Macromolecules

Volume 41, Number 3 February 12, 2008

Communications to the Editor

Polymer-Enhanced Stability of Glued Langmuir−Blodgett Monolayers

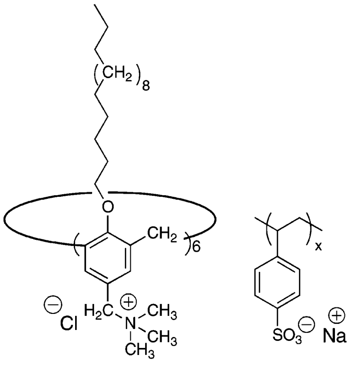
Yao Wang, Vaclav Janout, and Steven L. Regen*

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015

Received August 28, 2007
Revised Manuscript Received December 21, 2007

We have recently reported a new strategy for modifying hydrocarbon surfaces based on the use of glued Langmuir−Blodgett (LB) monolayers.[1−3] Specifically, we showed that a monolayer of **1**, which was ionically cross-linked (i.e., "glued") at the air/water interface with poly(styrenesulfonate) (PSS,) could be deposited onto a hydrocarbon surface by one LB down-trip (Chart 1). We further showed that a subsequent up-trip through a decompressed monolayer of **1** resulted in a modified surface without any additional surfactant being picked up from, or returned to, the air/water interface. This deposition behavior is in sharp contrast to conventional (i.e., non-glued) monolayers, where surfactants are often redeposited at the air/water interface on the up-trip under such conditions. In Figure 1, we show a stylized illustration of this difference.

Chart 1



1 **PSS**

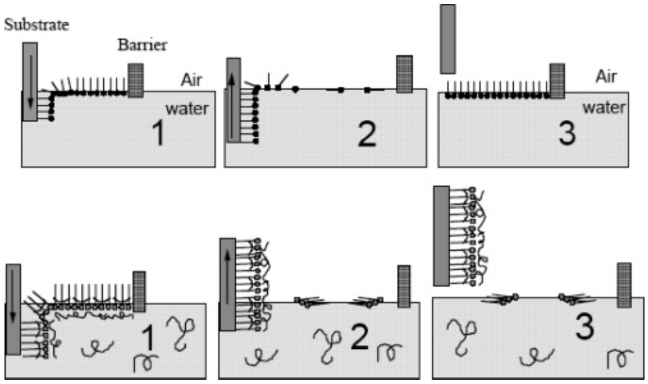
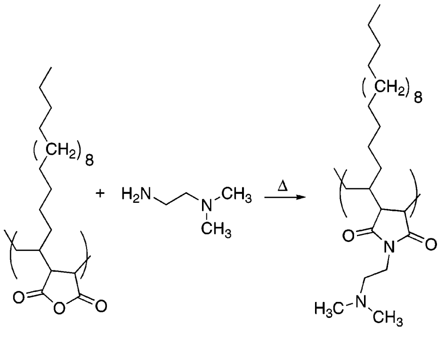


Figure 1. (A) Stylized illustration showing (1) a down-trip of a hydrophobic substrate through a compressed and non-glued surfactant monolayer, (2) decompression of the monolayer at the air/water interface, and (3) removal of substrate into air and return of surfactants to the air/water interface. Part B is the same as part A, except the surfactant monolayer is glued and remains intact as a monolayer upon removal into the air.

Scheme 1



POM **2**

Although the structure of this assembly was found to be stable after 24 h, as judged by atomic force microscopy (AFM) analysis, we have since discovered that extended contact with air results in a substantial change in surface structure. Apparently, the driving force for exposure of the hydrocarbon chains to air induces this rearrangement. In Figure 2, we show AFM

---

* Corresponding author. E-mail: slr0@lehigh.edu.

