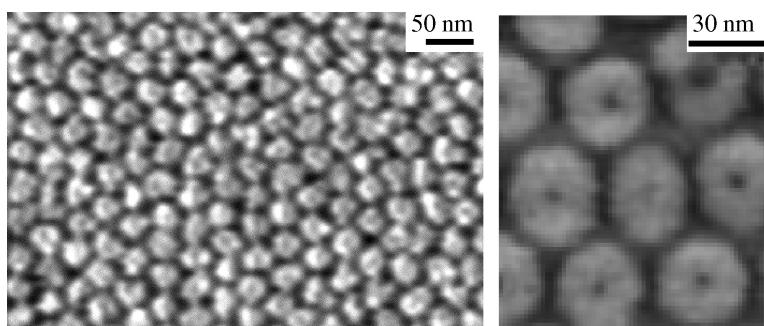


Occurrence, Shape, and Dimensions of Large Surface Hemimicelles Made of Semifluorinated Alkanes. Elongated versus Circular Hemimicelles. Pit- and Tip-Centered Hemimicelles

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Occurrence, Shape, and Dimensions of Large Surface Hemimicelles Made of Semifluorinated Alkanes. Elongated versus Circular Hemimicelles. Pit- and Tip-Centered Hemimicelles

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Abstract: The formation of large (~20–35 nm) surface hemimicelles in monolayers of semifluorinated alkanes, $C_nF_{2n+1}C_mH_{2m+1}$ (FnHm), observed after transfer onto silicon wafers, is a general phenomenon. F6H16 and F8H14 exclusively form highly monodisperse circular hemimicelles, organized in a hexagonal array. The other FnHm investigated form both circular and elongated hemimicelles. The longer FnHm is, the larger the area fraction of elongated micelles; both the hydrocarbon block (*H*-block) and the fluorocarbon block (*F*-block) affect this area fraction. The length of the elongated micelles increases with the total length of the diblocks. The diameter of the circular micelles increases with the length of the *H*-block but, unexpectedly, not with that of the *F*-block. Model calculations account for these observations. Close examination of the circular micelles showed that they generally present a pit or a tip at their center. The width of the elongated micelles is comparable to the radius of the circular micelles, suggesting that the latter arise from a partition of elongated micelles, followed by coalescence of the edges of the resulting fragments. The elongated micelles become shorter and fewer when surface pressure increases, further suggesting a conversion of elongated into circular micelles. This conversion is reversible. The surface pressure–molecular area isotherms do not present any feature that forebears the existence of hemimicelles. The obtaining of stable surface patterns from simple, “nonpolar” molecular fluorocarbon/hydrocarbon diblocks opens a new approach for producing featured nanostructures from organic templates.

Introduction

A current key objective of fundamental research is the design of “meso-scale” systems that have a spatial dimension comparable to the characteristic length of a physical, chemical, or biological process that involves interactions with multiple ensembles of molecules. Meso-scale system dimensions extend from that of macromolecules to that of viruses and eukaryotic cells (i.e., from ~10 nm to ~10 μ m).^{1,2} Meso-scale systems are pivotal in the development of application domains, such as microelectronics (ultradense data storage media), microfluidic devices, sensors, nanoelectromechanical systems, and drug and contrast delivery systems. Novel nanolithographic methods for fabricating and patterning sub-100 nm featured nanostructures are being developed based on the emergence of soft lithographic techniques (replica molding, microcontact printing, etc.).^{1,3} A promising alternative approach for further progress is the formation of patterns via the self-assembly of molecules. Self-assembly is more versatile than lithographic processes as it could

be used to form features on large surface areas of substrates, regardless of their nature and physical state (organic or biological materials with complex three-dimensional shapes can, in principle, be used). However, the use of self-assemblies of organic 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 self-assemblies. Various studies have been devoted to controlling pattern formation from high molecular weight diblock copolymers.⁴ Surface micelles, or more generally speaking “surface aggregates”, were found for copolymers with various hydrophilic blocks, including poly(4-vinyl pyridine) quaternarized with alkyl halides,⁵ poly(*tert*-butylacrylate), poly(*n*-butylacrylate),⁶ poly-(dimethylsiloxane),⁴ and poly(ethylene oxide).⁷ The hydrophobic block is usually poly(styrene). The known surface aggregates are circles (30–50 nm in diameter and ~5 nm high), ribbon-, or lamella-like aggregates, depending on the relative block

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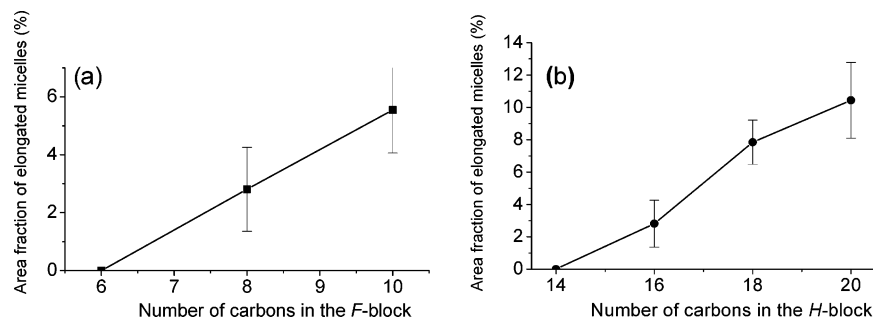


Figure 1. Variation of the area fraction of elongated micelles in transferred films of FnHm as a function of (a) the length of the *F*-block (for an *H*-block of 16 carbons), and (b) the length of the *H*-block (for an *F*-block of 8 carbons).

