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ATOMIC FORCE MICROSCOPY AND OPTICAL STUDIES OF ORGANIC THIN FILMS WITH HYDROGEN-BONDED NETWORKS

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Abstract

Brewster angle microscopy and atomic force microscopy were used to characterize the surface morphology of thin films *in situ* or after transfer onto solid supports. Two acids were studied, differing in carboxylic acid head groups, resulting in significantly different morphological features for thin films formed from these two amphiphiles on a Langmuir trough. Differences in self-assembly and domain sizes were correlated with the formation of hydrogen-bonded networks. The influence of surface hydrophobicity or hydrophilicity during deposition on morphology was also characterized, with spherulitic features appearing in some samples.

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Introduction

Ultrathin organic films have recently attracted attention due to their considerable importance in electrical rectification, conduction/redox activity, non-linear optics, and as templates for nucleation and growth of crystals [4, 5, 7, 8]. The organization of these films is different from those formed in bulk solution because the alkyl chains in the ultrathin organic films are packed and restricted to small spatial domains perpendicular to the film surface. Alkyl chain length influences the self-assembly of alkoxy substituted isophthalic acids (C_nISA) in the bulk and generates ribbon-, sheet and channel-type structures in the three-dimensional crystal lattice [2]. It is important to explore the arrangement of these molecules within organic thin films because they organize differently than conventional surfactants with pseudo-hexagonal lattices [4]. The organization of C_nISA within films is different due to a cross-sectional mismatch between the head and tail and their ability to form hydrogen-bonded networks.

In the present study, we directly observe the self-assembly of 5-hexadecyloxyisophthalic (C_{16}ISA, Fig. 1a) and assembly of 4-hexadecyloxybenzoic (C_{16}BA, Fig. 1b) acids on a water surface via Brewster angle microscopy (BAM). These observations are further explored with atomic force microscopy (AFM) on transferred monolayers to characterize surface morphology.

Material and Methods

The synthesis of C_{16}ISA and C_{16}BA and their physical properties are described elsewhere [2]. The C_{16}ISA is designed to have the flexibility of the alkyl substituents (hydrophobic end) coupled to hydrogen-bonding bulky head groups (hydrophilic end) to generate self-assembling, well-defined, periodic two-dimensional networks. The C_{16}ISA and C_{16}BA Langmuir monolayers were prepared on a water subphase in a Nima round trough (Nima Technology Ltd., Coventry, UK) which was mounted on a vibration isolation system MOD-2 {Nanofilm Technol. (NFT), Göttingen, Germany}. The

deionizer-active charcoal filter unit to a specific resistivity of 18.2 MΩ·cm. These monomolecular films were deposited at different surface pressures (10 and 20 mN/m) on either hydrophilic or hydrophobic surfaces of polished (001) silicon wafers by Langmuir-Blodgett (LB) technique according to a standard procedure [6, 7].

The direct visualization of the $C_{16}ISA$ and $C_{16}BA$ microstructures on various subphases was achieved with the BAM 1 plus (NFT) (resolution about 5 μm) and recorded on videotape [6]. The surface morphology of the monolayer films was characterized by AFM. Atomic force micrographs were obtained at ambient temperature with the Nanoscope IIIA-Dimension 3000 microscope (Digital Instruments, Inc., Santa Barbara, CA) according to an established procedures [10]. For scanning on a large scale, tapping mode was used to avoid damage of soft monolayer surfaces [10]. All AFM images were repeatedly observed and were stable under experimental conditions.