10.1021/ma701939p CCC: $40.75 © 2008 American Chemical Society
Published on Web 01/15/2008

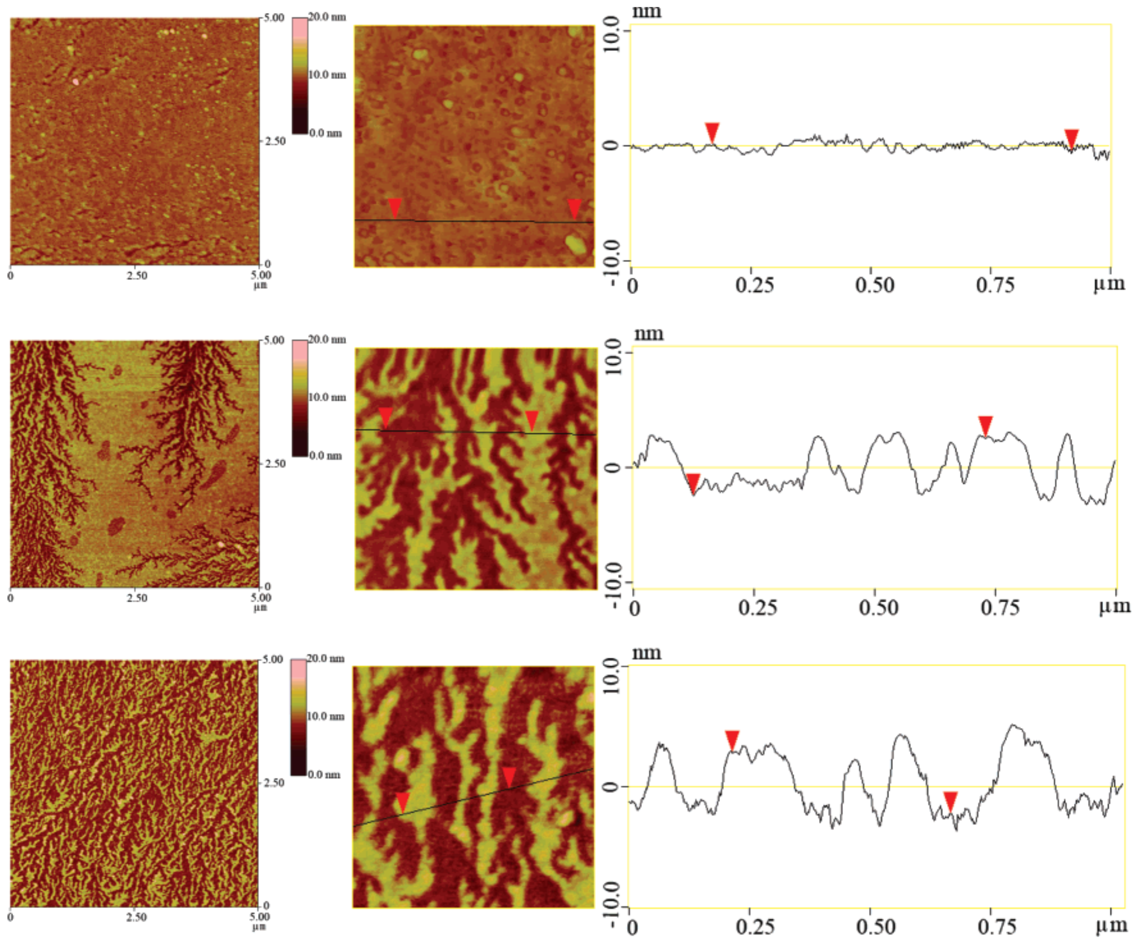


Figure 2. Height image (AFM, tapping mode 5 × 5 μm, left) and section profiles (1 × 1 μm, right) of a glued monolayer of **1** on a silicon wafer that had been silylated with *n*-octadecyltrichlorosilane after 22 h (top), 34 h (middle), and 73 h (bottom) exposure in air. Experimental conditions that were used to fabricate this film were similar to those previously described.[3,4]