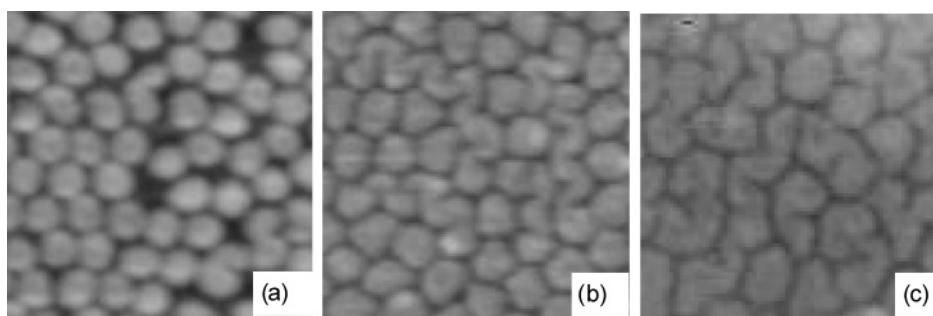


Figure 2. AFM images (250 × 250 nm) of transferred monolayers of (a) F8H16, (b) F8H18, and (c) F8H20 transferred onto silicon wafers at 5 mN m⁻¹.

length. Such polymer-patterned surfaces have been successfully used as nanolithographic masks.^{8–10} Low molecular weight surfactants have also been shown to self-organize onto various substrates (silica, gold, mica, and graphite) to yield circular aggregates, cylinders, or bilayers.^{11–13} These patterns are, however, quite small, their size being only ~5 nm wide and ~1 nm high, which is comparable to the size of three-dimensional surfactant micelles.

Perfluoroalkylated blocks provide an effective driving force for self-aggregation of amphiphilic molecules into molecular self-assemblies, such as micelles, vesicles, micro- and nanotubes,^{14,15} self-assembled monolayers (SAMs),¹⁶ as well as for the elaboration of infinite 1D chains and infinite 2D networks.¹⁷ We have established that, after transfer onto silicon wafers, Langmuir monolayers of the semifluorinated alkane, C₈F₁₇C₁₆H₃₃ (F8H16), consist of highly monodisperse surface hemimicelles having a diameter of 30 nm and a height of 3 nm.¹⁸ The *H*-blocks of the F8H16 molecules are directed toward the substrate, while the *F*-blocks are pointing outward, as shown by specular X-ray reflectivity. The F8H16 hemimicelles form well-ordered two-dimensional hexagonal arrays even for very low surface pressures of transfer (i.e., ~1 mN m⁻¹). More recently, we have shown, using grazing incidence small-angle

X-ray diffraction (GISAXS; European Synchrotron Radiation Facility (ESRF), Grenoble), that the surface hemimicelles of F8H16 already exist on the surface of water;¹⁹ that is, they are not formed during the transfer. Despite the many studies that have been conducted on Langmuir monolayers of semifluorinated alkanes,^{20–22} the existence of such surface micelles had not been anticipated.

The well-ordered, highly stable, hexagonally packed lattice of F8H16 hemimicelles may prove to be useful as a nanomask in the elaboration of patterned nanostructures. With this objective in mind, it was necessary to investigate the generality of the phenomenon, that is, whether other FnHm molecules also organize into surface hemimicelles and whether the shape and dimensions of these hemimicelles could be controlled by varying the lengths of the *F*- and *H*-blocks. We present here an investigation of the surface morphology of Langmuir monolayers of a series of FnHm molecular diblocks with *n* = 6, 8, and 10 and *m* = 14, 16, 18, and 20 after transfer onto silicon wafers.

Results and Discussion

Circular versus Elongated Micelles: Influence of the Molecular Structure of the FnHm Diblocks. The observation by atomic force microscopy (AFM) of FnHm Langmuir monolayers transferred onto silicon wafers established that all of the compounds investigated form surface micelles, hence, that surface micelle formation appears to be a general phenomenon for semifluorinated alkanes in these conditions. For some of the FnHm diblocks, elongated (or wormlike) micelles (see Figure 2) were found to coexist with circular micelles of the

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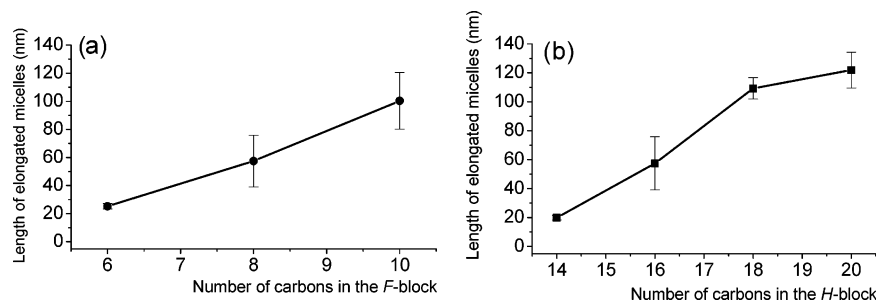


Figure 3. Variation of the length of the elongated micelles of FnHm as a function of (a) the length of the *F*-block (for an *H*-block of 16 carbons), and (b) the length of the *H*-block (for an *F*-block of 8 carbons).