Results and Discussion

Before deposition of the $C_{16}ISA$ and $C_{16}BA$ monolayers on solid substrates, *in situ* microstructures were characterized on the water subphase in the trough. Immediately after $C_{16}ISA$ was spread, we observed the formation of large ($\sim$ 0.5 mm^2) two-dimensional domains (Fig. 2) without applying surface pressure ($\sim$ 0 mN/m). These domains were homogeneous in thickness and had large areas of constant chain tilt, which was visualized by using the BAM analyzer. The areas of different molecular orientation exhibited strong optical contrast for certain positions of the analyzer [9]. The spontaneous appearance of large $C_{16}ISA$ domains could be caused by self-assembly processes via the formation of hydrogen-bonded networks. This network would form due to the presence of the meta-disposed carboxyl groups of the $C_{16}ISA$ benzene rings. In this model, each molecule resides in a rectangular lattice and interacts with two neighbors through hydrogen bonding along the *b* direction and a further two molecules via van der Waals forces along the *a* direction (Fig. 3). The $C_{16}ISA$ monolayer was very stable on the water surface and large domains were preserved even after several cycles of compression and decompression. In contrast, we did not observed any self-assembly for $C_{16}BA$ in the absence of applied surface pressure. The $C_{16}BA$ contains one carboxyl group in para-position to the alkyl chain of benzene ring versus the metadicarboxylic acids in the $C_{16}ISA$ (Fig. 1a). Based on molecular modeling and Fourier-transformed infra-red (FTIR) data (paper in preparation), $C_{16}BA$ would not be expected to form a self-organized hydrogen-bonded network under these conditions.
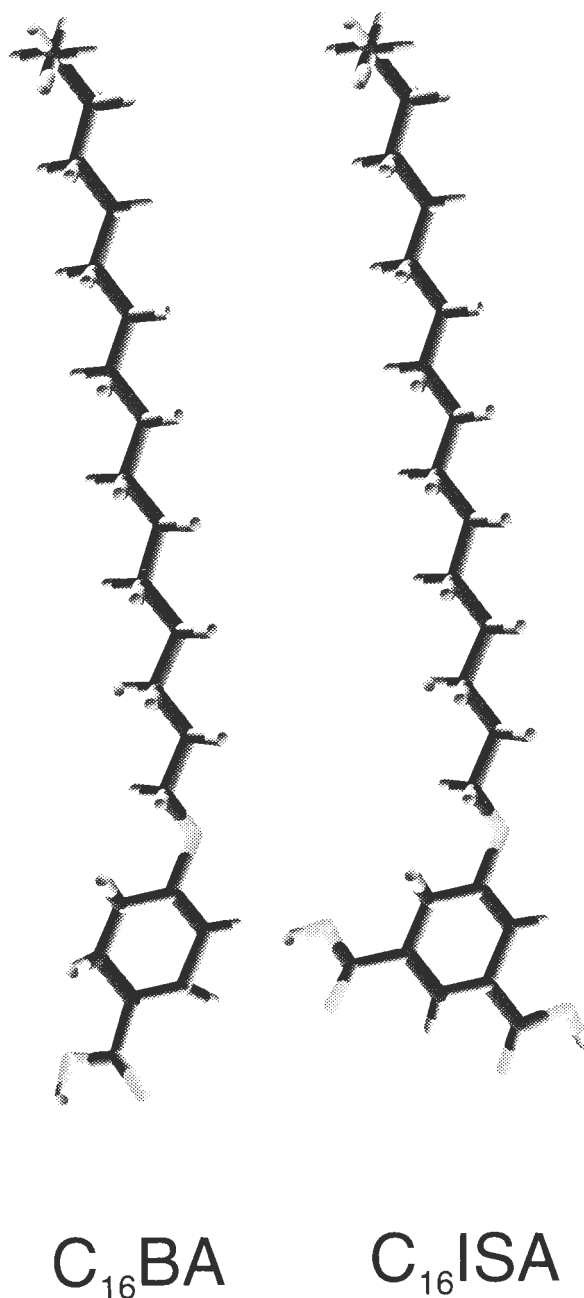

$C_{16}BA$ $C_{16}ISA$

Figure 1. Amphiphilic molecules used for monolayer formation: **(left)** 4-hexadecyloxybenzoic ($C_{16}BA$), and **(right)** 5-hexadecyloxyisophthalic ($C_{16}ISA$).

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amphiphiles were solubilized in ethyl alcohol and $CHCl_3$. The subphase temperature was kept constant at 21°C by circulating water around an aluminum support of the trough. The pure water for the subphase was first purified from tap water via reverse osmosis in a Milli-RQ 10 plus unit (Millipore Corp., New Bedford, MA) and then further refined by a Milli-Q plus recycling

