Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2007) 5391–5394
thin solid films
www.elsevier.com/locate/tsf

Formation of an epitaxial monolayer on graphite upon short-time surface contact with highly diluted aqueous solutions of 1-monostearoylglycerol

Carlos Escudero [a], Zoubir El-Hachemi [a], Ismael Díez-Pérez [b], Joaquim Crusats [a], Josep M. Ribó [a,*]

[a] Department of Organic Chemistry, University of Barcelona, Martí i Franquès 1, Barcelona, Catalonia, 08028, Spain
[b] Department of Physical Chemistry, University of Barcelona, Martí i Franquès 1, Barcelona, Catalonia, 08028, Spain

Received 6 June 2006; received in revised form 24 October 2006; accepted 12 December 2006
Available online 20 December 2006

Abstract

Short-time surface contact of highly diluted 1-monostearoylglycerol (1-MSG) aqueous solutions with highly oriented pyrolitic graphite results in the deposition of an epitaxial monolayer that can be detected by atomic force microscopy operating in tapping mode at the graphite–air interface. The monolayer obtained with the racemic mixture is then compared to that obtained with one of the pure enantiomers. The analogous behavior found for aqueous solutions of *rac*-1-MSG and 3-*sn*-MSG implies a two-dimensional self-assembly process with chiral discrimination. The results suggest that the monolayer originates from species located at the surface of the deposition drop. They also indicate that the simple experimental procedure reported, or more elaborate Langmuir–Schaefer methods, could be the method of choice to prepare other monolayers of similar surfactants.

Keywords: AFM; Deposition process; Chiral symmetry breaking; Monolayers

1. Introduction

Surfactant-based interfacial nanostructures have attracted widespread attention [1–5] because of their vast potential in many technological processes and functions such as molecular electronics, or as feasible surface self-assembled templates [6] that can selectively adsorb or induce the growth of other species. Indirectly, they also provide valuable information about the aggregated species present in solution. Therefore, great efforts are being made to obtain structured monolayers with regular architectures, especially since scanning probe microscopy (SPM) has recently become available for their characterization.

In the current work, we describe an efficient and simple procedure to prepare the yet unreported epitaxial 1-monostearoyl-*rac*-glycerol (*rac*-1-MSG) monolayer on highly oriented pyrolytic graphite (HOPG). The monolayer is obtained without the presence of any micellar-like structure on its top, and it is studied and characterized by atomic force microscopy (AFM) operating in tapping mode at the graphite–air interface.

We serendipitously came across the neat and fast formation of *rac*-1-MSG monolayers on HOPG by the identification of the monoglyceride as a contaminant in deposition solutions. Mere contact of water with brand-new disposable polyethylene laboratory material (e.g. screw-capped centrifuge tubes) was enough to produce a suitable solution that yielded the monolayer upon contact with the HOPG surface. Notice that *rac*-1-MSG is extensively used in the molding of organic polymers as a mold-release agent. In this respect, this report can also be considered a precautionary note for the sample preparation previous to SPM observations.

2. Materials and methods

2.1. Materials

1-monostearoyl-*rac*-glycerol (*rac*-1-MSG, Sigma, approximately 99%), 3-monostearoyl-*sn*-glycerol (3-*sn*-MSG, Bio-Chemika, >99%) and chloroform (J. T. Baker, p. a. grade)

* Corresponding author. Tel.: +34 934 021 251; fax: +34 933 397 878.
E-mail address: jmribo@ub.edu (J.M. Ribó).

0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.12.174

were used as received from the manufacturers without further purification. Ultrapure water (resistivity ≈18.2 MΩ cm) was supplied by a Purelab USF system. The basal plane of highly oriented pyrolytic graphite (HOPG, Advanced Ceramics, Cleveland, OH) was hand cleaved by using adhesive tape immediately before sample deposition.

2.2. Aqueous surfactant sample preparation

The following standard procedure was optimized to prepare suitable solutions yielding monolayers: 9.0 mg (25 mmol) of the monoglyceride (*rac*-1-MSG or 3-*sn*-MSG) were dissolved in 0.5 mL of chloroform in a Pyrex glass tube. Then, with the aid of a syringe, 15–30 μL of this organic solution (50 mM) was allowed to trickle down the sides of a 15 mL glass screw-cap test tube, near the liquid surface below, over 5 mL of freshly purified Milli-Q water. The mixture (150 μM, 3-*sn*-MSG or 300 μM, *rac*-1-MSG) was shaken and then the resulting suspension was left undisturbed for 30 min before proceeding to sample deposition (see Results and discussion section).

