STM observation of *N*-octadecylacrylamide and *N*-octadecylcinnamoylamide monolayers self-assembled on a graphite surface

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The STM observation of self-assembled *N*-octadecylacrylamide (ODA) and *N*-octadecylcinnamoylamide (ODC) on a graphite substrate clarified the head to tail alignment of the molecules and *s-trans* geometry of the alkene double bond and carbonyl group.

We have attempted to fabricate uniform Langmuir–Blodgett (LB) films having a well defined molecular orientation. In our previous study, we found that *N*-octadecylacrylamide (ODA) can form stable Langmuir monolayer and LB films on a solid substrate.[1–4] The X-ray diffraction study revealed that ODA forms two dimensional crystals in LB films.[5,6] Recently, we have observed the molecular arrangement of an ODA based LB film on a mica surface by atomic force microscopy (AFM) and obtained a molecular resolution image in which *N*-octyl chains are highly ordered to form two dimensional crystals.[7] The analysis of the AFM image and linear dichroism in polarized FTIR of the LB film[5,6] suggested that *N*-alkyl chains are tilted by *ca.* 28° against the film plane. Hydrogen bonding between ODA molecules was considered to be very important to stabilize the monolayer and the LB film. However direct evidence of intermolecular interaction between ODA molecules has not been clarified.

The scanning tunneling microscope (STM) is a powerful tool to image molecules at atomic resolution. Monolayers of physisorbed *n*-alkane and substituted alkanes on a flat substrate have been observed and the topological features of self-assembled two dimensional crystals discussed.[8–11] Different from LB films on mica, the molecules are aligned parallel to the graphite surface. This allows one to directly observe the molecular orientation and geometrical arrangement of monolayer. In the present study we applied the STM method to observe the molecular alignment of ODA molecules on the basal plane surface of highly oriented pyrolytic graphite (HOPG) to study their ordered structure and intermolecular interaction *in situ*. In addition, the molecular alignment of an ODA analogue *N*-octadecylcinnamoylamide (ODC) was also imaged.

ODA or ODC was dissolved in phenyloctane to near saturation and a drop of the solution was applied on the surface of freshly cleaved HOPG. The STM images were obtained in both constant current mode and constant height mode using Nano-Scope IIIa STM (Digital Instruments). The tunneling tip was a Pt–Ir tip purchased from Digital Instruments or a tungsten wire which was sharpened by electrolytical etching prior to use.

Fig. 1 shows the STM image of monolayer of ODA physisorbed on the HOPG surface (constant height mode). The two dimensional array of ODA molecules is clearly visible as stripes. The size of two dimensional crystals varies from a few 100 nm^2 to > 10 000 nm^2. Domain boundaries of adjacent crystals are observed with a rotation angle of 60°. This result suggests that ODA molecules are aligned by the influence of the graphite surface where the C–C–C atomic angle is 60°. Well ordered ODA molecules form stripe shaped lamella bands of *ca.* 2.7 nm width. A high resolution image of the monolayer is shown in Fig. 2 over a scan area of 8 × 8 nm (constant height mode). Increased brightness of the image corresponds to areas of higher electric conductance. Therefore the brighter parts can be attributed to the head groups containing conjugated π-electron systems and darker moieties to the alkyl chains. The molecular alignment is obviously in the head to tail structure. The alkene double bond appears to be downward to the molecular axis of ODA. The length of ODA observed along the molecular axis is roughly 2.7 nm which is consistent with that estimated by a CPK model. The separation of alkyl chains is *ca.* 0.47 nm. This value is slightly longer than that of two dimensional crystals of *n*-alkanes[8,9] presumably due to the presence of the bulky head group. The molecular axis of ODA

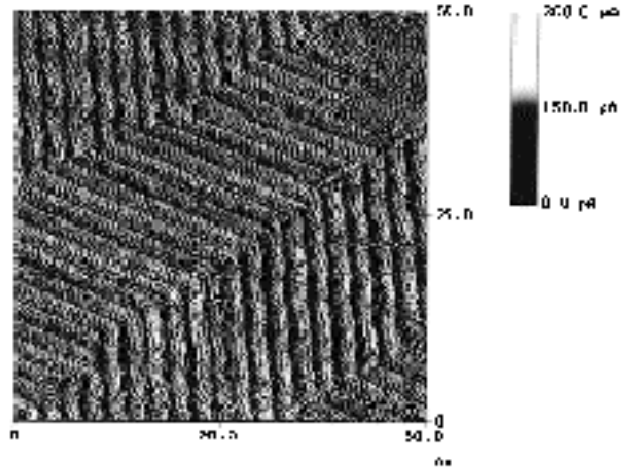

Fig. 1 STM image of a monolayer of ODA molecules self-assembled on a graphite surface. Image was taken in constant height mode. The area is 50 × 50 nm. Bias voltage is 1.1 V (tip positive) and current is 72 pA.

