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Communication

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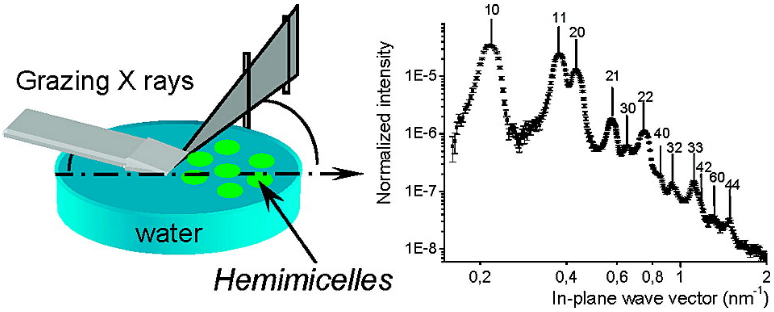

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Direct Evidence for Highly Organized Networks of Circular Surface Micelles of Surfactant at the Air−Water Interface

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We report the first direct evidence for the formation of surface hemimicelles at the air−water interface. As yet, surface micelles of molecular or polymeric surfactants have only been characterized on solid substrates,[1,2] in particular, after the transfer of Langmuir monolayers from the water surface onto a solid.[3,4] The hemimicelles of molecular surfactants reported here are circular and form highly organized hexagonal networks. The critical diameter of these domains is exceptionally large (30 nm), that is, much larger than that usually reported for hemimicelles made from molecular surfactants (∼5 nm).[5]

Because of their mesoscopic size, such networks may be useful as nanomasks to guide the growth or deposition of metals in the elaboration of patterned nanostructures. Novel top−down nanolithographic techniques for fabricating and patterning sub-100 nm featured nanostructures are being developed[6] that rely, in particular, on the emergence of soft lithographic techniques (replica molding, microcontact printing, etc.).[7] A promising alternative direction for further progress is the formation of patterns via self-assembly of molecules. Self-assembly is more versatile than classical lithographic processes. It is also a fructuous playground for chemists as the information that guides the organization of molecules into noncovalently bound structures is coded in the characteristics of the assembled molecules. However, the use of self-assembly of amphiphilic molecules to produce templates for nanostructures has so far been hindered by insufficient control of the order, domain size, density of defects, and stability of these templates. Recent studies have been devoted to controlling pattern formation from block copolymers.[2,8] Such polymer-patterned surfaces were successfully used as nanolithographic masks.[9]

We report now that well-organized arrays of monodisperse surface hemimicelles can be obtained by spreading a semifluorinated alkane, $C_8F_{17}C_{16}H_{33}$ (F8H16), at the air−water interface in a Langmuir trough. The techniques generally used to probe the air−water interface, including Brewster angle microscopy, specular X-ray reflectivity, or neutron reflectivity, are unable to differentiate a laterally homogeneous film from surface modulations with domain dimensions in the nanometer range. We found that grazing incidence small-angle X-ray scattering (GISAXS) can provide definite evidence for the existence of domains of 30 nm in diameter directly at the air−water interface. It is the first time that domains of that size, which is very large to the eye of GISAXS, are established by this method.

The semifluorinated alkanes utilized, $C_nF_{2n+1}C_mH_{2m+1}$ (FnHm diblocks), consist of a lipophobic fluorocarbon block and a fluorophobic hydrocarbon block. The mutual antipathy of these blocks results in a tendency for them to segregate, which can drive the self-organization of FnHm in bulk and in solution.[10,11] Many FnHm diblocks form stable Langmuir monolayers.[12] F8H16 was synthesized according to ref 13 and was thoroughly purified by repeated crystallizations from methanol. Its purity (>99%) was determined using thin-layer chromatography, NMR, and elemental analysis.

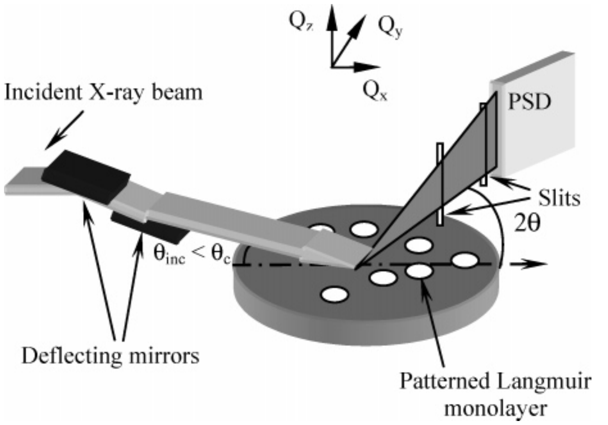

Figure 1. Experimental setting for direct investigation of patterned Langmuir films by GISAXS at the air−water interface.

The GISAXS experiments were conducted on the ID10B beamline of the ESRF synchrotron source (Grenoble, France). The dedicated PTFE Langmuir trough was equipped with a movable single barrier. The surface pressure, measured using the Wilhelmy plate method, was kept constant during a scan. The trough was enclosed within a gastight box (fitted with Kapton windows) that was filled with water-saturated helium. The temperature was regulated at 20 ± 0.5 °C. Monolayers were spread from 100 μL of a 1 mM chloroform solution of F8H16.