2.3. AFM imaging

AFM images were obtained at the Scientific-Technical Services UB using two Multimode microscopes (Digital Instruments, Santa Barbara, CA) controlled by a Nanoscope IV electronics (Digital Instruments, Santa Barbara, CA) operating in tapping mode in air at room temperature and typical relative humidity of 40%. The working setpoint amplitude and scan rate were between 2–3 nm (typical measured sensitivity of around 270 mV/nm for the cantilevers used) and 1.5–2 Hz respectively. The AFM probes were Silicon cantilevers with integrated conical-shaped Silicon tips (Nanosensors, Norderfried Richskoog, Germany), an average resonance frequency of 300 kHz, and spring constant of 35 N/m. Nominal tip radius and cone angle were 10 nm and 35° respectively. The reported topographical images correspond to the observation of several regions of many different samples deposited under the same experimental conditions and recorded at several points across their surfaces so as to obtain reliable measurements.

2.4. On the nature of the striped pattern in the AFM images

The monolayers obtained showed a striped pattern whose structural interpretation required several precautions before proceeding with their quantitative analysis. Regular sampling, as performed in the sweep procedure of AFM, can result in apparent periodicities at frequencies well below the resolution of the technique. According to Shannon's sampling theorem, aliasing occurs when a signal is sampled at a less than twice the highest frequency present in the signal (Nyquist criterion). We rule out aliasing or any effect of the instrument regular sampling raster (squared lattice) as the origin of the periodic modulation obtained in the reported AFM images, because: (a) the adsorbate morphology was invariant to changes in the scan size even at high image magnifications of 50×50 nm^2; (b) neither did the pattern disappear when we varied instrumental parameters so as to eliminate unwanted oscillations in the data due to possible aliasing of the linear scanning rate with the digital sampling rate or the feedback loop; and (c) the recorded periodicity of the stripes and the angles between them in different microdomains did not change when the tip scannings were rotated with respect to the underlying substrate. Notice that the former experimental observations, together with the reproducibility of the results using different electronics and probe platforms, confirm that the striped pattern observed has a completely different origin than the one exploited in under-sampled AFM techniques based on conventional analysis of fringe patterns obtained by moiré interferometry [7,8]. Once established that the striped patterns were not an experimental artifact, the structural parameters (stripe widths and angles between the stripes of different domains) were determined by averaging a large number of individual observations corresponding to pairs of top-to-bottom and bottom-to-top scans. The drift effects on the angle measurements were minimized using low image magnification (500×500 nm^2 scan size) in which the direction of the stripes could be still observed. This allowed us to measure angles with an accuracy of ±2°. The stripe width was better determined under low drift conditions and high image magnifications (down to 200×200 nm^2 of scan size). In this respect, the resolution of the technique determines that the stripes cannot be observed when the raster direction nearly coincides with that of the stripes. This is because the corrugation (peak to valley) in the direction perpendicular to the striped pattern is very low (0.1 nm).

3. Results and discussion

3.1. Sample deposition and AFM observation

In a typical experiment, 50 μL of the aqueous *rac*-1-MSG solution (see Materials and methods section) was deposited on a HOPG plate with a micropipette and blotted off with a filter paper tip. Any remaining solution was blown off with a nitrogen (99.99%) stream and imaged immediately afterwards. The solution was in contact with the graphite for less than 2 s. By following this simple procedure, motif images of 2-D arrays with a twofold symmetry axis were obtained (Fig. 1a). The images showed a striped pattern analogous to those previously described on HOPG for many organic compounds bearing linear polymethylene chains [9–11]. The AFM images in Fig. 1 correspond to the *rac*-1-MSG monolayer, whose identification and structural parameters are discussed in the next section. In addition to the monolayer, irregular nano-particles, or often platelet-like structures showing a flat surface with a uniform height of 4.0±0.2 nm (not resistant to the AFM contact mode, and without any motif pattern by AFM in tapping mode) were detected on the top of the monolayer. The 20–30 min delay between the preparation of the surfactant solution and its deposition (see Materials and methods section) proved to be a critical variable for monolayer detection: freshly prepared solutions generally did not form the adlayer, whereas older solutions resulted in the co-deposition of many interfering nano-

