

Highly Fluorinated Compounds Induce Phase Separation in, and Nanostructuration of Liquid Media. Possible Impact on, and Use in Chemical Reactivity Control

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ABSTRACT: Liquid perfluorocarbons-like supercritical CO₂-provide valuable reaction media that can facilitate the separation of reaction products and the recovery of catalysts. Chemistry in fluoruous media requires that some of the protagonist molecules, and in particular the catalysts, be grafted with one or more perfluoroalkylated chains. These chains, due to powerful hydrophobic and lipophobic effects, tend to self-

assemble and induce the formation of a variety of nanocompartmented supramolecular architectures and colloids, such as micelles, vesicles, tubules, monolayers, and emulsions, thus generating microheterogeneity in the reaction medium. Fluorinated amphiphiles are, for example, known to generate fibrous gels in fluoruous, organic, and aqueous media. Phase separation, nanocompartmentation, and interface-driven parameters

can thus complicate otherwise simple chemistry. Conversely, they can provide useful micro- and nano-reactors and templates. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 4251–4258, 2006

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nents of self-assembled molecular systems. Her present research includes the elaboration and study of multicompartimented micro- and nano-objects, nanocompartmentation being induced by fluorinated chains in organized systems such as monolayers, surface micelles, vesicles, tubules, microbubbles, and emulsions. The potential of such systems for biomedical applications (lung surfactant, tissue oxygenation, bioartificial pancreas, diagnosis) and in materials science (nanopatterned surfaces) is also explored. Dr. Krafft has published over 80 articles, including 4 book chapters, 10 invited reviews, 9 patents, and she has given numerous lectures. She sits on the Committees of the Nanosciences Program of the French National Research Agency, of the Division of Physical Chemistry, and of the French Network of Fluorine Chemistry. She coedits the Surfactant section of *Current Opinion in Colloid and Interface Science*.

INTRODUCTION

The synthesis of polymers having well-defined compositions, architectures, and functionalities is a major challenge of contemporary polymer science. Among the strategies used to achieve controlled/"living" radical polymerization, transition metal-mediated atom transfer radical polymerization (ATRP) has attracted considerable attention. ATRP allows effective control of the formation of a variety of macromolecular architectures, including block-copolymers, graft copolymers, comb and star polymers, and hyperbranched and dendritic polymers.^{1,2} One major constraint of the ATRP approach is the large amount of catalyst required to ensure suitable polymerization rates. Transition metal residues from catalysts need to be removed, as they tend to induce redox reactions and oxidative degradations of the polymers and, thereby, complicate ATRP implementation. More generally, the search for recoverable catalysts is a major concern of present-day chemistry.^{3,4}

Diverse solid/liquid separation methods have been proposed to recover metal-based catalysts, including immobilization of the ATRP catalyst onto polymeric supports.

Another strategy for catalyst recovery relies on the use of liquid–liquid separation procedures involving perfluorocarbons (PFC) or supercritical carbon dioxide (scCO₂). Chemical reactions in a PFC (fluorous chemistry) or scCO₂ generally imply the use of perfluoroalkylated* components, including substrates, reagents, or catalysts.

One key objective of this Highlight is to emphasize the fact that many of these reagents, catalysts, and so

forth once fitted with *F*-alkylated chains (*F*-chains) (The recently published Handbook of Fluorous Chemistry abounds in examples of such chemicals.⁶) are likely to become amphiphilic or to see an existing amphiphilic character be exacerbated. Hence, they become susceptible to adsorption at interfaces and to self-association into supramolecular and other colloidal systems. *F*-alkylated moieties, due to their combined hydro- and lipophobia, and consequent tendency to phase separate from both aqueous and organic media (or polar and hydrocarbonous moieties), are prone to generating nano-compartmentation within membranes and colloids. This phase separation also results in the development of large size interfaces. Phase separation, nanocompartmentation, and interface-driven parameters can thus complicate otherwise simple chemistry. Conversely, they can provide useful micro- and nanoreactors and templates.