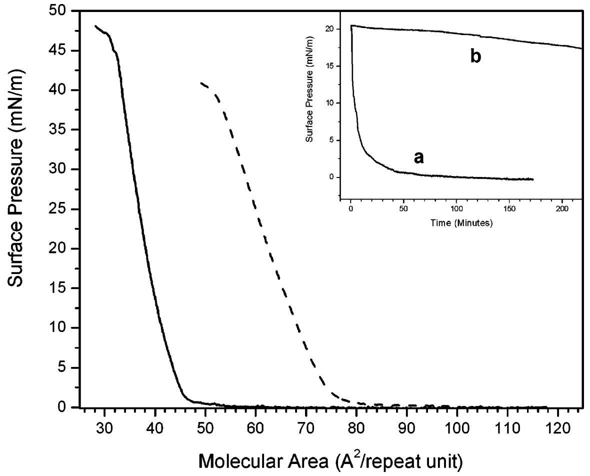


Figure 3. Surface pressure−area isotherms for **2** over water (solid line) and 5.0 mM PSS (dashed line) at 25 °C; inset shows surface viscosity over (a) water, and (b) 5.0 mM PSS after the monolayers were equilibrated at 20 dyn/cm for 60 min and subsequently exposed to a 6.0 mm slit opening of a canal viscometer.

images of such a surface after 22, 34, and 73 h in air. By extending this exposure time, initial “peak-to-valley” distances of ca. 0.5 nm increase to ca. 5.0 nm.

To improve the stability of such glued LB monolayers, we hypothesized that the substitution of **1** with a *polymeric* surfactant, having a large number of hydrophobic contacts with the substrate, would produce a more robust assembly. In this case, cooperative forces between the large number of hydrocarbon tails of the surfactant and the hydrocarbon surface would be expected to reduce the possibility of “turnover” and rearrangement of the assembly in air. In the work that is reported herein, we have tested this hypothesis using a simple imide derivative of commercially available poly(octadecylmaleic anhydride) (POM, average M_w ca. 40 000, Polysciences). Thus, **2** was readily obtained by treatment of POM with an excess of 2-dimethylaminoethylamine (Scheme 1).[5] At neutral pH, this polyamine is expected to be largely protonated and capable of being ionically cross-linked with PSS.

Prior to LB deposition, the monolayer properties and gluing behavior of **2** were first examined at the air/water interface. In Figure 3 are shown the surface pressure−area isotherms of **2** in the absence and in the presence of PSS in the aqueous subphase. Compression of **2** on the surface of pure water produced stable monolayers having a limiting area of ca. 42 ± 1 Å^2/repeat unit. Subsequent expansion and recompression cycles yielded the same surface pressure−area curve. Compression of **2** over an aqueous subphase containing 5.0 mM of repeat units of PSS (average M_w ca. 70 000, Aldrich) generated a similar surface pressure−area curve except that the limiting area increased to ca. 72 ± 1 Å^2/repeat unit.

We then tested the stability this glued monolayer of **2** in air, after being deposited onto a silicon wafer that had been silylated