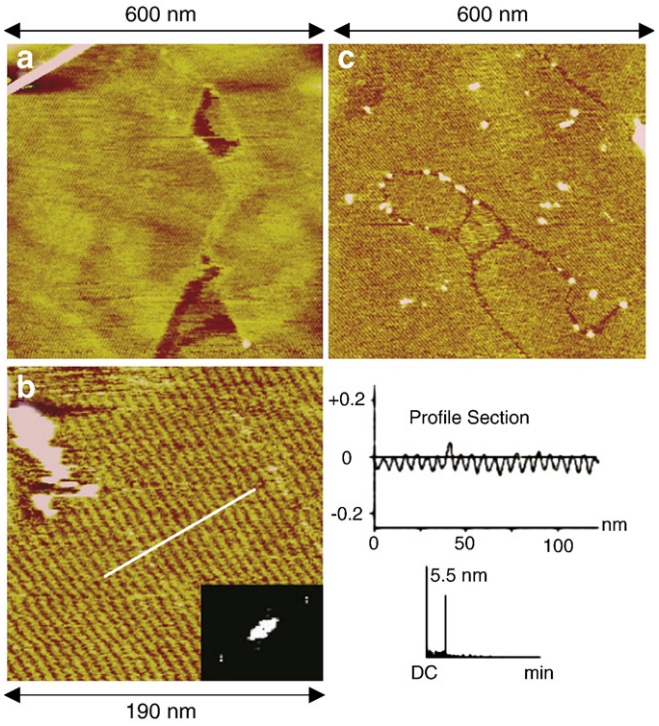

Fig. 1. Tapping mode AFM height images corresponding to monolayers of *rac*-1-MSG deposited onto HOPG from a 300 μM aqueous solution (a, b) and of 3-*sn*-MSG from a 150 μM solution (c). Panels (a) and (c) correspond to overviews of the monolayers in which the 60° relation between domains can be seen. (b) Measurements of the structural parameters. The inset shows the 2D Fourier transform of the pattern in the image. The pictures on the right correspond to the analysis of the sectional profile marked on the same image by a blank line (corrugation of the monolayer, upper panel) and the corresponding frequency histogram (lower spectrum).

and micro-particles. The reported deposition procedure, based on the preparation of suitable *rac*-1-MSG solutions, leads to the fast formation of monolayers, which in accordance with the Ostwald rule of stages [12] suggests the existence of metastable molecular assemblies for its success.

To test whether the species giving rise to the monolayer were sited at the air–water interface of the depositing drop we envisaged a different experimental procedure to attain surface contact: the drop of the surfactant solution was placed on a hydrophobic strip of a Parafilm M® sheet fixed on an vertically mobile micro-control platform. The sample was then placed beneath a carefully leveled horizontal support with a square HOPG plate to its lower side. The graphite was brought into contact with the upper part of the drop slowly raising the platform. Immediately after contact the sample was lowered slightly so as to obtain a cylinder-like water neck. The whole procedure took about 15 s. After a contact time of 30 s, the sample was blotted off with a filter paper tip and dried as described above. Following this inverse deposition procedure, large uniform striped domains were formed without unwanted massive particles interfering on their top, although some small fragments were still occasionally found on the sample. Probably, the hydrophobic film sheet on the bottom competes advantageously with the upper HOPG surface to adsorb the small solid particles which would otherwise pollute the monolayer. Taken together, all this suggests that the monolayer is built up from prearranged structures at the air–water interface of the drop. Notice also that such inverse deposition procedure corresponds, in fact, to a simplified approach of the Langmuir–Schaefer technique. In this respect, Langmuir monolayers of monostearoylglycerol have been previously reported [13–15].

In no case did we detect the presence of hemicylindrical hemimicelles or hemimicelles, which can be attributed to the high Krafft temperature of saturated long-chain monoacylglycerols [16]. Although there are numerous examples of periodic striped structures for ionic and non-ionic surfactants, they correspond to hemicylindrical hemimicelles. These previous reports assume that they grow on a primary monolayer which in most cases cannot be directly detected [1–5]. On the other hand, uncovered molecular epitaxial monolayers of compounds bearing long linear alkyl chains, without the interference of hemimicelle formation, have been obtained from near-to-saturated organic solvent solutions after long deposition times [9–11]. A distinctive aspect of our results is the fast formation of an uncovered monolayer by mere surface contact with highly diluted water solutions.

