

Gluing Langmuir–Blodgett Monolayers onto Hydrocarbon Surfaces

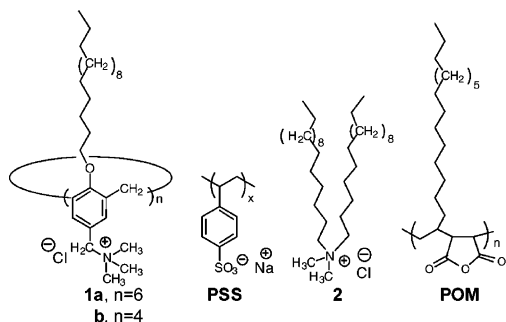
Junwei Li, Vaclav Janout, and Steven L. Regen*

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015

Received September 23, 2005; Revised Manuscript Received November 17, 2005; E-mail: slr0@lehigh.edu

Organic thin films are of considerable current interest for a wide range of applications, including the fabrication of optical devices, sensors, transducers, protective coatings, permeation-selective barriers, patternable surfaces, and biomaterials.^{1,2} Although the structure, composition and uniformity of the surface of such films play an important role in many of these applications, “brute-force” methods of surface modification (e.g., oxidation via corona discharge and plasma treatment) continue to be widely used.³ Devising mild and efficient methods for introducing functional groups to hydrocarbon surfaces, with precise control over their density and distribution, remains as a major challenge.^{4,5} Here, we describe one promising new approach that is based on the use of ionically cross-linked (i.e., “glued”) monolayers.⁶ Specifically, we show how Langmuir–Blodgett (LB) monolayers that have been assembled from a multiply charged, calix[6]arene-based surfactant (**1a**) and glued together with poly(4-styrene sulfonate) (PSS, MW 30,000–50,000) form a stable coating on hydrocarbon surfaces with their polar headgroups extending outward into air (Chart 1).^{6,7}

Chart 1



Consider a hydrophobic substrate that has been passed, vertically, down through a compressed monolayer of surfactant at an air–water interface. Normally, the substrate “picks up” the assembly and becomes hydrophilic while immersed in the subphase (Figure 1).⁷ If the monolayer that remains at the air/water interface is then decompressed, and the substrate withdrawn into air, the surfactant is expected to return to the water surface; that is, such processes are normally reversible.⁸ Now consider a hypothetical experiment, which uses a surfactant bearing multiple hydrocarbon chains and multiple ionic headgroups that have been ionically cross-linked by a polymeric counterion.⁶ Here, increased interaction between the substrate and the monolayer, and increased cohesiveness within the thin film, due to multiple hydrocarbon contacts and ionic cross-linking, has the potential for preventing the return of the surfactant to the water surface. In principle, this could lead to a modified surface in which the polar headgroups extend outward into air (Figure 1).

To test this hypothesis, a monolayer of **1a** was spread on the surface of an aqueous subphase containing PSS (5 mM repeat unit concentration, 25 °C), and compressed to 30 dyn/cm at a rate of 25 cm²/min. A silicon wafer, which had been previously silylated

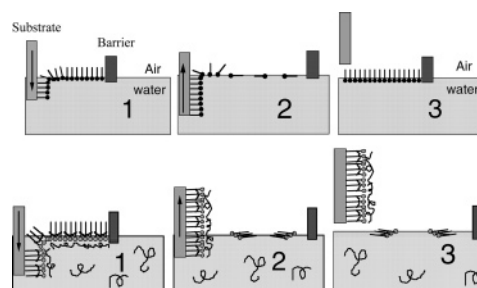


Figure 1. Stylized illustration. (Top): (1) Down-trip of a hydrophobic substrate through a compressed monolayer, picking up hypothetical surfactants, (2) decompression of the monolayer at the air/water interface, (3) removal of substrate into air, and return of surfactants to the water surface. (Bottom): Same as Top, except the surfactants bear multiple hydrocarbon chains and multiply charged headgroups, which are ionically cross-linked, resulting in retention on the substrate.