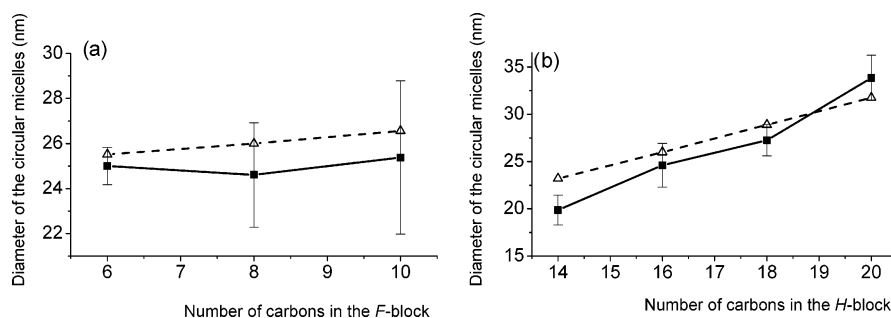


Figure 4. Variation of the mean diameter (solid lines) of the circular surface micelles of FnHm as a function of (a) the length of the *F*-block (for an *H*-block of 16 carbons), and (b) the length of the *H*-block (for an *F*-block of 8 carbons). Theoretical variations (dashed lines) are also shown.

Table 1. Characteristics of the Elongated Micelles Present in Transferred Monolayers of FnHm Molecules, As Assessed by Image Analysis

FnHm	surface pressure of transfer (mN m^{-1})	area fraction (%)	average length (nm)	average width (nm)
F6H16	5	0	0	0
F8H14	5	0	0	0
F8H16	2	12.5 ± 2.5	143.7 ± 8.6	<i>a</i>
	5	2.8 ± 1.4	57.4 ± 18.4	13.6 ± 2.6
F8H18	2	9.7 ± 4.6	132.3 ± 32.8	<i>a</i>
	5	7.8 ± 1.4	109.2 ± 7.4	17.2 ± 1.7
	8	6.2 ± 2.6	100.8 ± 10.5	16.9 ± 1.9
	12	3.3 ± 1.5	84.8 ± 7.5	15.2 ± 0.7
F8H20	5	10.4 ± 2.3	121.9 ± 12.4	20.6 ± 3.1
	18	2.8 ± 1	118.0 ± 15.8	18.4 ± 2.8
F10H16	5	5.5 ± 1.5	100.3 ± 20.1	17.2 ± 1.7
	10	1.6 ± 0.8	80.8 ± 5.9	10.7 ± 1.6

^a Could not be determined.

type found in the transferred films of F8H16. To assess the effect of the molecular structure of FnHm on the shape and dimensions of the surface micelles, we determined quantitatively, by image analysis, the relative amount of elongated micelles present. The area fraction, average length, and average width of elongated micelles formed are displayed in Table 1. The length of the elongated micelles was determined by measuring the length of their backbone.

It can be seen that the shortest FnHm (F6H16 and F8H14) exclusively form circular micelles. For the other compounds, the area fraction of elongated micelles ranges from ~ 2.8 to $\sim 12.5\%$. Figure 1 shows that, at a given surface pressure of transfer π_t (5 mN m^{-1}), the relative proportion of elongated micelles increases with the length of both the *F*-block and the *H*-block.

Figure 2 illustrates the effect of the overall FnHm length on the occurrence of elongated micelles.

While circular micelles are present almost exclusively in films of F8H16, some elongated surface micelles are seen in F8H18

Table 2. Mean Diameter of the Circular Micelles in Transferred Monolayers of FnHm Molecules Measured with NanoScope Software (D_1), Visilog Software (D_2), and Calculated (D_{calcd}) (see part c of Results and Discussion)

FnHm	surface pressure of transfer (mN m^{-1})	D_1 (nm)	D_2 (nm)	D_{calcd} (nm)
F6H16	5	30.1 ± 0.2	25.3 ± 0.8	22.5
F8H14	5	25.7 ± 1.2	19.9 ± 1.6	24.1
F8H16	2	35.1 ± 1.2	27.8 ± 1.0	26.0
	5	30.5 ± 1.2	24.6 ± 2.3	26.0
F8H18	2	34.5 ± 0.8	27.5 ± 0.7	27.8
	5	32.8 ± 0.9	27.2 ± 1.6	27.8
	8	34.7 ± 1.6	29.3 ± 1.7	27.8
	12	33.6 ± 2.0	29.1 ± 3.0	27.8
F8H20	5	38.6 ± 2.4	33.9 ± 2.4	28.7
	18	35.8 ± 2.5		28.7
F10H16	5	30.2 ± 2.3	25.4 ± 3.4	29.3
	10	39.0 ± 2.1	27.0 ± 3.9	29.3

films; they become more numerous with F8H20. Quantitative image analysis determined that the elongated micelles become longer when the total length of the FnHm increases. Figure 3 shows that the longer the *F*- or *H*-blocks, the longer the elongated micelles.

Circular Micelles: Size and Organization. (a) Diameter of the Circular Micelles. Table 2 collects the average diameters of the circular micelles as measured with the usual NanoScope software and with the Visilog image analysis software. The NanoScope software only provides a mean diameter for the domains present, whether circular or elongated, indistinctly. Visilog, which allows removing the elongated micelles from the investigated field, provides an analysis of the circular micelles only. The Visilog data (D_2), which are significantly lower than the Nanoscope values (D_1), are, therefore, expected to better reflect the actual values.