3.2. Structure of the monolayer

The AFM images of the adlayer show domains in the micrometer range with a striped pattern running along well-defined directions. The structured pattern corresponds to parallel stripes with a regular distance of 5.6±0.1 nm, whose corrugation is about 0.1 nm for the peak to valley value (Fig. 1b). The domain height from the graphite surface to the top of a peak is 0.45±0.05 nm (measured by sectional analysis in areas in which the domain boundary is clearly seen), implying that the monolayer is formed by flat-lying molecules. Notice that the thinness of the film precludes the existence of any micellar or hemicellar structure formed by molecules perpendicular to the substrate plane.

The fact that the stripes follow fixed angular dependencies with degenerate domains interchangeable by 60° rotations, in accordance with the six-fold symmetry of the graphite underneath, unequivocally indicates epitaxial growth. Moreover, the salient AFM resolution obtained in the case of the monolayer must be the signature of a marked atomic-force map, as expected for an epitaxial superstructure formed between graphene and the monoglyceride monolayer. Recall at this point that the regular 4.0 nm thick platelet-like structures described above did not show any structural details on their surface.

The large size of the domains, and the fact that their size increases after 48 h (Ostwald ripening), indicates high stability of the assembly. However, the monolayer is not resistant to AFM working in contact mode since the tip sweeps away the deposited adlayer even at forces as low as a few hundreds pN (with softer SiN cantilevers).

Up to now we have been unable to record scanning tunneling microscopy (STM) images of the monostearoylglycerol monolayer of reasonable quality at the solid–air interface. The high bias voltage necessary for tunneling or charge injection in such

highly dielectrical materials can lead to unwanted electrochemical processes in the presence of oxygen and water. Notice that previous reports on STM images of monolayers of neutral molecules have been obtained under ultra high vacuum conditions or in organic solvents. Nevertheless, the parameters obtained from the AFM motif allow us to propose a packing model that takes into account the epitaxial relation between the 2-D organic crystal and the HOPG surface. There are numerous examples demonstrating that the common parallel stripes appearing in physisorbed monolayers of organic compounds bearing long alkyl chains are due to a head-to-head and tail-to-tail arrangement of the adlayer molecules forming rows and columns [1–5,9–11]. Owing to commensurate interactions between the all-trans alkyl chains and the graphite surface, there is a good geometrical matching of the H atoms of the methylene groups with the hexagonal rings of graphene [17]. The physisorbed molecules are bound with their long axis C–C backbone parallel to the surface, following the principal symmetry axes of graphene, in such a way that the AFM periodicity corresponds approximately to twice the extended molecular length [1–5,9–11]. In the case at hand, because of the large size of the glycerol headgroups and the existence of hydrogen bonds between them (both inside rows and between columns) the axis of the stripe is not expected to be perpendicular to that of the polymethylene chain (lateral molecular offset within the lamella), in concordance with the 5.6 nm periodicity of the AFM images. The existence of a network of hydrogen bonds is predictable from the structure of monostearoylglycerol crystals in the bulk [18–20]. In addition, the commesuration between the long chain H–C units and the hexagonal rings of the substrate should be extended to the H–C backbone units of the glycerol residue. Consequently, the asymmetric –CHOH group must determine an epitaxial ordering that distinguishes the diastereotopic faces of the carbonyl group and the diastereotopic hydrogen atoms of the $–CH_2–O–$acyl and $–CH_2–OH$ groups. Thus, significant differences in free energy between homochiral or heterochiral head-to-head orderings should be expected. Then, in considering the structure of the monolayer, the question arises as to whether the growth of the 2-D domains on HOPG from the racemic mixture gives rise to racemic domains or whether they spontaneously resolve into mirror domains identical to those coming from the enantiomerically pure material, i. e., conglomerate formation. In attempt to discern between these possibilities we performed similar experiments with 3-monostearoyl-*sn*-glycerol, obtaining monolayers (Fig. 1c) whose structural parameters do not differ from those determined for the racemic mixture. However, the size of the domains tends to be larger in the case of 3-*sn*-MSG. Another significant difference is that solutions of 3-*sn*-MSG at lower concentrations give comparable monolayers to those obtained with *rac*-1-MSG at higher concentrations (e.g. 150 μM compared to 300 μM). In any case, the structural similarity between both adlayers points to spontaneous resolution in the case of *rac*-1-MSG. Notice that the number of reports on chiral discriminations from racemic mixtures and on the formation of chiral monolayers from achiral organic compounds shows a continuous increase, suggesting that these processes are not uncommon. In addition, fatty acid 1-monoglycerides show a well-known tendency to crystallize in conglomerates [18–20]. More work is in progress to further investigate the 2-D conglomerate formation of the *rac*-1-MSG mixture on HOPG.

