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Bilayer and Odd-Numbered Multilayers of Octadecylphosphonic Acid Formed on a Si Substrate Studied by Atomic Force Microscopy

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Introduction

Amphiphilic molecules tend to self-organize in water¹ or on a support medium.² It has been known that amphiphilic molecules in aqueous media aggregate to form various structures.¹ A Langmuir–Blodgett (LB) technique^{3–6} or a simpler method of solution spreading⁷ can be used to form amphiphilic molecular layers on a support. Bilayers consisting of two amphiphilic molecular layers with their hydrophobic tails facing together are the fundamental structure of membranes. A bilayer formed on a support^{8–11} or between a surface and a probe¹² can be used as a model system for investigations of its utilization in biological or man-made systems. Understanding molecular layer formation is thus important for any application of a bilayer structure on a support.

Recently, there have been reports of the use of octadecylphosphonic acid (OPA) molecules to form monolayers on mica^{13–15} and sapphire¹⁶ surfaces. When a diluted solution of OPA was used to wet the mica substrate, a monolayer of OPA was observed using atomic force microscopy (AFM). The headgroup of OPA molecules is found to be bonded to the mica surface, resulting in a monolayer having a great potential for application as an ordered surface providing hydrophobic chemistry.^{13–15} The monolayer on a mica substrate is very stable upon heating at temperatures up to 80 °C,¹⁴ indicating that the interaction between the hydrophilic headgroup and the mica surface is quite strong.

In this article, we describe experiments which explored another interesting aspect of OPA molecules on a Si

surface: the movement of these molecules due to their amphiphilic nature. We demonstrate OPA as a model system for understanding molecular movement and multilayer formation. To investigate this aspect of OPA molecules, a much higher concentration of ethanolic OPA solution was used than for preparing monolayers on mica.

AFM studies have revealed the formation of bilayer^{5,6} LB films, detailed molecular chain packings³ of LB films, and reorganization⁴ in LB films submerged in an aqueous medium. In the present study, we report a different system of OPA molecular layers prepared on a silicon substrate by a solution spreading method. Our OPA samples consisted of stacks of small layers and small dotlike structures. The OPA molecules were found to be highly mobile as evidenced by the experimental observation of a reorganization of layers and a formation of rodlike structures on bilayer surfaces at room temperature. Moreover, we observed a drastic change of morphology, that is, a formation of bilayers and odd-numbered multilayers, caused by a recrystallization of OPA molecules on a silicon substrate at elevated temperatures. In addition, friction force imaging using a silicon tip was able to distinguish the amphiphilicity of OPA molecular layers, identifying whether a layer is terminated by the hydrophilic headgroup or the hydrophobic tail.

Materials and Methods

A silicon wafer and a cleaved mica substrate were used as the support for preparing OPA samples. A concentration of 5 mM OPA (Alfa Aesar, Ward Hill, MA) solution in ethanol was used for preparing OPA samples on the Si surface, while a 2 mM solution was used for monolayer formation on the mica surface. A drop of OPA solution was placed on the support, and within 30 s the solution was blown away. Such an OPA sample prepared on a Si substrate was then heated to 50–60 °C for ~30 s using a thermoelectric module. The temperature of the sample surface was directly measured with a pyrometer (Omega OS-160).

Dynamic force mode AFM (Explorer, TopoMetrix) was employed to image OPA films prepared on the substrate before heat treatment. A rectangular silicon cantilever with a nominal spring constant of 40 N/m and resonant frequency of ~300 kHz was used. The cantilever was 125 μm long, 35 μm wide, and 4 μm thick. The tip integrated on the cantilever had an apex radius of ~20 nm. The oscillation amplitude in free space was on the order of 40 nm, and the set point (oscillation damping) for imaging was 50%.¹⁷

