Atomic Force Microscopic Observation of Random Molecular Arrangement in Dialkyl Guanidinium Monolayer

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Molecular arrangement in an amorphous monolayer which was prepared on pure water at 293 K and transferred onto a mica substrate, was successfully observed for the first time with an atomic force microscope (AFM) in the case of dialkyl guanidinium, **DG**.

AFM has enabled us to observe the material surface at a nanometer level.[1] The molecular arrangements in monolayers prepared by the Langmuir-Blodgett (LB) method have been directly observed with AFM.[2-4] However, AFM molecular images were obtained for monolayers only in a crystalline state in which component molecules are regularly arranged. Cohesive force among molecules is much weaker in amorphous monolayers, and they are generally destroyed by tip during scanning.[5] It is, therefore, indispensable to prepare mechanically stable monolayers in order to obtain molecular AFM image of amorphous monolayers. In this study, an amorphous monolayer with a relatively high mechanical stability was prepared from a guanidinium amphiphile with long dialkyl chains by LB method. The required molecular resolution was achieved by AFM observation of the transferred film.

Synthesis of ((dioctadecyl)carbamoylmethyl)guanidinium *p*-toluenesulfonate (**DG**) amphiphile shown in Figure 1 is reported elsewhere.[6] We spread **DG** in benzene/ethanol at a concentration of 5.7×10^{-4} M on pure water at a subphase temperature of 293 K. The monolayer was compressed up to a surface pressure of 30 $mN \cdot m^{-1}$ and was maintained as such for one hour, in order to prepare mechanically stable monolayers sufficient for obtaining the molecular-resolution AFM image.[3,4] The monolayer was transferred onto a freshly cleaved mica and a SiO substrate for AFM and transmission electron microscopic observation, respectively, by the horizontal drawing-up method.[7] The hydrophilic SiO substrate was prepared by vapor-deposition of SiO onto a Formvar thin layer with which an electron microscope grid was covered on a glass slide. The transfer ratio for each monolayer was unity, indicating that those substrates are completely covered with monolayers. The AFM image of the monolayer was obtained with a SFA300 (Seiko Instruments) in air at 293 K. A 0.8 μm x 0.8 μm scan head and a silicon nitride tip on a cantilever with a spring constant of 0.022 $N \cdot m^{-1}$ were used. Images were recorded in the "constant-height" mode; that is, feedback electronics and software were used to measure

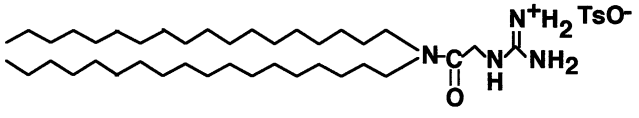


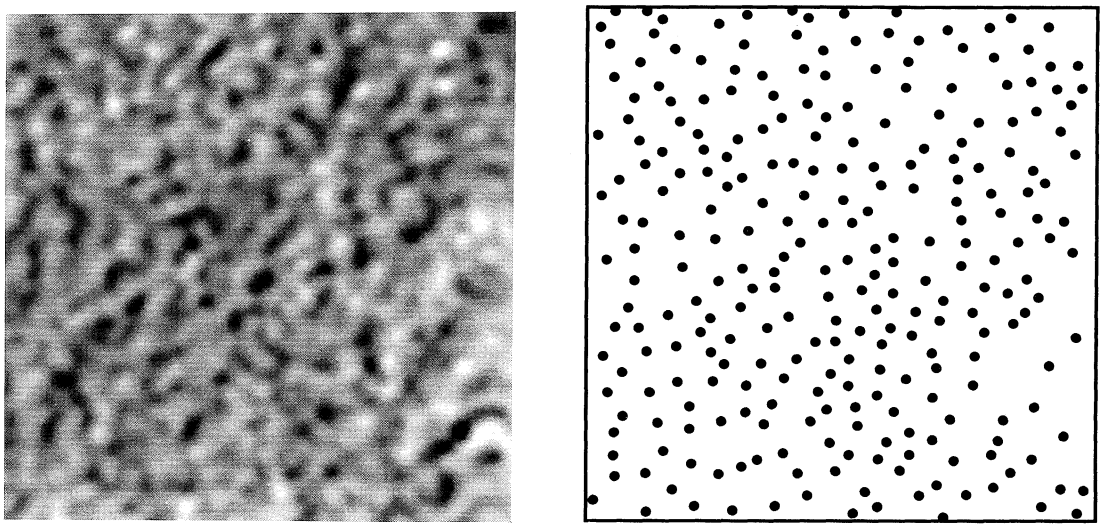
Figure 1. Chemical structure of **DG** molecule.