Figure 4 displays the variations of the mean diameter of the circular micelles as a function of the lengths of the *F*-block and *H*-block.

Figure 4 shows that increasing the length of the *F*-block, while keeping the *H*-block's length constant, has surprisingly little effect on the diameter of the micelles. On the other hand, this diameter increases strongly with the length of the *H*-block (at constant *F*-block length). Consequently, for a given total chain length, increasing the weight of the *F*-block in the molecule results in a decrease in micelle size. Thus, at 5 mN m⁻¹, the diameter of the micelles formed by F6H16 (25.3 ± 0.8 nm) is larger than that formed by F8H14 (19.9 ± 1.6 nm).

In the case of partially fluorinated carboxylic acids,²³ the mean diameter of the surface micelles, as assessed using the NanoScope software, also increased with the *H*-block's length and did not change with the *F*-block's length. Qualitatively, the shape of the micelles was reported to change from circular to so-called "irregular". The average diameter of the surface micelles formed by F8H16COOH (~33 nm) was similar to that of surface micelles of F8H16 (30.5 ± 1.2 nm) when measured using the NanoScope software in this work.

Several points need to be highlighted here. First, the diameters of the circular surface micelles of semifluorinated amphiphiles (either semifluorinated alkanes or semifluorinated carboxylic acids) are much larger (~20–35 nm) than those of the surface micelles formed by nonfluorinated surfactants (~5 nm).^{11,12} The driving force for their formation is likely to be different. The fact that discrete curved objects are formed, rather than the flat monolayers observed with classical surfactants, is in itself remarkable. It can be ascribed to the forced coexistence, within the hydrophobic tail, of *F*- and *H*-blocks, which have different cross-sections. The packing of F_nH_m in a conventional flat monolayer would result in a lack of density in the hydrocarbon sheet within the monolayer. This lack of density is relieved by the formation of aggregates, the bending of the edges toward the interface, resulting in an increase of the density of the hydrocarbon sheet. Finally, it is remarkable that the organization into hemimicelles is driven solely by the hydrophobic segments, not by the polar head. The formation of hemimicelles from simple semifluorinated alkanes indicates that when a carboxylic headgroup is present in the amphiphile, it likely plays little or no role in the formation of hemimicelles.

Interestingly, the diameters of the hemimicelles involving small semifluorinated molecules are comparable to those of surface micelles obtained from block copolymers several orders of magnitude larger. These diameters fit well within the presently accepted range of sizes desired for organic templates intended for the elaboration of nanostructures.

Hexagonal arrays of similarly sized circular hemimicelles of F8H16 and F8H18 have also been observed when the monolayers were transferred onto glass plates rather than silicon wafers. The fact that the morphology of the patterns does not depend on the nature of the substrate is another point of resemblance of semifluorinated compounds with diblock copolymers. By contrast, the shape of the patterns formed by standard surfactants in self-assembled monolayers is strongly influenced by the nature of the substrate.¹³

(b) Influence of the Surface Pressure of Transfer on Circular Micelles. Figure 5 shows that varying π_t does not influence the diameter of the circular micelles significantly. For all of the F_nH_m compounds investigated, it was found that the

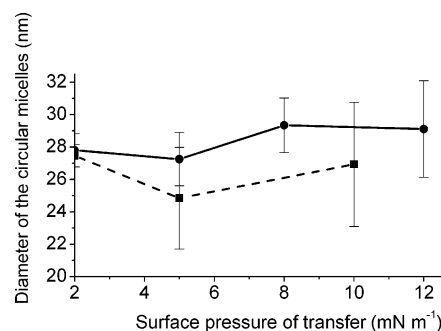


Figure 5. Variation of the diameter of circular micelles made from F8H16 (solid line) and F8H18 (dashed line) as a function of the surface pressure of transfer.

surface micelles progressively come closer together during compression; that is, their arrangement becomes more compact, but their diameter does not change. Importantly, no coalescence between micelles was ever observed to occur, even at the highest π_t values.

Grazing incidence small-angle X-ray diffraction (GISAXS) experiments directly conducted on the surface of water also showed that the diameter of surface micelles of F8H16 was not affected by variations of the surface pressure.¹⁹

(c) Model. We propose a disklike model that allows calculation of the mean radius of the micelles, *R*. In this model, the interfacial area between the hydrocarbon and fluorocarbon layers within the surface micelle, $S_{\text{interface}}$, is being calculated (eq 1):

$$S_{\text{interface}} = \pi (R - L_{\text{FnHm}})^2 + \pi^2 (R - L_{\text{Fn}}) L_{\text{Hm}} = S_{\text{FnHm}} \times N_{\text{FnHm}} \quad (1)$$

where L_{Hm} , L_{Fn} , L_{FnHm} are the lengths of the fully stretched *H*-block, *F*-block, and F_nH_m molecule, respectively.