with *n*-octadecyltrichlorosilane (OTS), was then *immediately* passed, vertically, down through the monolayer at a speed of 2 mm/min. The transfer ratio was 1.0 ± 0.1 . After allowing the substrate to remain submerged for 60 min, the residual monolayer at the air/water interface was decompressed to 0 dyn/cm and the substrate removed, vertically, from the subphase. None of the surfactant returned to the water surface, as evidenced by the fact that recompression of the film to 30 dyn/cm showed the same occupied area as that found after the down-trip. After rinsing substrate with pure water, examination by atomic force microscopy (AFM) revealed a surface that was uniform on a micrometer-scale (Figure 2). The advancing contact angle for water was $46^\circ \pm 2^\circ$. Exposure to the laboratory ambient for an additional 48 and 120 h resulted in contact angles of $49^\circ \pm 1^\circ$ and $51^\circ \pm 1^\circ$, respectively. Retention of surface hydrophilicity was also evident after six repetitive washing cycles with pure water, where a contact angle of $51^\circ \pm 2^\circ$ was observed (the same value was observed after three washing cycles). The contact angle for water on the OTS-modified silicon wafer, itself, was $108^\circ \pm 2^\circ$. The ellipsometric thickness of this glued monolayer (2.6 ± 0.03 nm) was comparable to half the thickness of glued and unglued LB bilayers of **1a**, which were 2.82 and 2.4 nm, respectively.⁶ Further examination by X-ray photoelectron spectroscopy (XPS) revealed a S/N atomic ratio of ca. 1.3, which was independent of the “take off” angle used, from 11.5 to 53.1° (Figure 3). Also, an enrichment of both of these elements at the outer surface of the film was clearly evident.

A similar surface modification was performed with an OTS-modified silicon wafer, except that the monolayer of **1a** was transferred after first being incubated over the PSS subphase for 60 min at 30 dyn/cm. In separate experiments, we have found that the surface viscosity of such monolayers increases to a maximum during this time. In this case, the down-trip resulted in a transfer ratio of 0.7 ± 0.1 , indicating a less-than-perfect transfer. On the up-trip, none of the surfactant was returned to the water surface. Examination of this substrate by AFM showed the presence of defects, and a “peak-to-valley” distance of ca. 3 nm, which is consistent with ellipsometry measurements for such film (Figure

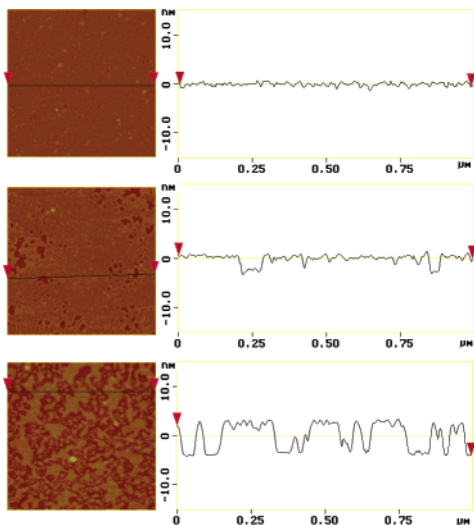


Figure 2. Height image and section profiles (AFM, tapping mode, $1 \mu\text{m} \times 1 \mu\text{m}$) of a deposited monolayer of **1a** on an OTS-modified silicon wafer using: (Top) an aqueous subphase containing 5 mM PSS; (Middle) same as Top, except that the monolayer was held for 60 min at 30 dyn/cm prior to transfer; (Bottom) a pure water subphase was used. All transfers were made using a speed of 2 mm/min and a surface pressure of 30 dyn/cm. Monolayers that were deposited from a PSS subphase were washed with water (three times, 10 min per rinse); the monolayer shown here, which was deposited from a pure water subphase, was examined without washing.