SOME KEY ATTRIBUTES OF *F*-CHAINS

F-chains have outstanding chemical inertness that results from the strength of the C—F bond (the strongest single bond encountered in organic chemistry), the low polarizability, and electron-attracting character of the fluorine atom, which reinforces the C—C backbone, and the dense electron shield that protects the molecule against the approach of reagents.^{5,7,8} *F*-chains also differ from hydrogenated chains (*H*-chains) by their bulkiness (cross sections of $\sim 28 \text{ \AA}^2$ vs. 20 \AA^2 , respectively). The mean volumes of the CF₂ and CF₃ groups are estimated as 38 and 92 \AA^3 vs. 27 and 54 \AA^3 for CH₂ and CH₃, respectively. To alleviate steric hindrance, *F*-chains adopt a helical conformation rather than the planar "zigzag" structure of *H*-chains. Because of reduced conformational freedom, *F*-chains are also more rigid than *H*-chains.

The low polarizability of fluorine results in very weak van der Waals interactions among *F*-chains and, consequently, to low cohesive energy within liquid PFCs.

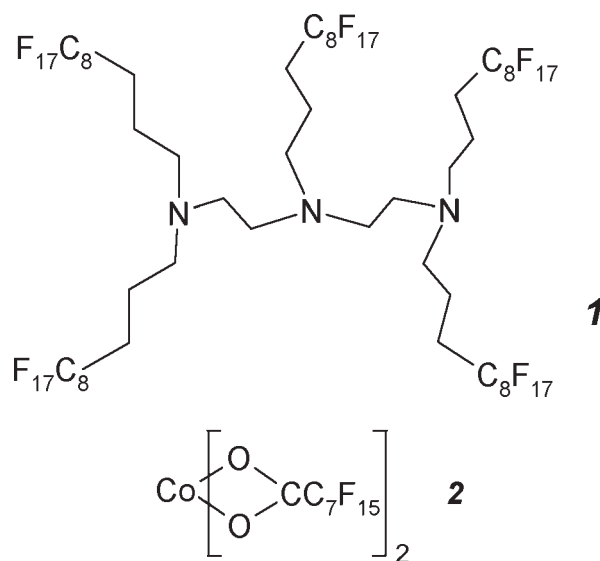
*(*F*-alkylated; The IUPAC-authorized *italized* prefixal symbol *F*-means perfluoro, as in *F*-alkyl = perfluoroalkyl. By extension, it will be used here to designate entities (*F*-chains, *F*-amphiphiles, *F*-colloids, etc.) that comprise a highly fluorinated moiety or phase, responsible for effects different from those found for hydrogenated analogs.⁵)

F-chains are considerably more hydrophobic than *H*-chains. Being less water-soluble than their hydrogenated counterparts, *F*-alkylated surfactants form micelles at much lower concentrations, as reflected by critical micellar concentrations that are typically two orders of magnitude lower. Interfaces made from *F*-amphiphiles generally exhibit lesser curvatures than those found for nonfluorinated analogs, thus favoring, for example, vesicles over micelles and tubules over vesicles. *F*-self-assemblies are also less dynamic than those made from nonfluorinated analogs: the exchange of components among micelles or vesicles is significantly slower. Permeability across fluorinated membranes tends to be lower than that for their hydrogenated counterparts. Fluorinated surfactants can decrease the surface tension of water down to values ($15\text{--}20\text{ mN m}^{-1}$) that cannot be reached by any hydrogenated surfactant. The interfacial tension between an aqueous solution of an *F*-surfactant and a PFC is also very low (typically $0\text{--}5\text{ mN m}^{-1}$). In addition to extreme hydrophobicity, *F*-chains exercise a pronounced lipophobic effect, which was estimated at about one third in magnitude of their hydrophobic effect.⁹