Since $S_{\text{interface}}$ must be equal to the product of the cross-section area of the F_nH_m diblock (S_{FnHm}) by the number of molecules (N_{FnHm}) that constitute one micelle, and since $N_{\text{FnHm}} = V_{\text{H}}/V_{\text{Hm}}$ (V_{Hm} is the volume of the *H*-block), one obtains eq 2 that allows calculation of *R*, knowing that $S_{\text{FnHm}} = 28.3 \text{ \AA}^2$.²⁴

$$(R - L_{\text{FnHm}})^2 + \pi (R - L_{\text{Fn}}) L_{\text{Hm}} = S_{\text{FnHm}} \left\{ [(R - L_{\text{FnHm}})^2 L_{\text{Hm}} + \pi/2 (R - L_{\text{FnHm}}) L_{\text{Hm}}^2 + 2/3 L_{\text{Hm}}^3]/V_{\text{Hm}} \right\} \quad (2)$$

Figure 4 shows that the calculated diameter values are in good agreement with the experimental values. In particular, the model adequately reflects the fact that increasing the *F*-block length does not increase the micelle's diameter in any substantial way.

Pit- and Tip-Centered Micelles. Close scrutiny of the AFM images of the circular micelles shows that their surface is not flat. In most cases, they exhibit a pit at their center, that is, they have a doughnut-shaped morphology. In other cases, they present a tip at their center. Figure 6a shows an AFM image of surface micelles of F8H18 (transferred at 8 mN m⁻¹) showing pits. The pit is clearly visible on the AFM profile analysis. The depth of the pit could, however, not be determined quantitatively due to the limitations of the AFM method (probe size, convolution by the AFM tip). It can also be seen in Figure 6a that some of the doughnut-shaped micelles are not totally closed up, as if the formation process had remained incomplete. Figure

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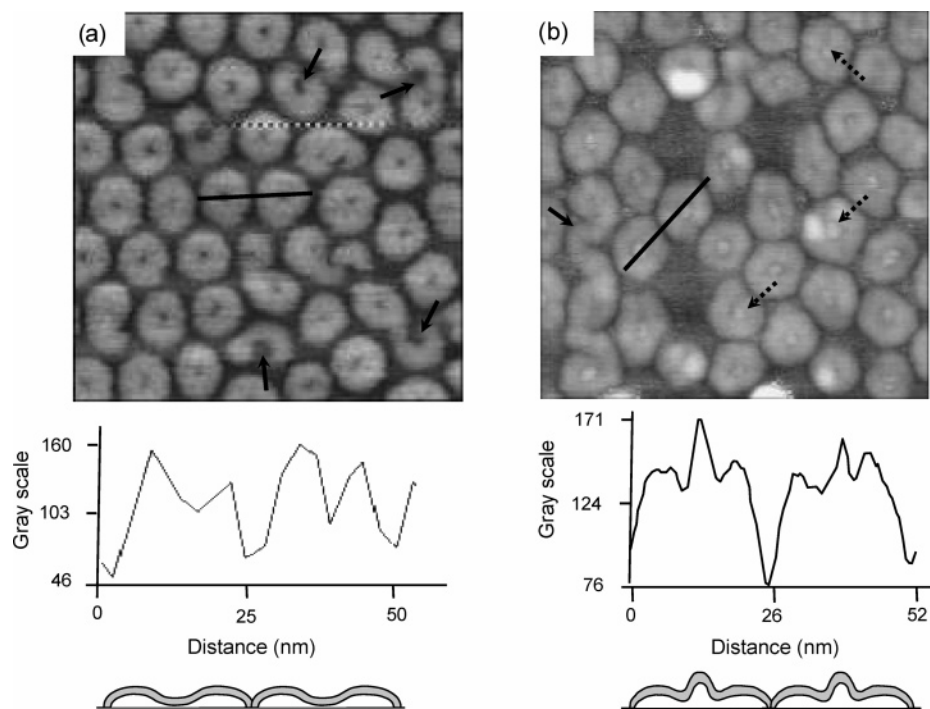


Figure 6. AFM images (336×336 nm) of films of F8H18 transferred at (a) 8 mN m^{-1} and (b) 12 mN m^{-1} . Below each panel are the corresponding image analyses of the AFM profiles along the solid lines shown in the images, as well as schematic representations of surface hemimicelles displaying (a) a pit and (b) a tip at their center. In (a), the arrows show doughnut-shaped surface micelles that are not completely closed up. In (b), the solid arrow shows an elongated micelle, and the dotted arrows show micelles with a tip at their center that may result from the protrusion of one of the edges during curling.

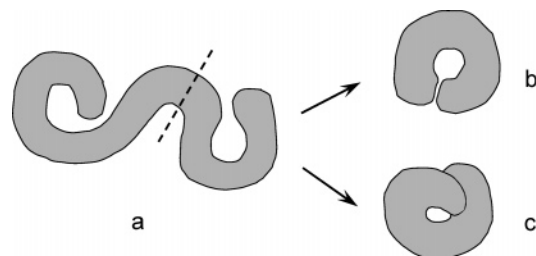
6b shows an AFM image of surface micelles of F8H18 transferred at 12 mN m^{-1} . In this case, the profile analysis shows the presence of a tip at the center of the micelles. The possibility of these features (pits or tips) being artifactual can be discarded because they were observed reproducibly and because they are reproducibly located at the very center of the micelle.

To our knowledge, this is the first observation of such morphologies in surface micelles. It was, therefore, desirable to get some insight on the mechanism of formation of these surface micelles. Mastering micelle morphology is, indeed, a key issue when the objective is to use them as templates for the elaboration of nanostructured materials.

