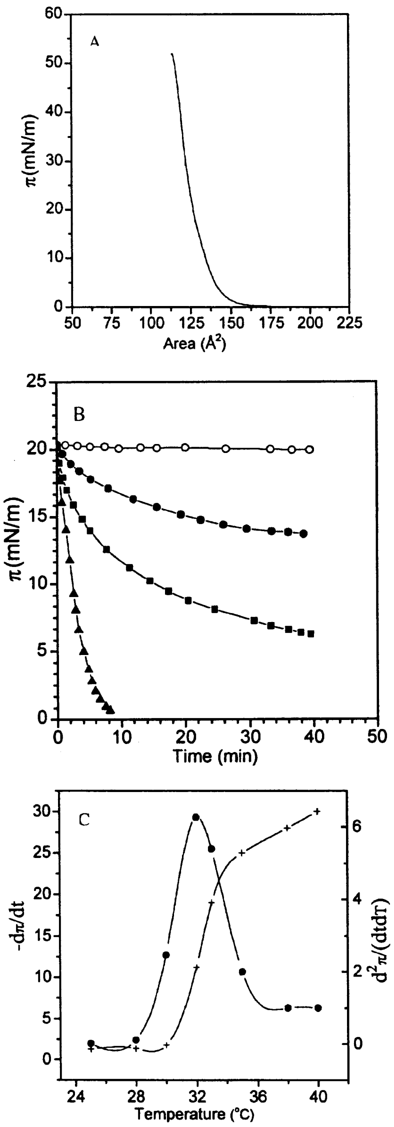

Figure 1. (A) Surface pressure−area isotherm for **1** over a water subphase at 25 °C under an argon atmosphere. (B) Surface pressure as a function of time for monolayers of **1** that have been maintained under an argon atmosphere at 25 °C (●), 32 °C (■), and 40 °C (▲), or air (after incubating in air for 60 min) at 25 °C (○), and then exposed to a 6.5 mm slit opening of a canal viscometer. (C) Initial rate of surface pressure decrease as a function of temperature for monolayers of **1** (+); also shown is a second derivative plot of these data (●).

Table 1. Permeance of He and SF_6 across Surfactant Monolayers[a]

monolayer on PTMSP	transfer method	$10^6 P/l$ (cm³/cm² s cm Hg) He	SF_6	$(P/l)_{He}/(P/l)_{SF6}$
none		784	320	2.5
		825	315	2.6
polymerized **1**	A	825	77.1	10.7
	A	689	57.4	12.0
	B	724	65.3	11.1
	B	770	68.7	11.2
2		684	123	5.6
		663	137	4.8

[a] Permeance values (P/l) were calculated by dividing the observed flux (F) by the area of the membrane and the pressure gradient used (10 psig). All measurements were made at ambient temperatures. Values were obtained from 5 to 10 measurements; the error in each case was <5%. All transfers were made using a subphase temperature of 25 °C. PTMSP supports were typically 15 μm in thickness.

permeation selectivity that we have found for monolayers of **2** was characteristic of Knudsen diffusion; bare PTSMP exhibited a lower degree of selectivity.[12] It is presumed that cross-linking contributes to the relatively high compactness of polymerized monolayers of **1**.

To demonstrate improved robustness resulting from cross-linking, a monolayer of **1** was tranferred to a silicon wafer (previously treated with *n*-octadecyltrichlorosilane) by the LS method. In one experiment, the monolayer was maintained under argon before and after the transfer. Gentle rinsing with chloroform resulted in the complete removal of the calix[6]arene layer, as indicated by ellipsometry. In contrast, a transferred monolayer, which had been allowed to polymerize in air for 2 h prior to rinsing, showed a thickness of ca. 2.6 nm (estimated via ellipsometry), which is one-half the value of a Langmuir−Blodgett bilayer (ca. 5.3 nm) obtained by one vertical down- and one vertical up-trip.

The fabrication of a 2.6 nm-thick polymeric membrane, having a gas permeation selectivity that exceeds Knudsen diffusion, represents a milestone in the area of gas separations. It also raises the intriguing possibility that similar membranes may be obtainable by use of self-assembly methods. Efforts currently in progress are aimed at exploring such a possibility.

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Supporting Information Available: Procedures for the synthesis of **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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