To study the friction force between the tip and OPA films on the Si surface after heat treatment, contact mode AFM was also used. A soft silicon cantilever with a sharp tip on its free end was used to detect the interaction between the tip and the sample surface. The rectangular silicon cantilever had a nominal spring constant of 0.05 N/m. The cantilever was 1.0 μm thick, 35 μm wide, and 300 μm long with a tip whose nominal apex radius was ~20 nm. A friction force image was obtained simultaneously with a topographic image. Typical imaging forces were repulsive and in the range of 1–5 nN. The output of the photodetector (photoinduced current in nA units) corresponding to the torsional movement of the cantilever was directly used to express friction force.¹⁸ All images were obtained in air with a typical relative humidity of about 50%. Each image consisted of 500 lines with 500 pixel points per line. The scan rate for images was 10 and

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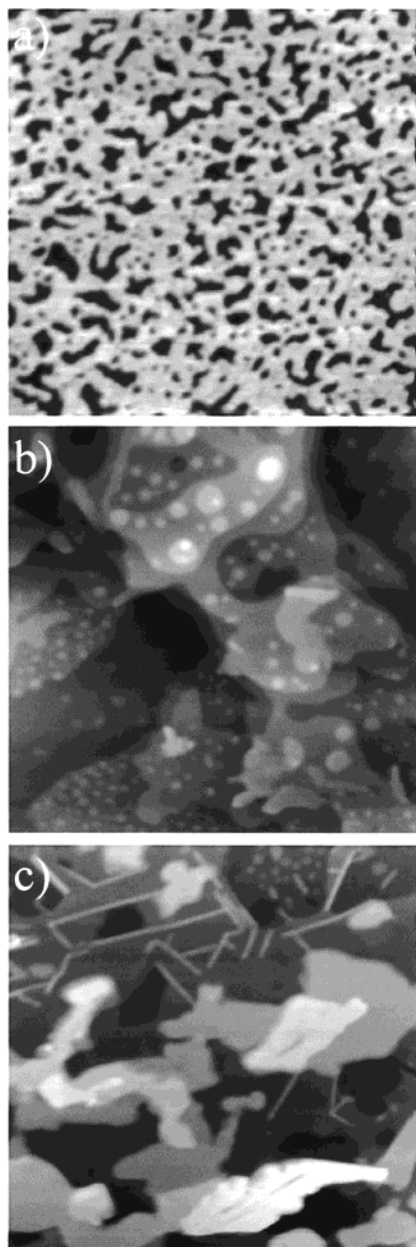


Figure 1. AFM images of (a) the monolayer prepared with a 2 mM ethanolic OPA solution on a mica substrate, (b) the flakelike layered structure of OPA prepared with a 5 mM ethanolic OPA solution on a Si substrate, and (c) crystallization of OPA after the sample shown in (b) was left in air for 4 days. The scan area is $1\ \mu\text{m} \times 1\ \mu\text{m}$ for (a) and $2\ \mu\text{m} \times 2\ \mu\text{m}$ for (b) and (c). The gray scales for the three images in (a)–(c) are 0 to 2, 18, and 14 nm, respectively.

40 $\mu\text{m/s}$ for the dynamic force and contact mode AFM, respectively.

Results and Discussion

Shown in Figure 1a is a dynamic force mode image of an OPA monolayer prepared in this laboratory on a mica substrate. The morphology and thickness ($\sim 1.5\ \text{nm}$) of the monolayer are similar to those reported elsewhere.^{13–15} By contrast, in Figure 1b an OPA sample freshly prepared on a Si substrate showed a stacked flakelike structure with small round dotlike features. The majority of the layers were found to have a thickness of $2.4 \pm 0.1\ \text{nm}$; this is close to the fully extended OPA molecular length of 2.5 nm.¹³ The dotlike features have a flat surface, and their thickness was found to be $2.8 \pm 0.1\ \text{nm}$. The monolayer