Mechanism of Formation of Surface Micelles. (a) Conversion of Elongated Micelles into Spherical Micelles. The AFM images suggest that the circular micelles likely originate from elongated micelles that have partitioned into smaller segments. In support of this hypothesis is the observation that the width of the elongated micelles is close to half the diameter of the circular micelles (Tables 1 and 2). This observation is valid for all the FnHm molecules and under all the surface pressure conditions investigated. The segments that result from the sectioned elongated micelles may then curl and their two extremities fuse together, thus forming pit-centered micelles, as shown in Figure 6a (see also Scheme 1). In certain cases, the curling of the segments is not complete, resulting in the formation of open doughnut-shaped structures. It may also happen that the two extremities of the sectioned elongated micelle do not curl in the same plane, one of them staying in contact with the substrate while the other extremity spirals upward. This may result in the formation of a tip-centered micelle (Figure 6b and Scheme 1).

It can be inferred that the conditions of transfer should influence the occurrence of pits or tips in surface micelles; low

Scheme 1. Schematic Representation of the Partition of an Elongated Micelle (a) to Yield Formation of (b) a Pit-Centered Micelle and (c) a Tip-Centered Micelle, Depending on the Conditions of Transfer



surface pressures of transfer would induce the formation of pits, while high surface pressure would favor the formation of tips. This is indeed the case for F8H18 (Figure 6).

(b) Influence of the Surface Pressure of Transfer on the Area Fraction and Length of the Elongated Micelles. To determine whether elongated micelles can convert into circular micelles, we have investigated whether the relative proportions of elongated versus circular micelles were sensitive to the surface pressure of transfer.

Figure 7a shows that the higher π_t is, the smaller is the area fraction of elongated micelles (see also Table 1). It was also found that the length of the elongated micelles decreases with the surface pressure (Figure 7b). In addition, when the monolayer was allowed to re-expand following compression, the area fractions and lengths of elongated micelles were found to be comparable to the values found before compression. This indicates that a dynamic conversion process of the elongated micelles into circular micelles is at work, the former ones disappearing to the benefit of the latter ones when surface pressure increases, the phenomenon being reversible.

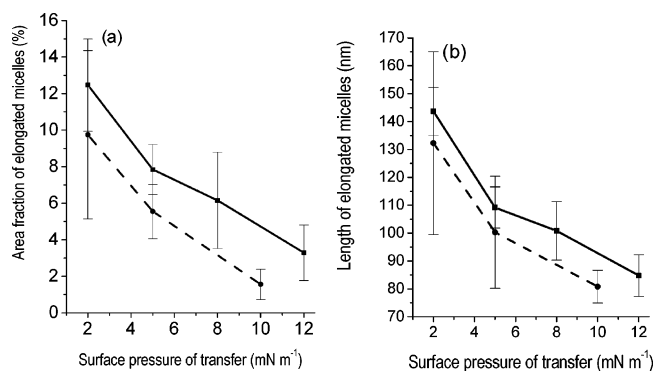


Figure 7. Variation of (a) the area fraction and (b) the length of the elongated micelles as a function of the surface pressure of transfer for F8H18 (solid lines) and F10H16 (dotted lines).

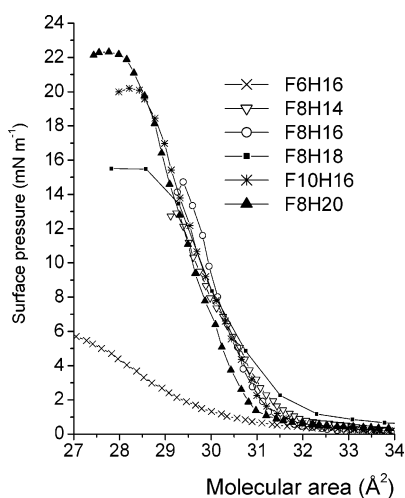


Figure 8. Surface pressure–molecular area compression isotherms of the FnHm diblocks at the air/water interface at 20 °C.

Surface Pressure–Molecular Area (π - A) Compression Isotherms of FnHm Diblock Monolayers. Figure 8 collects the isotherms of the FnHm diblocks investigated. Although the isotherms of some of these compounds have been published,^{18,20–22} the relative effects of the *F*- and *H*-blocks on the monolayer behavior have not been determined. Figure 8 shows that, except for F6H16 (which, along with F8H14, is the shortest

diblock used, but also the compound having the shortest *F*-block), all the FnHm investigated form stable Langmuir monolayers.

The collapse pressures, π_c , range from ~ 12 to 22 mN m⁻¹. The longer the FnHm molecule, the higher π_c and the more stable the monolayer. When comparing diblocks of the same total length, it is that compound with the longest *F*-block that always gives the most stable monolayer. Thus, F8H14 forms a stable monolayer ($\pi_c = 12$ mN m⁻¹), while F6H16 progressively desorbs from the water surface during compression. Also illustrative is the fact that F10H16 has a π_c higher than that of F8H18 (~ 20 vs 15 mN m⁻¹, respectively).