Figure 2. Brewster angle micrograph of $C_{16}ISA$ monolayer on a water surface without applying surface pressure ($\sim$ 0 mN/m).
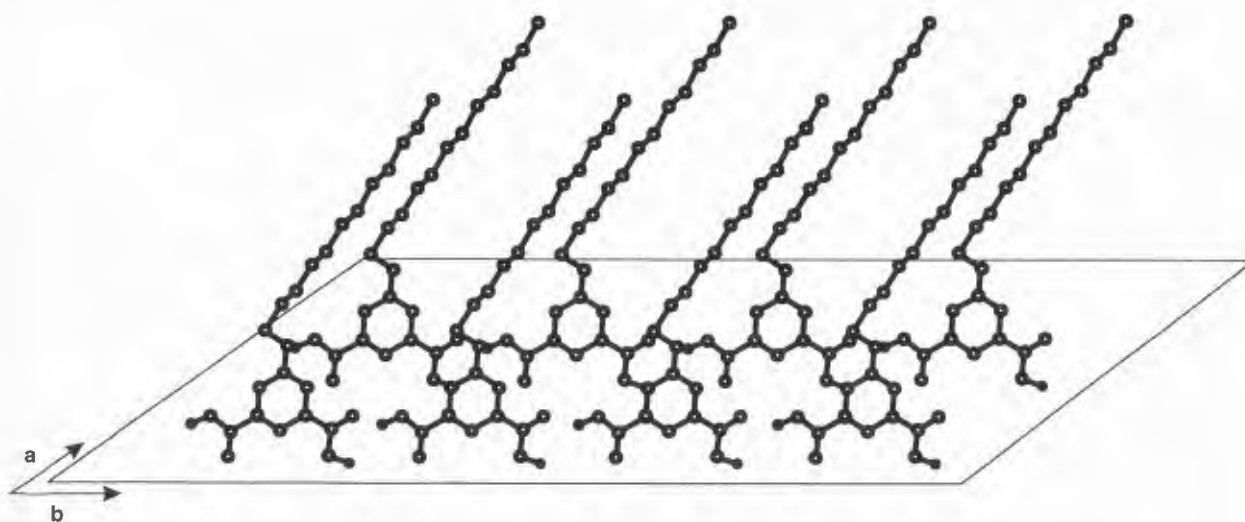

Figure 3. Schematic representation of the $C_{16}ISA$ molecular arrangement within the monolayer. In this model, each molecule resides in a rectangular lattice and interacts with two neighbors through hydrogen bonding along the b direction and a further two molecules via van der Waals forces along the a direction.

In the absence of applied surface pressure, $C_{16}BA$ exhibited growing crystallites that were thread-like in appearance and not homogeneous (Fig. 4). The growth was no longer isotropic, several "threads" grew from a common point, in comparison with the one-dimensional growth of $C_{16}ISA$ from a common center in different directions. Under applied pressure (starting from 20 mN/m), the monolayer formed relatively large (0.2 mm^2) homogeneous domains that tended to disappear after decompression.

The combination of BAM with AFM analysis was effective in characterizing the monolayer surface morphology and organization. The AFM study of the $C_{16}ISA$ and $C_{16}BA$ monolayers deposited on hydrophilic substrates agrees well with BAM observations of these monolayers on the water subphase. The monolayers deposited on the silanized hydrophobic substrate show different surface textures than those on the hydrophilic substrate. The reason for the different observations is that the interfacial interaction between the hydrophilic
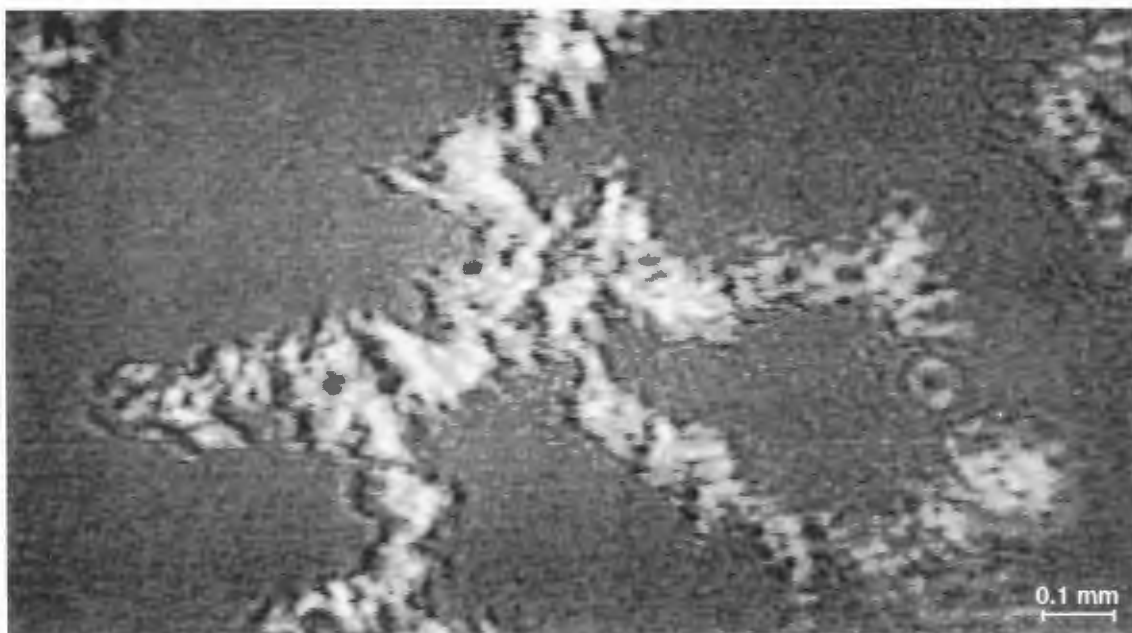
Figure 4. Brewster angle micrograph of $C_{16}BA$ monolayer on a water surface without applying surface pressure ($\sim$ 0 mN/m).