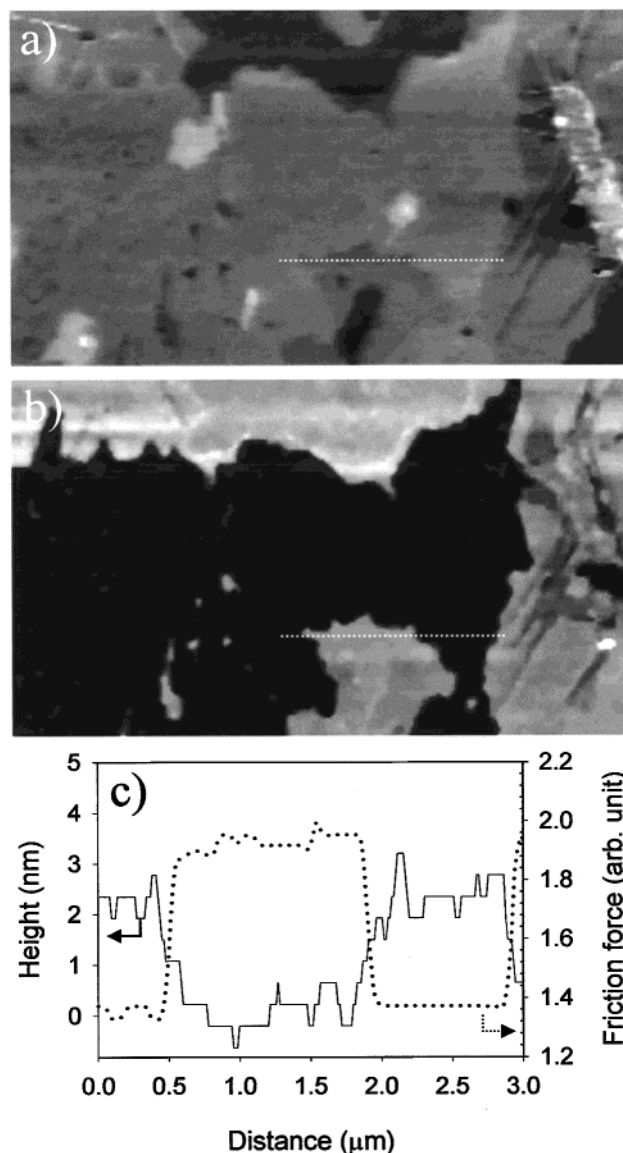


Figure 2. Topographic (a) and friction force (b) images (scan area, $8.0\ \mu\text{m} \times 4.5\ \mu\text{m}$) for the OPA sample prepared with a 5 mM ethanolic OPA solution on a Si substrate after a heat treatment at $50\text{--}60\ ^\circ\text{C}$. Shown in (c) are profiles indicated by inserted dotted lines in (a) and (b) for the height and friction force. The gray scale is 0–15 nm for (a) and 1.3–2.3 nA for (b). The friction force was directly expressed by the output of the photodetector (photoinduced current in nA units) corresponding to the torsional movement of the cantilever.

on a mica surface was previously found to have a thickness of only $\sim 1.6\ \text{nm}$,^{14,15} indicative of a tilted orientation. By contrast with this behavior on mica, OPA molecules oriented on silicon are fully extended.

After the OPA sample was left in air for 4 days, a clear change in morphology occurred as shown in Figure 1c: various shapes of crystalline domains with a thickness of 2.4 ± 0.1 or $4.7 \pm 0.1\ \text{nm}$ were observed; this corresponds to the monolayer and bilayer structures, respectively. Also, many rodlike structures were formed. These interesting rodlike structures seen in Figure 1c are $23 \pm 2\ \text{nm}$ wide and $150\text{--}650\ \text{nm}$ long, and their apparent height is $2.2\text{--}4.5\ \text{nm}$. From Figure 1b,c, it seems that the rodlike structure is formed by the rearrangement of the dotlike structure into one particular direction of growth. Also, the rodlike structure seems to be formed only on the bilayer surface. These changes in surface structure clearly indicate