Except for F6H16, all of the isotherms display comparable limiting molecular areas (A_0) of 31 ± 0.5 Å². This A_0 value is significantly lower than those found for *partially* fluorinated carboxylic acids, C_{*n*}F_{*2n+1*}(CH₂)_{*m*}COOH ($n = 8, 10; m = 10, 16, 22$), which typically range from 35 to 40 Å².^{23,25} By contrast, the A_0 values of FnHm are only slightly larger than those commonly measured for *perfluoroalkylated* surfactants (29 Å²), which, in turn, is very close to the usually accepted value for the cross-section of a perfluorinated chain (28.3 Å²).²⁶ In Langmuir monolayers, the liquid condensed (LC) phase structures of perfluoroalkylated carboxylic acids, perfluoroalkylated alcohols, or perfluoroicosane all consist of molecules vertically packed in a well-organized 2D hexagonal lattice with a unit cell area of ~ 29 Å², as determined by grazing incidence X-ray diffraction.²⁶

The larger disorder commonly observed in the packing of partially fluorinated amphiphiles, as compared to that of perfluorinated compounds, is generally assigned to the combined effects (1) of the cross-sections mismatch between the fluorinated terminal chain and the hydrogenated spacer within the hydrophobic chain, and (2) of the repulsive interactions between the dipoles associated with the CF₂–CH₂ linkages. Such disorder can result in the apparition of a liquid expanded (LE) phase in their phase diagram. The occurrence of such an LE phase is inhibited for *perfluorinated* surfactants by the rigidity of the *F*-chain.²⁶ The fact that simple FnHm molecules are better organized than semifluorinated carboxylic acids with similar hydrophobic chains indicates that the polar head is also, unexpectedly, a factor of disorder.

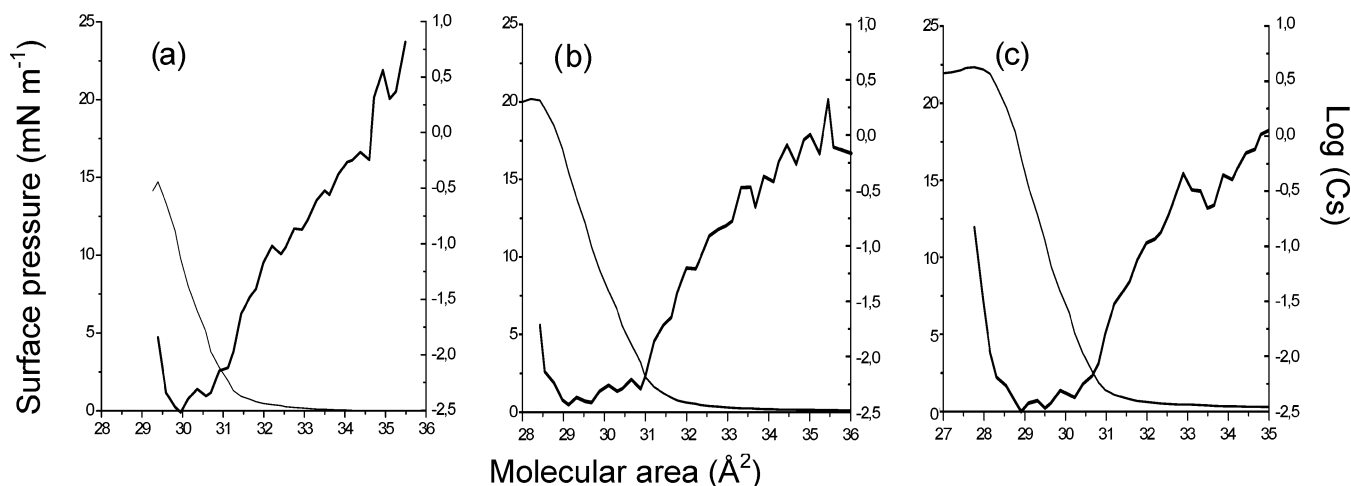


Figure 9. Variation of the surface pressure (thin lines) and isothermal compressibility coefficients (heavy lines) as a function of molecular area for (a) F8H16, (b) F10H16, and (c) F8H20.

Table 3. Values of Surface Pressure and Molecular Area Corresponding to Minimum Compressibility Values, $C_{s\min}$, in FnHm Langmuir Monolayers

FnHm	surface pressure (± 1.0 mN m $^{-1}$)	molecular area (± 0.7 Å 2)	$C_{s\min}$ ($\times 10^{-3}$) (± 1.4 m mN $^{-1}$)
F8H14	10.6	29.4	4.6
F8H16	9.6	30.1	3.3
F8H18	10.7	30.3	5.2
F8H20	15.7	28.4	3.2
F10H16	15.3	29.1	4.5

The isothermal compressibility coefficients (C_s) of FnHm monolayers were calculated from π - A isotherms according to $C_s = (-1/A)(dA/d\pi)$, where A is the area per molecule and π the surface pressure (Figure 9). The minimum compressibility values, $C_{s\min}$ (Table 3), do not vary significantly with the molecular structure. These values, which range from 3.2 to 5.2×10^{-3} m mN $^{-1}$, are lower than those (5.4 – 6.2×10^{-3} m mN $^{-1}$) reported for partially fluorinated carboxylic acids of similar F - and H -block length.²⁵ The compressional moduli (the reciprocal quantity of C_s), C_s^{-1} , range from 192 to 312 mN m $^{-1}$, indicating that the FnHm monolayers are in an LC state.²⁷

It is noteworthy that the surface hemimicelles have no detectable effect on the surface pressure–area isotherms, and that their existence could not be inferred from the isotherms.