PERFLUOROCARBONS AND SUPERCRITICAL CO₂

Liquid PFCs and scCO₂ share some common features. Both media have extremely low cohesive energy. Both exhibit a unique capacity for dissolving highly fluorinated compounds. The concept of fluorous biphasic catalysis has been introduced in 1994.¹⁰ In its initial form, the catalyst, on which *F*-chains have been grafted, is confined in the PFC phase (the “fluorous” phase), while the substrate and reaction products are dissolved in an organic solvent. Biphasic at low temperature, the system becomes homogeneous when heated. Cooling of the medium at the end of the reaction allows easy separation of the reaction products from the catalyst, which returns to the PFC phase. In the recent years, chemistry in fluorous biphasic systems has evolved into a well-established, self-standing discipline that provides new, up and coming procedures for organic synthesis.^{6,11} For example, the fluorinated catalyst based on the equimolar mixture of Cu(I)Br and the fluorous polyamine ligand **1**, initially developed for atom transfer radical additions (ATRA),¹² was efficient for copper(I)-mediated ATRP of methyl methacrylate.¹³ The *F*-catalyst was efficiently recycled after hydrocarbon/PFC extraction. Likewise, cobalt(II) *F*-octanoate (**2**)-catalyzed ATRP and reverse ATRP allowed preparation of oligostyrene with low dispersity.¹⁴

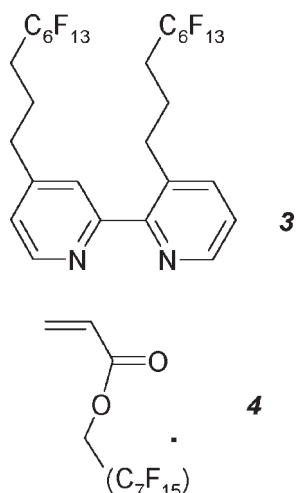
One definite trend, designated as “light fluorous chemistry”, is now to use the minimum amount of fluorine needed to reach the intended goal. As a limiting



case, one can cite fluorous catalysts whose solubility-based thermotropic properties in organic solvents are exploited to achieve homogenous fluorous catalysis without a PFC solvent.¹⁵ Light fluorous chemistry has also found its way in separation science. For example, the hydrophobic and lipophobic interactions that “bind” *F*-chains, used as tags, have allowed immobilization of DNA fragments on *F*-alkylated silicagel for purification of oligonucleotides.¹⁶

In parallel, the use of scCO₂ as a polymerization medium has been widely investigated during the last decade.¹⁷ In addition to being an environmentally benign alternative to volatile organic solvents, scCO₂ offers the advantages of having low solution viscosity, effective inertness (no detectable chain transfer to solvent), and tunable solvent strength. In particular, scCO₂ was shown to be an excellent solvent for radical polymerization.

Complementary use of scCO₂ and an *F*-monomer or *F*-catalyst or *F*-surfactant opens further interesting perspectives. Thus, one can cite the living carbocationic polymerization in CO₂ of vinyl ethers, for which the lowest polydispersity was obtained with a vinyl ether bearing a fluorinated side chain.¹⁷ ATRP was successfully carried out in CO₂ for the polymerization of *F*-(meth)acrylates.¹⁸ Well-controlled polymerizations have been achieved with the *F*-alkyl-substituted 2,2'-bipyridine ligand **3** (used in equimolar amount with CuCl). As a further example that involves both CO₂ and *F*-components, one can mention the dispersion polymerization of methyl methacrylate (MMA) using ATRP in scCO₂ in the presence of a fluorinated polymeric surfactant stabilizer obtained from 1,1-dihydro-*F*-octyl acrylate **4**. This reaction successfully produced poly(MMA) latex particles with controlled molecular weight and narrow distribution.¹⁸



F-CHAINS PROMOTE SELF-ASSEMBLY AND STABILIZE COLLOIDAL SYSTEMS IN BOTH AQUEOUS AND ORGANIC MEDIA

The remarkable ability of compounds comprising an *F*-chain to induce microstructuration derives from the possibility of combining up to three antinomial affinities at the molecular level, namely fluorophilic, lipophilic, and hydrophilic, within the same molecule (Scheme 1). Such arrangements are actually found in many compounds involved in fluorous synthesis, including precursors, intermediates, surfactants, ligands, catalysts, labels (or tags), protecting groups, scavengers, supports, or polymers.