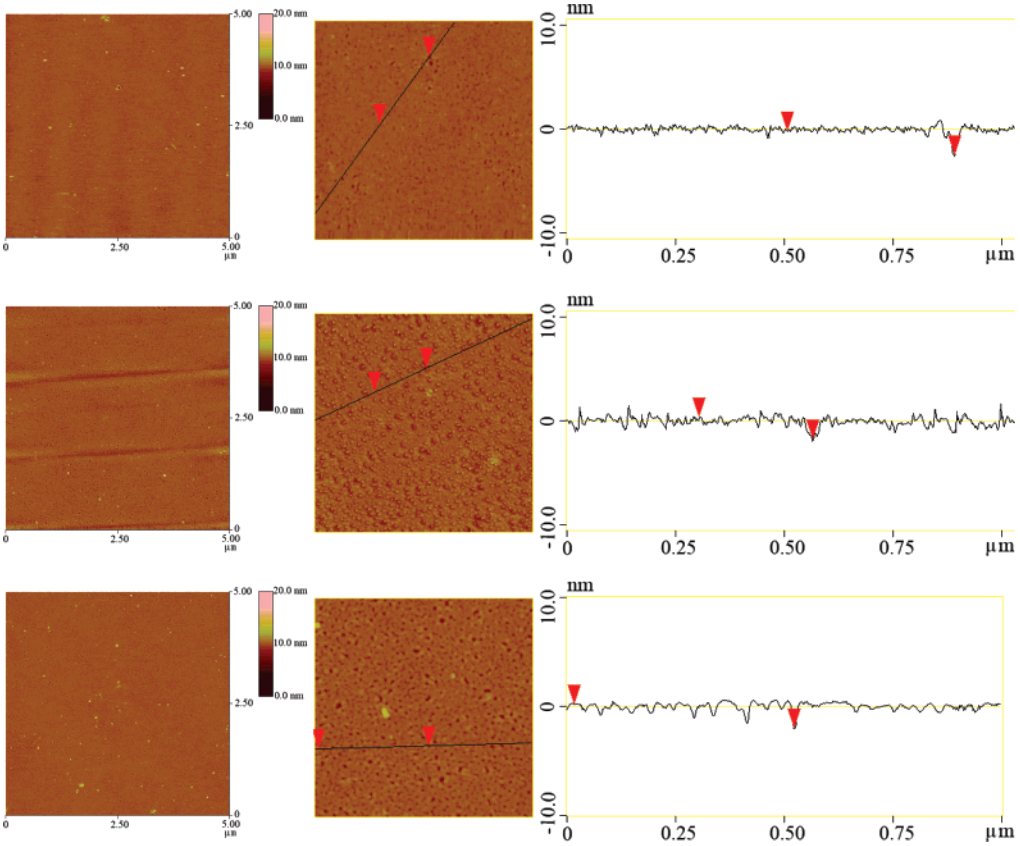


Figure 4. Height image (AFM, tapping mode 5 × 5 μm, left) and section profiles (1 × 1 μm, right) of a glued monolayer of **2** on a silicon wafer that had been silylated with *n*-octadecyltrichlorosilane and exposed to air for 24 h (top), 190 h (middle), and 274 h (bottom).

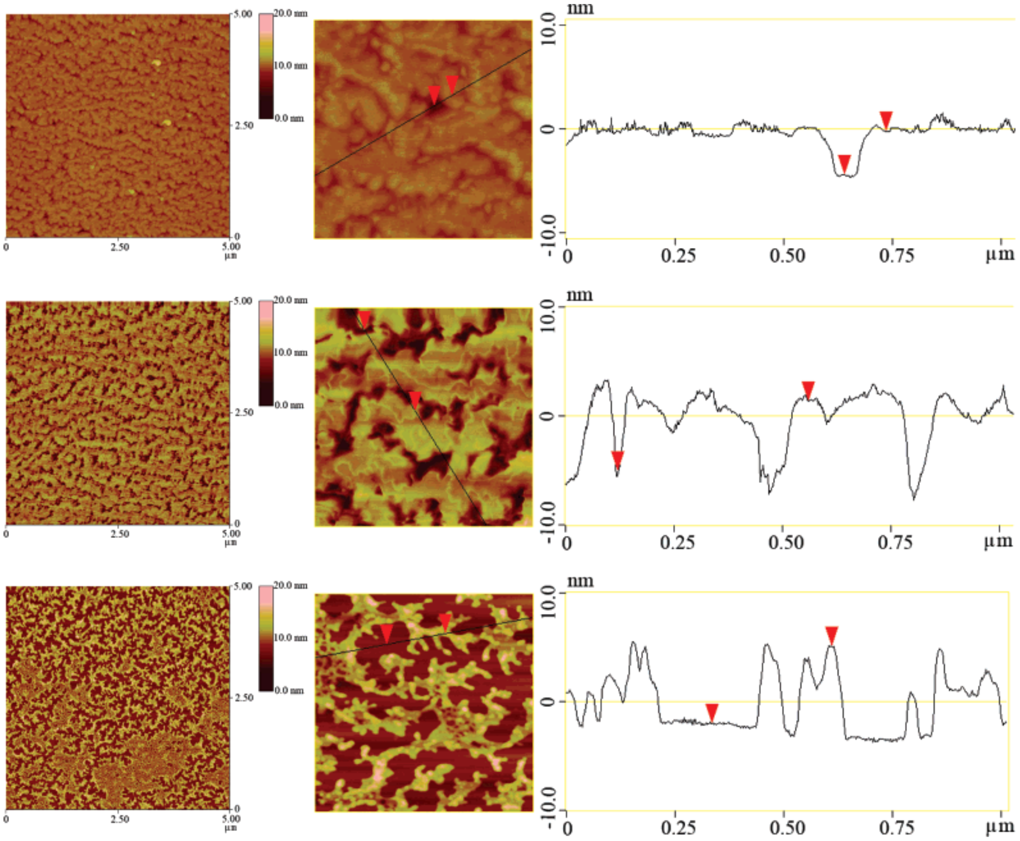


Figure 5. Height image (AFM, tapping mode 5 × 5 μm, left) and section profiles (1 × 1 μm, right) of a non-glued monolayer of **2** on a silicon wafer that had been silylated with *n*-octadecyltrichlorosilane and exposed to air for 24 h (top), 190 h (middle), and 274 h (bottom).