Conclusions and Perspectives

We have established that Langmuir monolayers of semifluorinated alkanes $C_nF_{2n+1}C_mH_{2m+1}$ (FnHm, $n = 6, 8, 10; m = 14, 16, 18, 20$), transferred onto silicon wafers, consist of surface hemimicelles rather than of classical, laterally featureless monolayers. The size of these hemimicelles is in the 20–35 nm range, that is, much larger than those of the micelles obtained from classical molecular surfactants. Depending on the molecular structure of the FnHm diblocks, the hemimicelles are circular or elongated. Increasing the FnHm length favors the formation of elongated micelles at the expense of the circular ones. Highly monodisperse circular hemimicelles are formed by F8H16 and F8H20. When transferred at high surface pressure, these hemimicelles form highly organized and stable hexagonal networks. It is remarkable that the hemimicelles do not shrink nor coalesce and retain their circular shape when compressed at surface pressures close to collapse, while the much smaller surface micelles formed by conventional surfactants are deformed and eventually coalesce upon compression. The diameter of the circular micelles is controlled by the length of the H -block, while the length of the F -block has no significant influence. The formation of these surface micelles cannot be predicted from the surface pressure–molecular area isotherms. However, the experimental data are in good agreement with a model based on the fact that the interfacial area between the hydrocarbon and fluorocarbon layers within a circular surface micelle is equal to the product of the cross-section area of the FnHm molecule by the number of FnHm per micelle. This model allows prediction of the micelle diameter for a given FnHm. It also shows that the size of the micelles is only controlled by the density mismatch between the F -block and

the H -block. The limiting molecular area of the FnHm molecules is lower than those found for carboxylic acids that have similar partially fluorinated hydrophobic chains, indicating that the former compounds are better organized and that the polar head is a factor of disorder.

We also found that the circular surface micelles have a hole or a tip at their center, two morphologic features that had never been reported for any surface micelles. The width of the elongated micelles, when present, is very close to the radius of the circular micelles. An interconversion between the two types of objects appears to occur, by which circular micelles are formed from elongated ones. This hypothesis is supported by the fact that the occurrence of elongated micelles is reduced when surface pressure of transfer is high. The phenomenon is reversible.

The formation of stable, large nanometric surface hemimicelles from simple fluorocarbon/hydrocarbon amphiphiles devoid of a polar head may provide a new approach to organic templates for the elaboration of metallic or polymeric nanostructures and deserve further investigation. X-ray-induced radiolysis of metal ions present in the subphase of nonpatterned Langmuir monolayers is being explored,²⁸ and the potential of the arrays of hemimicelles of FnHm diblocks as nanomasks using this method is under investigation.

Experimental Section

Materials. FnHm diblocks were synthesized according to ref 29 and were thoroughly purified by repeated crystallizations from methanol. Chemical purity (>99%) was determined by TLC, NMR, and elemental analysis. Polarization microscopy established that the compounds were crystalline when pure. Spreading solutions of FnHm (1 mmol L $^{-1}$ for LB transfer and 0.5 mmol L $^{-1}$ for surface pressure–area isotherm measurement) were prepared in analytical grade chloroform. Water was purified using a Millipore system (surface tension = 72.1 mN m $^{-1}$ at 20 °C; resistivity = 18.2 MΩ cm).

Monolayer Isotherms: Transfer of the Monolayers. Surface pressure versus molecular area (π - A) isotherms were recorded on a Langmuir minitrough (Riegler & Kirstein GmbH, Potsdam, Germany) equipped with two movable barriers (compression speed = 0.1 nm 2 min $^{-1}$ molecule $^{-1}$). The surface pressure was measured using the Wilhelmy plate method. Temperature was regulated at 20.0 ± 0.5 °C; 25 μ L of FnHm solution was spread on the water surface and 5 min was allowed for solvent evaporation.

The monolayers were compressed up to the desired surface pressure and transferred onto a silicon wafer previously treated with a piranha solution (concentrated H $_2$ SO $_4$ + 30% H $_2$ O $_2$ 3:1), using the Langmuir–Blodgett technique (one monolayer is transferred; lift speed = 1 mm min $^{-1}$).

AFM Images. The transferred films were analyzed with an atomic force microscope (NanoScope III, Digital Instruments, Santa Barbara, CA) in tapping mode. The cantilever (Olympus) was fitted with a very sharp tip (5 nm). The resonance frequency was 300 kHz and the spring constant 42 mN m $^{-1}$. At least three different samples were analyzed, and several positions were scanned on the wafer for each sample.

Image Analysis. The mean values of the parameters that characterize the micelles (diameter or width, area, length, area fraction) were measured on the AFM images using the NanoScope software and the Visilog Image Analysis Software (Noesis, Les Ulis, France). The average values of these parameters and standard deviations (SD) were calculated from the analysis of at least three images. The NanoScope

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software allowed automatic determination of the mean diameter of the domains in the image, but did not allow discrimination between circular and elongated micelles nor calculation of their dimensions independently. The digitized AFM images were analyzed with the Visilog Image Analysis Software using filtering techniques, a morphological gradient method, mathematical morphology functions, and adaptive thresholding.³⁰ Visilog allowed determination of the parameters of both circular and elongated micelles independently by extracting selectively

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the desired domains, that is, circular or elongated, by filtering them with a shape factor.

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