F-chains provide an effective driving force for self-aggregation in aqueous media of amphiphilic molecules into micelles, vesicles, micro and nanotubules, and other more or less complicated supramolecular systems.^{5,19} The force of this self-assembling capacity is, for example, illustrated by the ability of single chain *F*-surfactants to form stable vesicles rather than micelles in water. Likewise, tubules were obtained from nonchiral *F*-amphiphiles, while chirality was deemed indispensable

for promoting the formation of elongated structures from nonfluorinated amphiphiles. The fluorophobic effect has been exploited efficiently to both generate and amplify nonbonding inter- and intramolecular interactions, thus allowing the design of unprecedented supramolecular structures.^{5,20–22} Similar phenomena are observed in two-dimensional self-assembled films.

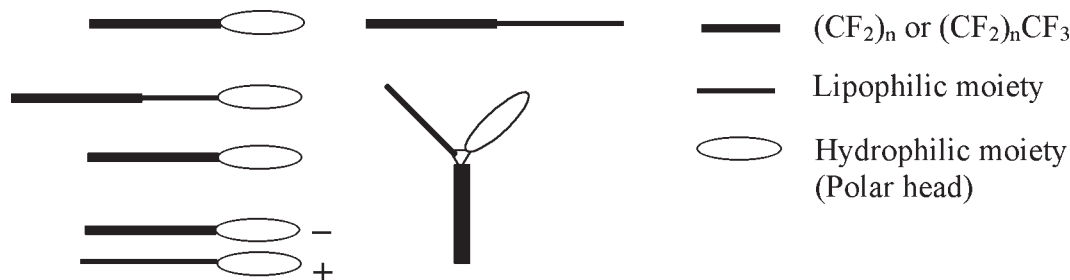
Because of their lipophobic character, *F*-amphiphiles can also self-assemble in organic media. Thus, even the structurally very simple, nonpolar semifluorinated alkanes $C_nF_{2n+1}C_mH_{2m+1}$ (FnHm) form micelles in both hydrocarbons and fluorocarbons. Such diblock molecules constitute a class of nonconventional surfactants that exhibit surface activity at the interface between a fluorocarbon and a hydrocarbon.

As a rule, films and membranes made of *F*-surfactants are more stable than those of their hydrogenated analogs. Ordering within these films or membranes tend to be more pronounced. A range of emulsions, miniemulsions, microemulsions, and multiple emulsions with an internal, median, or external PFC phase are being investigated as contrast agents for diagnosis, oxygen carriers, and drug delivery systems.⁷ The extremely low water solubility of PFCs allows osmotic stabilization of the injectable gaseous microbubbles used as contrast agents for ultrasound diagnosis.²³ Osmotic bubble stabilization by an internal gaseous PFC and membrane stabilization by an *F*-phospholipid can even be synergistic.²⁴

Altogether, the likelihood that media containing *F*-components be microheterogeneous are high, with possible consequences on the rate and outcome of chemical reactions.

FLUORINATED AMPHIPHILES ARE POTENT GELATORS

F-amphiphiles were often observed to cause gelification of aqueous, organic, or PFC media. These gels consist of self-assemblies of the *F*-amphiphile into a variety of fibrillar phases (fibers, strands, tapes, etc.) that form



Scheme 1. Examples of combinations of fluorophilic (hydrophobic and lipophobic), lipophilic, and hydrophilic moieties that are prone to generate microheterogeneity in aqueous and organic media.