Figure 2. ED pattern of the **DG** monolayer.

the cantilever deflection by keeping the sample height constant. The applied force on scanning was about 10^{-10} N in an attractive force region. In order to reduce the noise component in raw AFM images, only a low-pass filter treatment was carried out. Electron diffraction (ED) pattern was taken with a Hitachi H-600 transmission electron microscope which was operated at an acceleration voltage of 75 kV, a beam current of several μA and a beam spot size of several μm.

Figure 2 shows the ED pattern of the **DG** monolayer. The ED pattern was an amorphous halo, indicating that the **DG** monolayer is in an amorphous state. The ED pattern results from two-dimensional assembly of scattered bodies of the **DG** molecule (one **DG** molecule corresponds to one scattered body) because the total path difference of scattered waves by carbon atoms in one **DG** molecule is smaller than one wavelength of electron beam.[8] Then, the amorphous state indicates that the center of gravity of **DG** molecule are irregularly arranged in the monolayer. The average intermolecular distance was evaluated to be about 0.50 nm, by applying Bragg's law to the peak position on the amorphous halo. The O/N value obtained by X-ray photoelectron spectroscopic analysis of a multilayered film of the monolayer revealed that the hydrophilic groups of **DG** molecules are dissociated with OH^- counterion.[9] The amorphous state of the **DG** monolayer may be caused by electrostatic repulsion among ionic hydrophilic groups of **DG** molecule.[10]

Figure 3(a) shows a typical AFM image of the **DG** monolayer on pure water with a scan area of 10 nm x 10 nm, as prepared under the same condition as the ED sample. Brighter portions may correspond to methyl terminals of **DG** molecules, because the hydrophobic end of **DG** molecule in the monolayer at high surface pressure of 30 $mN \cdot m^{-1}$ on a mica substrate are oriented toward air because the monolayer was transferred onto a hydrophilic mica surface by the horizontal drawing-up method. It is significant that the molecular image could be obtained without damage by repeated tip scanning. Apparently, the amorphous **DG** monolayer is mechanically stable owing to a high cohesive force



(a) (b)

Figure 3. (a) AFM image of **DG** monolayer with a scan area of 10 nm x 10 nm. (b) Distribution of brighter portions in Figure 3(a), which is expressed by dots.

of hydrophobic dialkyl chains. The AFM image reveals that **DG** molecules are irregularly arranged. The average intermolecular distance between **DG** molecules in the monolayer was evaluated to be about 0.52 nm, by using a two-dimensional radial distribution function (RDF)[11] of Figure 3(b) of which dots correspond to brighter portions in the AFM image of Figure 3(a). This value agrees closely with the intermolecular distance of 0.50 nm which was estimated from the ED pattern of Figure 2. The slight discrepancy between these values may be due to a small statistical ensemble on RDF analysis of AFM image.

It has been considered that the molecular arrangement in amorphous monolayer cannot be observed with AFM owing to damage of monolayers during the scanning operation. The present report is the first example of the molecular AFM image in the case of amorphous monolayers prepared by the LB method. Examination of the distribution of molecular arrangement in monolayer may provide a possibility to study physics of random systems and chaos in two-dimensional systems.

References and Notes

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11 After choosing a certain dot as an origin, the length, r between the origin and neighboring dots were measured. The same measurement was repeated by changing the origin to other dots in AFM image. An increase in the number of measured point due to an increase in r was canceled by giving an equal weight to the number of the measured point. Details of the analysis will be reported elsewhere.