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groups of the monolayer and the hydrophobic surface becomes weaker with an increase in the surface energy difference. Therefore, the corresponding crystalline state of the monolayer on the water surface could not be transferred and maintained on the hydrophobic substrate since the surface energy of the substrate is different from that of the water surface.

The $C_{16}ISA$ monolayer deposited at 10 mN/m on a hydrophilic silicon surface uniformly covered the substrate with relatively large domains (Fig. 5, top). This micrograph agreed qualitatively with the BAM observations described earlier. On the micrometer scale, the monolayers of $C_{16}ISA$ obtained at 10 mN/m on a hydrophilic substrate were relatively smooth, with a roughness of 0.4 nm determined by variation of the monolayer thickness. The monolayers featured a number of holes ($\sim$ 0.2 μm diameter) homogeneously distributed over the surface area. The distribution of these holes was non-random based on Fourier-transformation of monolayer surfaces (Fig. 5, bottom). Diffuse halos on the Fourier-image indicated the presence of short-range positional ordering with an average distance between holes of 0.7 μm. The depth of the monolayers is about 0.8 nm and this may indicate propagation of the holes through only part of monolayer.

The $C_{16}ISA$ monolayer deposited on the hydrophilic support at a pressure of 20 mN/m shows typical morphology of a collapsed monolayer with very uneven surface roughness rising to 0.9 nm. The observation of this

behavior could be due to the fact that, in this pressure range, the rigidity of the hydrogen-bonded network becomes maximal and interferes with the deposition process. Apparently, during the deposition process, this film starts to break up in spite of its stability on the water surface.

The surface morphology of the $C_{16}ISA$ monolayers deposited at higher surface pressures (20 mN/m) on a hydrophobic silicon wafer surface (Fig. 6) differs dramatically from that discussed earlier. Surface roughness increased to 1.3 nm and a significant portion of the monolayer had spherulitic-like features. These "two-dimensional spherulites" ($\sim$ 1-2 μm across) were composed of two curved beams grown from one nucleus. The thickness of the beams was about 4.4 nm, very close to the expected thickness of a bilayer with close to normal orientation of the alkyl tails. A number of materials in which spherulitic crystallization has been observed before include high polymers crystallized from the melt and substances which, in certain temperature ranges, exist as liquid crystals [1, 3].