The energy of the incoming X-ray beam, 8 keV (0.154 nm), was selected using a double diamond crystal monochromator. The incident beam was deflected downward by a double mirror setup to an incidence angle of 2 mrad, slightly below the critical angle for total external reflection of X-rays at the air−water interface (∼2.5 mrad) (Figure 1). The dimension of the incident beam was adjusted to 0.25 mm horizontally and to 0.1 mm vertically.

An evacuated tube and a collimator made of two vertical slits were installed in front of the detector. Scattered photons were recorded using a vertical gas-filled (Xe−CO_2) position-sensitive detector (PSD) covering a Q_z range from 0 to 5 nm^{-1}. Scans were performed as a function of the in-plane component of the scattering wave vector, Q_{xy}. The in-plane resolution was 1 mrad.

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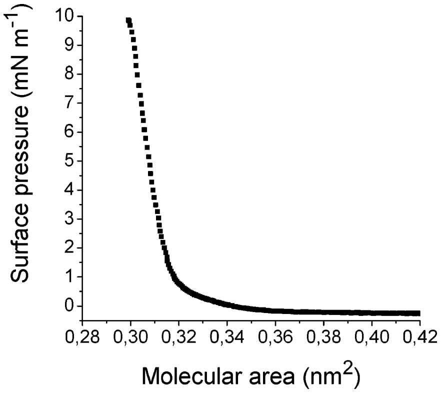

Figure 2. Surface pressure versus molecular area isotherm obtained by compressing F8H16 at the air−water interface at 22 °C.

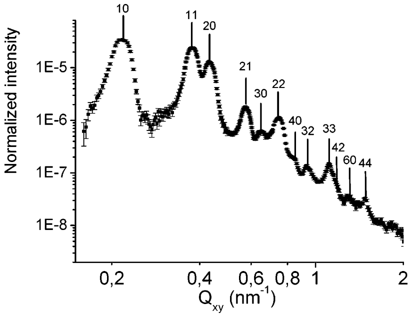

Figure 3. Diffraction spectrum for a monolayer of F8H16 compressed at 5 mN m^{-1}. The intensity is integrated along Q_z from 0 to 5 nm^{-1}. Peaks are indexed in the hexagonal lattice of parameter 33.5 nm.

Surface pressure versus molecular area isotherms of F8H16 indicate that the monolayer remains stable up to ∼10 mN m^{-1} (Figure 2). The limiting area of 0.31 ± 0.5 nm^2, which is significantly larger than the cross-section of a typical hydrogenated chain (0.2 nm^2), corresponds to the reported cross section of a perfluorinated chain.[10]

At 5 mN m^{-1}, a set of 12 peaks was obtained (Figure 3) that were fitted by Lorentzian curves. These peaks were indexed using a hexagonal lattice with a cell parameter of 33.5 nm (Table 1). This indexation establishes that the observed 2D structure consists of circular domains of 33.5 nm in diameter positioned on a hexagonal lattice. Similar results were obtained at 7 mN m^{-1} and as low as 0.5 mN m^{-1}. At 0 mN m^{-1}, no diffraction peaks were observed.

These data demonstrate unambiguously that hemimicelles of F8H16 diblocks exist on the water surface, at least at nonzero surface pressure. We cannot tell whether the micelles exist at zero surface pressure, that is, at very large molecular area since they would probably not be sufficiently organized to diffract the X-ray beam.

Once transferred onto silicon wafers, Langmuir monolayers of F8H16 consist of monodisperse disklike hemimicelles, as visualized by AFM.[4] The transferred hemimicelles of F8H16 had the same diameter (30 ± 2 nm) as was now found on the water surface. The size of the transferred micelles of FnHm diblocks was shown to be controlled by the density mismatch between the fluorocarbon and hydrocarbon blocks and depends mainly on the length of the hydrocarbon block.[14] It is likely that the same control can be exercised at the air−water interface, which is valuable when patterning applications are contemplated. X-ray-induced radiolysis of metal ions present in the subphase of nonpatterned Langmuir monolayers is being explored,[15] and the potential of the arrays of hemimicelles of FnHm diblocks as nanomasks using this method is under investigation.

Table 1. Peak Positions (Q_{xy}) and Widths (W) Deduced from a Lorentzian Fit of the Diffraction Peaks[a]

Q (nm^{-1})	W (nm^{-1})	indexation (hexagonal lattice)
0.2159	0.0249	(1 0)
0.3772	0.0303	(1 1)
0.4333	0.0307	(2 0)
0.575	0.033	(2 1)
0.6509	0.0299	(3 0)
0.747	0.0467	(2 2)
0.8478	0.0222	(4 0)
0.939	0.044	(3 2)
1.113	0.0524	(3 3)
1.172	0.0362	(4 2)
1.293	0.068	(6 0)
1.482	0.0438	(4 4)

[a] Last column is the indexation of the peaks in a hexagonal lattice with a parameter of 33.5 nm.

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