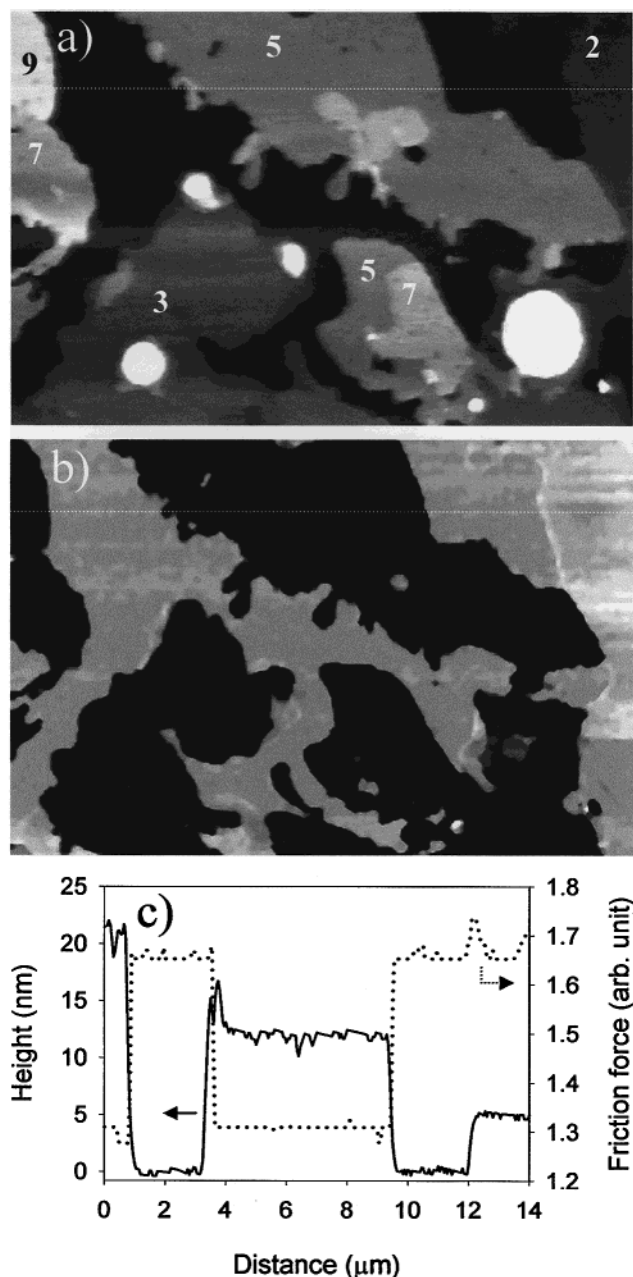


Figure 3. Topographic (a) and friction force (b) images (scan area, $14.0\ \mu\text{m} \times 8.8\ \mu\text{m}$) from the same sample used in Figure 2, showing the bilayer and odd-numbered multilayers. Numbers shown in (a) indicate the number of molecular layers in the multilayers. Shown in (c) are profiles indicated by inserted dotted lines in (a) and (b) for the height and friction force. The gray scale is 0–40 nm for (a) and 1.3–2.0 nA for (b). The friction force was directly expressed by the output of the photodetector (photoinduced current in nA units) corresponding to the torsional movement of the cantilever.

that the OPA molecules have a certain degree of freedom to move at room temperature. This contrasts with the monolayer on a mica surface which is very stable at temperatures up to $80\ ^\circ\text{C}$.¹⁴

Inspired by the observation that OPA molecules move even at room temperature, we explored the effects of a further increase in temperature on the molecular orientation. Shown in parts a and b of Figure 2 are topographic and friction force images, respectively, for an area on the OPA sample following a heat treatment at $50\text{--}60\ ^\circ\text{C}$ for ~ 30 s. A complete change of surface morphology was produced: the stacks of OPA layers such as those observed

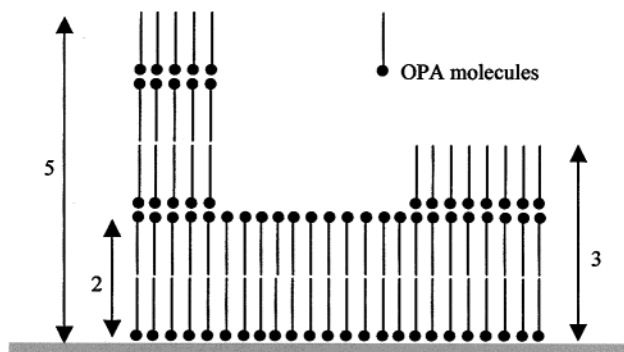


Figure 4. Schematic illustration showing a bilayer (2), a trilayer (3), and a 5-fold layer (5) of the OPA molecules on a support. Filled circles represent the hydrophilic headgroups of the amphiphilic molecule.

in Figure 1b were replaced by the large area layers shown in Figure 2a. Areas of bare Si substrate, for example, the dark area near the top in Figure 2a, are seen and hence are used as a reference to estimate OPA layer thickness. From a number of measurements on many areas, the thinnest layers have a thickness of 4.7 ± 0.3 nm. On the basis of this height estimation, it is believed that a bilayer was formed on the Si substrate following the heat treatment.