with *n*-octadecyltrichlorosilane (OTS). Experimental procedures that were used were similar to those previously described for the deposition of **1** on a similar surface.[1] In brief, a monolayer of **2** 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 30 cm^2/min. An OTS-modified silicon wafer 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 AFM revealed a surface that was uniform on a micron-scale (Figure 4).[1] The static and advancing contact angles for water on this surface were 56 ± 2 and 88 ± 1°, respectively.[7] By comparison, the static and advancing contact angles for water on the OTS-modified silicon wafer, itself, were 105 ± 2 and 116 ± 3°, respectively. Further examination of this surface by AFM after 190 and 274 h still showed the retention of a high quality of film. (Figure 4). In sharp contrast, a time-dependent AFM study revealed that a non-glued monolayer of **2** had poor stability in air (Figure 5).

Taken together, the present findings demonstrate that the use of a polymeric surfactant (**2**), in place of a non-polymeric surfactant that is capable of being ionically cross-linked (i.e., **1**), leads to significantly enhanced stability of a glued LB monolayer. Given the importance of surface structure and composition for a wide range of applications (e.g., optical devices, sensors, transducers, protective coatings, permeation-selective barriers, patternable surfaces, and biomaterials), the glued LB film approach for the modification of hydrocarbon surfaces offers a mild alternative to “brute-force” methods that continue to be widely used; that is, oxidation via corona discharge and plasma treatment.[8,9]

Acknowledgment. This work was supported by the Department of Energy (Grant DE-FG02-05ER15720).

References and Notes

(1) Li, J.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **2006**, *128*, 682−683.

(2) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience, New York, 1966.

(3) Ulman, A. *An Introduction to Ultrathin Films: From Langmuir-Blodgett to Self-Assembly*; Academic Press: New York, 1991.

(4) Heindel, R. A.; Nomura, E.; Janout, V.; Regen, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 6909−6918.

(5) To a solution of 0.325 g of poly(maleic anhydride-*alt*-1-octadecene) (Polysciences, MW 30000−50000 Da, 0.928 mmol) in 1.0 mL of toluene was added 0.420 g (4.77 mmol) of 2-(*N*,*N*-dimethylamino)-ethylamine. The mixture was sealed under an argon atmosphere, stirred for 24 h at 125 °C, and then cooled to room temperature. The resulting polymer was isolated by precipitation by adding the mixture to 100 mL of acetone. Further purification was by carried out by dissolving the polymer in 3 mL of chloroform and then precipitating it by dilution with 100 mL of acetone (three times). Subsequent drying (24 h, room temperature, 0.3 Torr) afforded 0.299 g (71%) of **2** as a colorless solid. ^{1}H NMR ($CDCl_3$/MeOD, 1/3, v/v): 3.55 (bm, 2H), 2.40−3.00 (bm, 4H), 2.21−2.40 (bs, 6H); 1.20−1.90 (m, 33H), 0.85 (t, 3H). IR (film): 3918, 3868, 1769, 1699 $cm^{-1.}$ Anal. Calcd for $C_{26}H_{48}N_2O_2 \cdot 1H_2O$: C, 71.23; H, 11.50; N, 6.39. Found: C, 71.44; H, 10.07; N, 6.79.

(6) Li, J.; Janout, V.; McCullough, D. H., III; Hsu, J. T.; Troung, Q.; Wilusz, E.; Regen, S. L. *Langmuir* **2004**, *20*, 8214−8219.

(7) The static and advancing contact angles for water on a similar surface that was modified with a glued monolayer of **1** were 52 ± 1 and 82 ± 1°, respectively.

(8) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932−950.

(9) Koberstein, J. T. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 2942−2956.

MA701939P