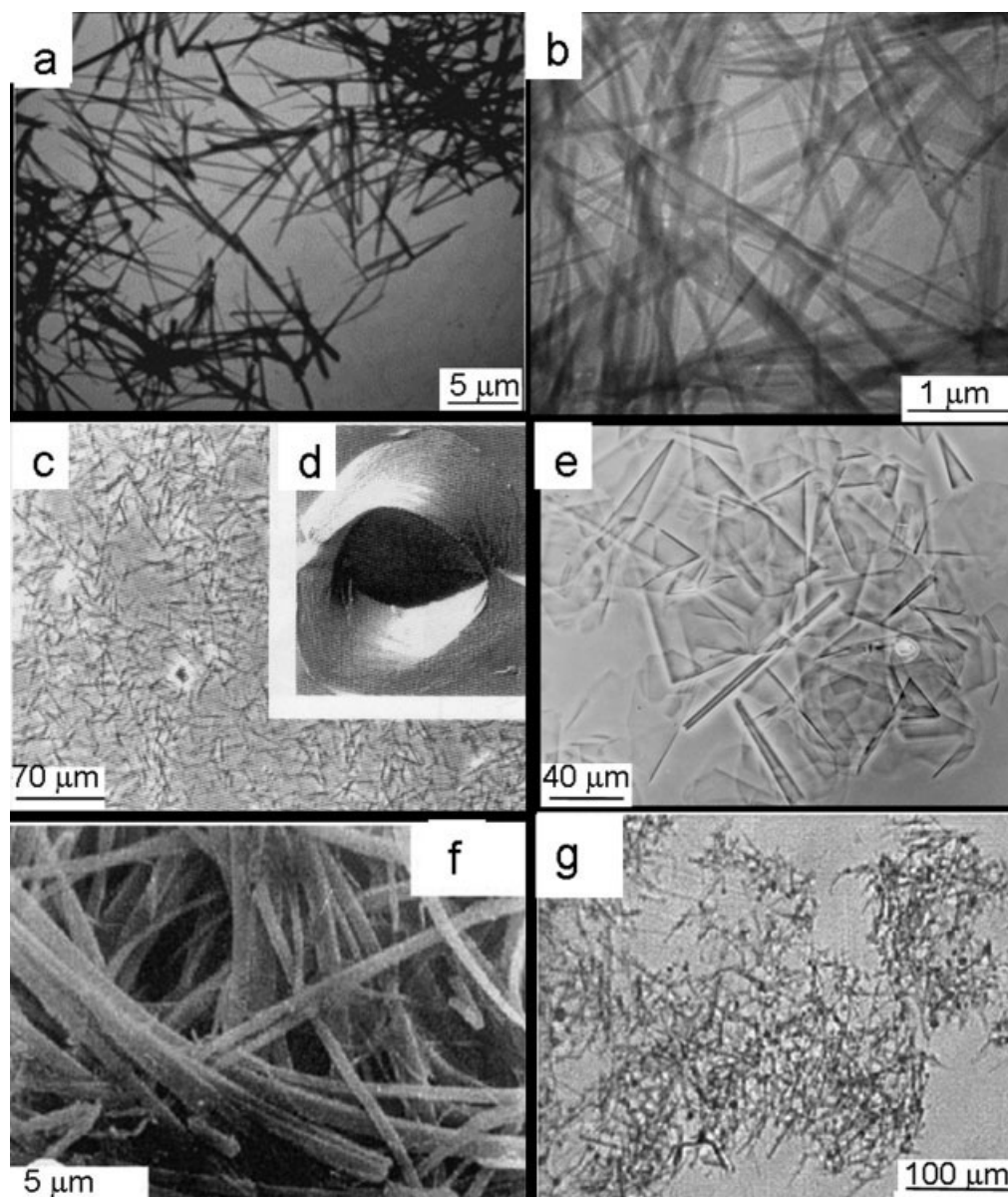
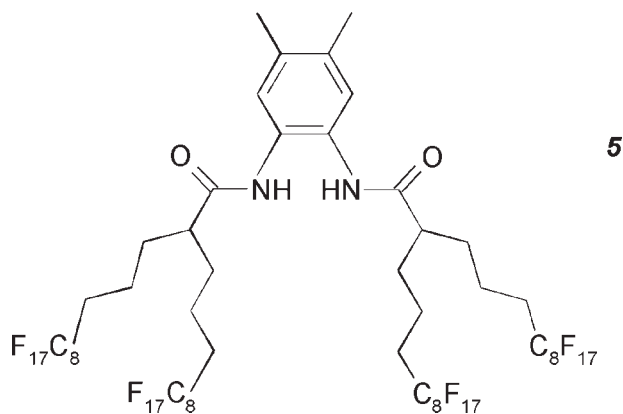