The $C_{16}BA$ monolayer deposited at 10 mN/m on a hydrophilic silicon surface showed non-uniform surface coverage with significantly smaller domains than the $C_{16}ISA$ monolayer (Fig. 7). These data agree qualitatively with BAM observations. The surfaces of the $C_{16}BA$ monolayer deposited on different substrates are relatively smooth (roughness of 0.2-0.4 nm) but unstable under the local pressure produced by the AFM tip. The
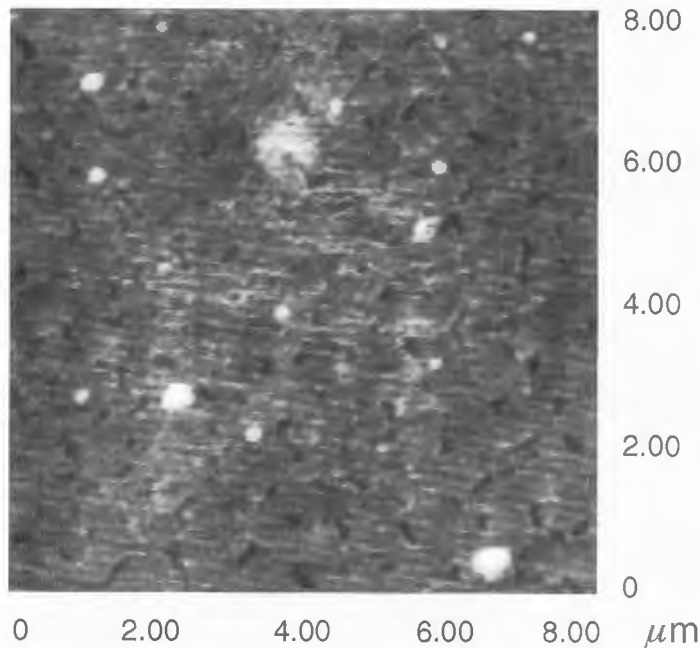
organic molecule self-assembly on a water surface. By changing the position of the BAM analyzer with respect to the polarizer from 0° (only the p-polarized light is allowed to pass through the analyzer) to 90° (only the s-polarized light is allowed to pass through the analyzer), areas of different molecular orientation were observed for C_{16}BA monolayers and were not observed for homogeneous C_{16}ISA monolayer domains (Litvin *et al.*, submitted to Langmuir). The C_{16}ISA is self-assembling on a water surface via formation of a hydrogen-bonded network with very large 2-D domains (~ 0.5 mm^2) and these domains are preserved after several cycles of compression and decompression. The C_{16}BA is not self-assembling and forms relatively large homogeneous domains under the applied pressure but they tend to disappear after decompression. AFM surface morphology data of C_{16}ISA and C_{16}BA monolayers qualitatively agreed with the BAM observations. We observed a uniformly covered silicon substrate with relatively large domains for C_{16}ISA and non-uniformly covered substrate with significantly smaller domain size for C_{16}BA. Spherulitic-like organization has been observed for C_{16}ISA monolayers deposited on a hydrophobic substrate.

depth of the holes produced as a result of plastic deformation of the monolayers is about 1.3 nm and 2.4 nm for the hydrophilic and hydrophobic supports, respectively. At higher surface pressure (~ 20 mN/m), for this monolayer deposited on the hydrophilic support, we observed the formation of mono- and multilayer areas with thicknesses from 2.3 nm, 4.4 nm and 5.5 nm. These areas are relatively smooth (root-mean-square roughness is about 0.4 nm) and stable under the scanning conditions.