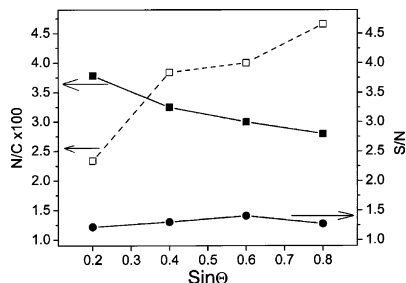


Figure 3. Atomic ratios of N/C ($\times 100$) for glued (\blacksquare) and unglued (\square) monolayers of **1a**, as well as S/N atomic ratios for glued monolayers (\bullet) determined by angle-resolved XPS. Monolayers were transferred to OTS-modified silicon substrates using a transfer speed of 2 mm/min and a surface pressure 30 dyn/cm. Here, Θ is the takeoff angle for XPS data collection. Prior to XPS analysis, the glued monolayer was washed with water (three times, 10 min per rinse); the nonglued monolayer was analyzed without rinsing.

2). A similar transfer of a monolayer of **1a** that was carried out in the absence of PSS showed a transfer ratio of 1.0 ± 0.1 and no return of the surfactant to the water surface on the up-trip. Before being rinsed with water, this surface was found to be rich in defects (Figure 2). The presence of such defects, together with a “peak-to-valley” distance of ca. 6 nm implies that the assembly has undergone rearrangement to bilayers. Examination by XPS, using various takeoff angles, showed a nitrogen content that was greater beneath the surface of the film (Figure 3). This result lends further support for a bilayer structure. Upon rinsing with water, **1a** was completely removed from this surface, as evidenced by a combination of ellipsometry and AFM measurements. Taken together, these results indicate that six alkyl chains per surfactant are sufficient to maintain contact with the OTS-modified silicon wafer during the up-trip, but that ionic cross-linking is essential for producing a stable assembly, which can retain its structure and orientation in air.

Control experiments that were carried out using a conventional double-chain surfactant (**2**), bearing one quaternary ammonium group, resulted in a transfer ratio of 1.0 ± 0.1 on the down-trip into aqueous PSS. On the up-trip, however, all of the surfactant

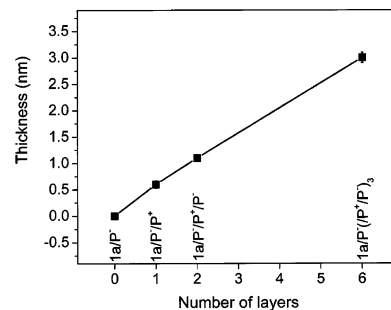


Figure 4. Plot of ellipsometric film thickness versus number of layers of polymeric counterions deposited onto a silylated silicon wafer that was modified with **1a**/PSS. Here, P^- is PSS and P^+ is PDADMA.

was returned to the air–water interface. When a polymeric surfactant [poly(octadecylmaleic anhydride), **POM**] was transferred to an OTS-modified silicon wafer, the transfer ratio on the down-trip was 1.0 ± 0.1 , and none of the surfactant was returned to the water surface on the up-trip. However, examination by AFM revealed a film that was rich in defects and a peak-to-valley distance of ca. 4.6 nm, implying that the assembly had undergone rearrangement, most probably to a bilayer structure (Supporting Information). Attempted use of **1b**, bearing four alkyl chains and four quaternary ammonium groups resulted in a transfer ratio of 1.0 ± 0.1 for the down-trip, but a significant return of the surfactant (ca. 30–50%) to the surface on the up-trip, in the absence and in the presence of PSS. Apparently, more than four alkyl chains and four quaternary ammonium groups are necessary to produce a stable coating.

In preliminary studies, we have found that glued monolayers of **1a** on OTS-modified silicon wafers, can be used to anchor alternating layers of PDADMA and PSS ions by conventional layer-by-layer dipping.^{9,10} Figure 4 shows the observed ellipsometric film thickness as a function of number of deposited layers. These thickness values, and the advancing contact angle for water of 55° for the final deposited layer of PSS are in good agreement with previous literature reports using hydrophilic substrates.¹¹

Studies that are currently in progress are being aimed at defining the full scope of this technique with a view toward the development of ultrathin, permeation-selective barriers.

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Supporting Information Available: Synthesis of **1b**, silylation, LB and layer-by-layer deposition, surface viscosity data, and AFM scans. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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