Figure 1. Gel formation induced by *F*-compounds in PFCs, organic media, and aqueous media. Fibers from the *F*-bis-benzamide **5** in (a) isopropanol and (b) *F*-tributylamine, as visualized by transmission electron microscopy.³¹ Hollow tubules made from an *F*-derivative of dimorpholino-phosphate in (c) water and (e) an ethanol/water mixture, as visualized by optical microscopy.³³ The insert (d) shows the hollow core of a tubule (freeze fracture electron microscopy). (f) Fiber-gel formed by an *F*-alcohol in methanol (scanning electron microscopy; Giulieri and Krafft, unpublished). (g) Fiber-gel formed by an *N*-alkyl *F*-alkanamide in tetramethyltetraphenylsiloxane.³⁰

extended networks. These networks immobilize the solvent, primarily through surface tension and capillary forces.²⁵ Viscous fibrous dispersions, made of stable, hollow tubular microstructures, were, for example, formed in water from anionic glucophospholipids in which a mixed fluorocarbon/hydrocarbon hydrophobe was present.⁸ Viscoelastic, transparent water-in-PFC

gels, that can accommodate up to 98% of water, have been obtained with *F*-polyethoxylated alcohols.²⁶ FnHm solutions form swollen gels in hydrocarbons and mixtures of *F*-octane and octane.^{27,28} The microfibrils present in these gels result from an arrangement of diblock molecules in a lamellar structure. Microfiber gels of FnHm diblocks were also reported to form in scCO_2 .²⁹

N-alkyl *F*-alkanamides are efficient gelators of a variety of hydrocarbons and PFCs.³⁰ The *F*-bis-benzamide **5** was reported to gelify isopropanol and *F*-tributylamine.³¹



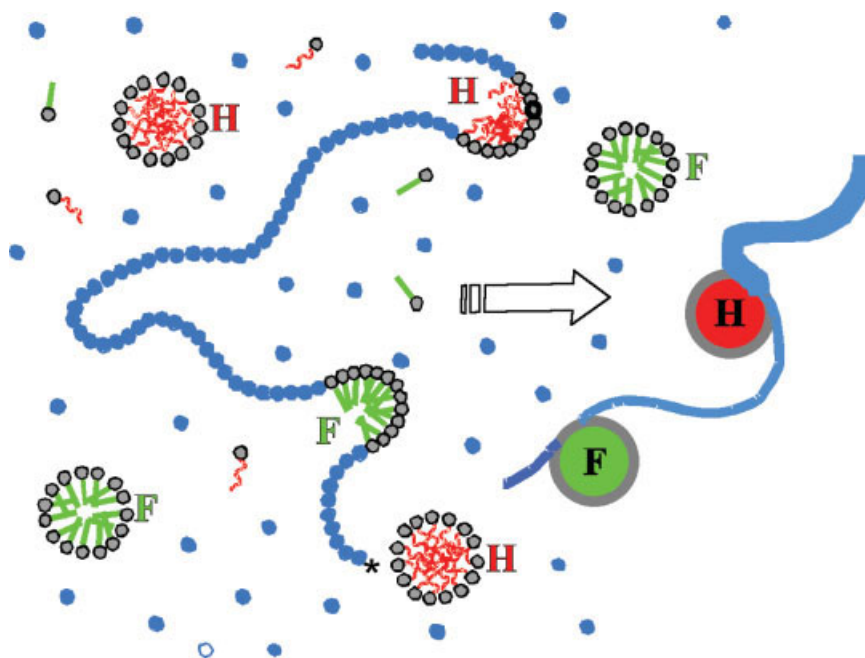
F-alkyl(alkyl) alcohols were also shown to form gels in methanol (Giulieri and Krafft, unpublished). Further bilayer-based fibrous gels were obtained in organic solvents from amphiphiles with two *F*-chains and one *H*-chain grafted on the chiral *L*-glutamate residue.³² More generally, it is possible to obtain stable gels and bilayers in organic media when using fluorinated “solvophobic” amphiphiles with appropriate molecular design. Examples of gels obtained with *F*-compounds are illustrated in Figure 1.