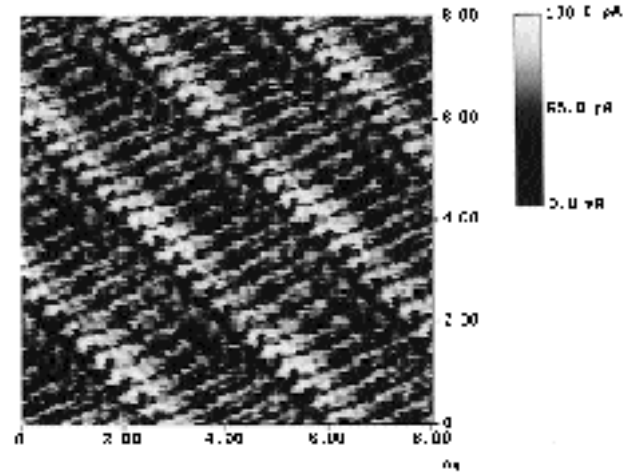

Fig. 2 STM image of a monolayer of ODA molecules self-assembled on a graphite surface. Image was taken in constant height mode. The scan area is 8 × 8 nm. Bias voltage is 1.0 V (tip positive) and current is 292 pA.

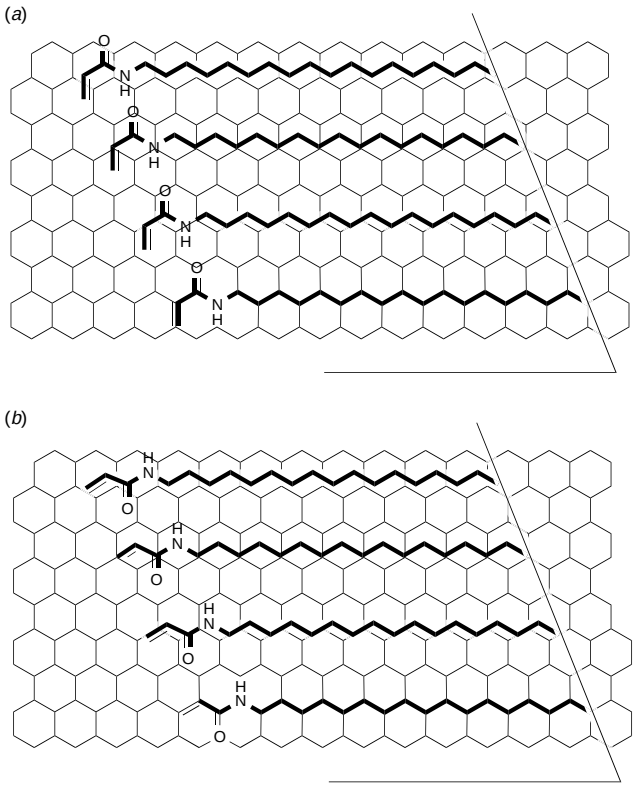

Fig. 3 Possible molecular arrangements of ODA with (*a*) an *s-trans* geometry and (*b*) an *s-cis* geometry, on a graphite surface. There are 18 carbon atoms in the alkyl chain of an ODA molecule.

appears to be inclined with an angle of *ca.* 70° *vs*. the orientation of the lamella band.

Possible molecular alignments of ODA on the graphite surface are schematically represented in Fig. 3(*a*) and 3(*b*) by which the observed inclination between the molecular axis of ODA and lamella band can be reproduced. Those two models are rotational isomers of ODA with respect to the amide group. The *s-trans* geometry [Fig. 3(*a*)] can consistently explain the observed alignment of ODA molecules where the intermolecular hydrogen bonds effectively link ODA molecules to form a molecular network. Such hydrogen bonds are unlikely to take place in *s-cis* geometry because the amide proton is then spatially remote from the carbonyl oxygen of an adjacent ODA molecule. The imaged morphology of the monolayer provides structural information of the constituent molecule and the observed inclination is very similar to that of the LB film deduced by FTIR and X-ray diffraction studies.[5,6]

Fig. 4 shows the high resolution STM image of ODC (scan area 8 × 8 nm, constant current mode) where a phenyl group is attached to an alkenic terminal of ODA. We can clearly distinguish the benzene rings and alkyl chains. The molecular ordering is again of head to tail structure as found in ODA. The head to tail distance is *ca.* 3.1 nm which agrees with the

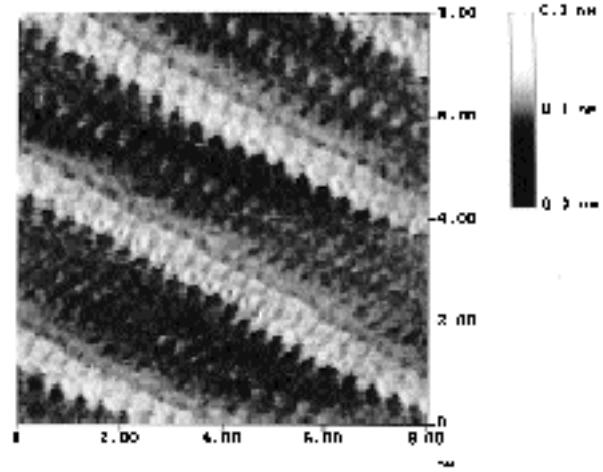

Fig. 4 STM image of a monolayer of ODC molecules self-assembled on a graphite surface. Image was taken in constant current mode. The scan area is 8 × 8 nm. Bias voltage is 0.85 V (tip positive) and current is 340 pA.

molecular length of ODC. Here also an inclination of ODA is observed against the lamella bands and the *s-trans* geometry around the amide group can explain the observed molecular arrangement.

The present STM observations have clarified the geometrical configuration of self-assembled ODA and ODC molecules where the intermolecular hydrogen bond in the amide group plays an important role in controlling the morphology of the molecular alignment.

Notes and References

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