Conclusions

Brewster angle microscopy was used to observe

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Figure 6. Atomic force micrograph of $C_{16}ISA$ monolayer deposited at 20 mN/m on hydrophobic silicon surface.
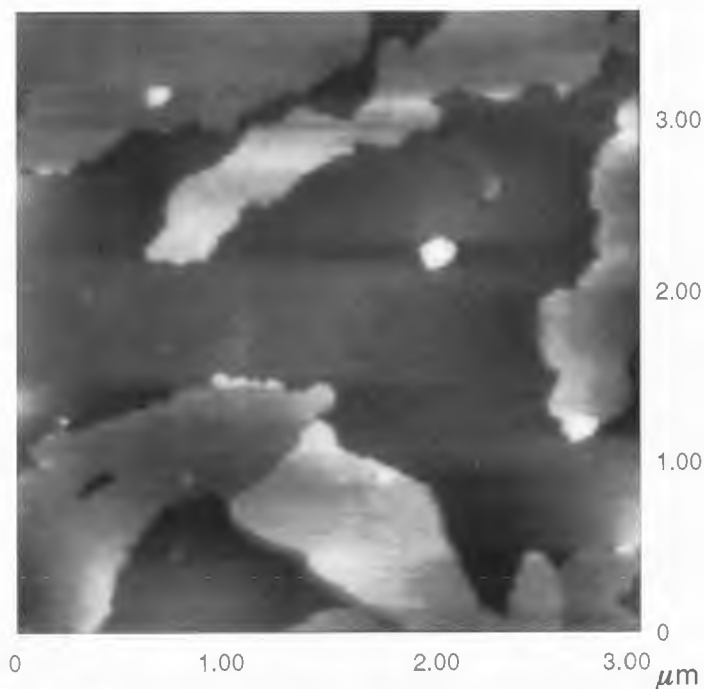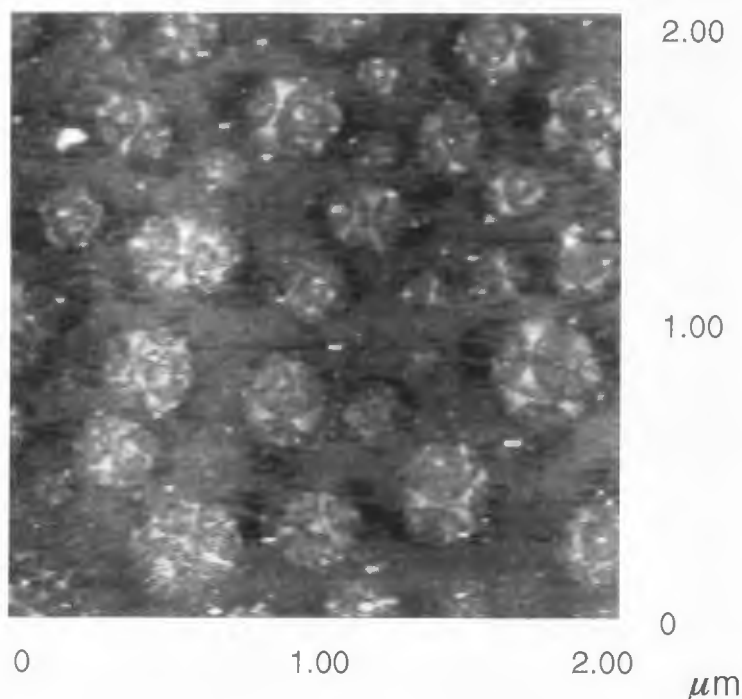

Figure 7. Atomic force micrograph of $C_{16}BA$ monolayer deposited at 10 mN/m on hydrophilic silicon surface.

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Discussion with Reviewers

Reviewer I: How were the wafers made hydrophobic?
Authors: Substrates were cleaned by ultrasonication, first in hot chloroform for 15 minutes and then in a hot 1:1:5 solution of $NH_4OH/H_2O_2/H_2O$ for 30 minutes. After rinsing in Millipore water and drying in nitrogen flow, the surfaces were rendered hydrophobic by placing the substrates in atmosphere of 1,1,1,3,3,3-hexamethyldisilazane for 24 hours.

Reviewer II: Variations in the monolayers thickness could be related to the roughness of the substrate.
Authors: All silicon wafers used had atomically smooth surfaces with a typical microroughness of about 0.15 nm within a 1 μm x 1 μm area. This is smaller than the thickness of a monolayer.

Reviewer III: It would be helpful to have some explanation of the contrast expected in Brewster angle microscopy with respect to the orientation of the molecular optic axis.
Authors: Figure 2 shows formation of large domains at low pressure where the water subphase appears as a dark strip. The denser domains in a monolayer appear brighter than the ambient subphase. This contrast arises from the formation of a monolayer with a refractive index different from that of the subphase. The monolayer areas with different molecular orientation exhibit strong optical contrast which indicate areas of constant chain tilt [12]. BAM limitations with regard to the interference pattern caused by the optical components of the system and the coherent laser light should be taken into account. By watching the video display during formation and compression of the monolayer, this pattern and the solu-

tion subphase (black area) can be clearly distinguished from the signal produced by the monolayer. This is more difficult when looking at a particular snapshot. Despite this limitation, BAM has been successfully used since its invention [12] for qualitative and quantitative monolayer characterization [5, 6, 9, 11].

Reviewer II: Why are the holes in the monolayer in Fig. 5 not randomly distributed?
Authors: Presence of an amorphous hallo in a Fourier transform (diffraction image) of the AFM picture shows certain correlation in distribution of characteristic features (holes in our case) on the surface of the film. This correlation is not strong and includes only first coordination circle of neighbours. Nevertheless, it is well pronounced and can be clearly distinguished from the case of random distribution. This is very interesting observation and further work is now in progress to understand this phenomenon.

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