***F*-AMPHIPHILES INDUCE NANO-COMPARTMENTATION**

The unusual combination of hydrophobic and lipophobic effects engendered by *F*-chains can promote phase separation and compartmentalization at meso-, micro-, and nano-scales in molecular systems that contain *F*-species. Examples of such behavior include polymeric micelles that comprise two types of mutually incompatible segregated domains, some fluororous, the others hydrocarbonous, attached to the same water-soluble polymeric backbone (Scheme 2).³⁴ The molecular frustration resulting from the combination of three mutually immiscible polymeric components (poly(ethylene oxide), poly(perfluoropropylene oxide), and poly(ethylethylene)) in a mixed-arm star block terpolymer has recently led to a previously unknown class of multicompartment micelles.³⁵

Segregation of hydrogenated and fluorinated domains within liposomes^{36,37} and Langmuir monolayers have also been reported. Both laterally and vertically phase-separated zones within bilayers and films have been obtained.³⁸

Even simple molecular FnHm diblocks, when spread on the surface of water or on a silicon wafer, do not form the *a priori* expected continuous homogenous film of surfactant. Instead, they arrange into a highly ordered hexagonal array of monodisperse surface micelles (Fig. 2).³⁹ Unprecedented faceted surface micelles have



Scheme 2. Terpolymerization of a polymerizable hydrocarbon surfactant, a polymerizable fluorocarbon surfactant, and acrylamide led to multicompartmented micelles.³⁴

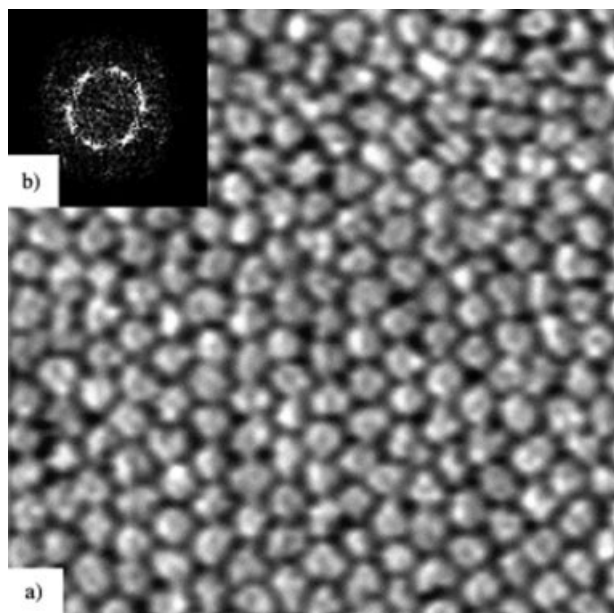


Figure 2. (a) AFM image ($0.5 \times 0.5 \mu\text{m}^2$) of surface micelles in a monolayer of F8H16 transferred onto a silicon wafer. (b) Two-dimensional Fourier transform of (a), showing two rings characteristic of hexagonal close-packing.

recently been obtained from a triaffine amphiphile (Sanchez Dominguez et al., unpublished).

Such situations can be exploited advantageously. Surfaces decorated with regularly arranged hemi-micelles can provide templates, for example, for the obtaining of metal dots.⁴⁰ Polymerization of a hydrophobic monomer, such as isodecylacrylate or styrene, within the bilayer of a vesicle made from an *F*-phospholipid allowed obtaining of spherical capsules,⁴¹ a result that could not be achieved with vesicles made from regular phospholipids; in the latter case, phase separation occurs, resulting in the formation of latex beads, rather than a capsule. In these experiments, the *F*-vesicles provided an appropriately shaped confinement microreactor for the polymerization reaction.

A clear understanding of the occurrence and basic properties of fluorinated self-assembled supramolecular systems and interfaces should be valuable to any chemist using fluorous phases and fluorous components for synthesis and separation, since these properties determine phase separations, the occurrence of micro-heterogeneities in reaction media, the development of large size interfaces, and the possible constitution of micro- or nanoreactors and templates.

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