4. Conclusions

We have described a simple procedure to form a monolayer of 1-MSG on HOPG from highly diluted aqueous solutions. The results indicate that the monolayer originates from species ordered at the air–water interface of the deposition drop. Consequently, the detection of 2-D conglomerates on graphite implies that chiral discrimination already occurs at the air–water interface. This is consistent with earlier reports on the chiral discrimination of racemic fatty acid monoglycerides in Langmuir monolayers [15,21]. In addition, the simple experimental procedure reported, or more elaborate Langmuir–Schaefer methods, could be the method of choice to prepare monolayers of similar surfactants.

Acknowledgements

This work was financed by the Spanish Government (Grant No. MAT2003-430 and AYA2006-15648-01) and belongs to the action COSTD27 (WG0004-02) of the European Commission. J. C. and C. E. acknowledge financial support from the Spanish MEC Ramón y Cajal and FPU programs, respectively.

References

[1] Z. Király, G.H. Findenegg, Langmuir 21 (2005) 5047.
[2] H. Kawasaki, M. Shinoda, M. Miyahara, H. Maeda, Colloid Polym. Sci. 283 (2005) 359.
[3] R. Atkin, V.S.J. Craig, E.J. Wanless, S. Biggs, Adv. Coll. Interface Sci. 103 (2003) 219.
[4] I. Sokolov, H. Yung, G.A. Ozin, G.S. Henderson, Adv. Mater. 9 (1997) 917.
[5] S. Manne, H.E. Gaub, Science 270 (1995) 1480.
[6] G. Mao, D. Chen, H. Handa, W. Dong, D.K. Kurth, H. Möhwald, Langmuir 21 (2005) 578.
[7] Z.W. Zhong, G.L. Lu, Int. J. Adv. Manuf. Technol. 23 (2004) 462.
[8] D.E. Angelescu, C.K. Harrison, M.L. Trawick, P.M. Chaikin, R.A. Register, D.H. Adamson, Appl. Phys., A 78 (2004) 387.
[9] J.P. Rabe, S. Buchholz, Science 253 (1991) 424.
[10] D.M. Cyr, B. Venkataraman, G.W. Flynn, A. Black, G.M. Whitesides, J. Phys. Chem. 100 (1996) 13747.
[11] M. Hibino, A. Sumi, I. Hatta, Jpn. J. Appl. Phys. 34 (1995) 3354.
[12] W. Ostwald, Z. Phys. Chem. 22 (1897) 289.
[13] D.A. Cadenhead, D.M. Balthasar, J. Colloid Interface Sci. 107 (1985) 567.
[14] K. Meine, D. Vollhardt, G. Weidelmann, Langmuir 14 (1998) 1815.
[15] U. Gehlert, D. Vollhardt, G. Brezesinski, H. Möhwald, Langmuir 12 (1996) 4892.
[16] N.J. Krog, T.H. Riisom, L. Latsson, in: P. Becher (Ed.), Encyclopedia of Emulsion Technology, vol. 2, Marcel Dekker, New York, 1983, p. 321.
[17] F. Tao, Y. Cai, S.L. Bernasek, Langmuir 21 (2005) 1269.
[18] M. Goto, K. Kozawa, T. Uchida, Bull. Chem. Soc. Jpn. 61 (1988) 1434.
[19] K. Larsson, Acta Chem. Scand. 20 (1996) 2255.
[20] D.R. Kodali, T.G. Redgrave, D.M. Small, D. Atkinson, Biochemistry 24 (1985) 519.
[21] N. Nandi, D. Vollhardt, G. Brezesinski, J. Phys. Chem., B 108 (2004) 327.