We also observed areas where there appear to be trilayers. A trilayer appears very faintly in the topographic image in Figure 2a because the height range is quite large compared to the thickness of a monolayer. However, the trilayer is clearly distinguished from the bilayer in the friction force image shown in Figure 2b. Profiles for the height and friction force at the same location indicated by dotted lines in Figure 2a,b are shown in Figure 2c. A thickness of 2.4 nm and a difference in friction force were measured between the bilayer and the trilayer. The friction force on the bilayer is larger than that on the trilayer and is similar to that on the bare Si substrate. From this, we surmise that the bilayer is terminated by the hydrophilic headgroup and the trilayer is terminated by the hydrophobic tail. The tip used to probe the different chemistry on the OPA sample is made of silicon. The silicon tip is covered by a native oxide layer, which is hydrophilic. Therefore, the contrast shown in Figure 2b is consistent with the difference in the hydrophilicity¹⁹ of the bilayer and trilayer.

Formation of multilayers greater than a trilayer was also observed in some areas of the OPA sample. Shown in parts a and b of Figure 3 are topographic and friction force images, respectively, obtained on an area where multilayer formation is observed. Shown in Figure 3c are one of the profiles measuring the thickness of the multilayers and the corresponding profile for friction force at the location indicated by dotted lines in Figure 3a,b. It is clear from the thickness measurement that, except for the bilayer, multilayers are of odd-numbered layers, that is, 3, 5, 7, and 9. The friction force image in Figure 3b clearly shows that those odd-numbered layers have an identical friction force much smaller than that of the bilayer, confirming that they are terminated by hydrophobic tails.

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The observation we made on the bilayer and odd-numbered multilayers can be explained in terms of the amphiphilic nature of OPA molecules. Because the hydrophilic headgroup has to be bonded with the hydrophilic silicon substrate, it is thus required that the second layer orient its hydrophobic tail with the hydrophobic tail of the first layer, leaving the hydrophilic headgroup of the second layer pointing outward. The third layer hence has its hydrophilic headgroup bonded to the second layer, resulting in a surface with a chemistry of hydrophobic tails. After the third layer, interestingly, it is not the 4-fold layer (i.e., double bilayer) but the 5-fold layer that was observed. Similarly, further multilayers were found to be 7-fold and 9-fold layers and so forth. This experimental fact shows that the increment after the trilayer is not a monolayer but a unit of an inversed bilayer, in which the hydrophilic headgroups are facing together and the surface is thus always terminated by the hydrophobic tail. A schematic illustration is depicted in Figure 4, showing the bilayer (2), trilayer (3), and the 5-fold layer (5). A surface terminated by a hydrophobic tail has a lower surface energy compared to that with a hydrophilic headgroup.

Conclusions

Self-assembled OPA layers were prepared on a silicon substrate by a solution spreading method and studied using AFM. OPA molecules were found to be mobile at room temperature as evidenced by the experimental observations of (1) reorganization of the stacked flakelike OPA layers to form small crystalline domains and (2) reorientation of OPA molecules to form rodlike structures. Following heat treatment of the sample at 50–60 °C, a complete change of morphology, that is, the formation of large area bilayer and multilayers, was clearly observed. Except for the bilayer, the multilayers observed were only odd-numbered (e.g., 3, 5, 7, 9) layers. The odd-numbered layers exhibited a significantly smaller friction force than the bilayer as measured by a silicon tip. Our experimental results indicated that a hydrophobic tail-terminated surface is more favorable than a hydrophilic headgroup-terminated surface, though the hydrophilic headgroup-terminated bilayer is the platform for other multilayers.

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