Existence of Two-Dimensional Physical Gels even at Zero Surface Pressure at the Air/Water Interface: Rheology of Self-Assembled Domains of Small Molecules

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Abstract: *Films of mesoscopic domains self-assembled from fluorocarbon/hydrocarbon diblock copolymers (FnHm) at the air/water interface were found to display highly elastic behavior. We determined the interfacial viscoelasticity of domain-patterned FnHm Langmuir monolayers by applying periodic shear stresses. Remarkably, we found the formation of two-dimensional gels even at zero surface pressure. These monolayers are predominantly elastic, which is unprecedented for surfactants, exhibiting gelation only at high surface pressures. Systematic variation of the hydrocarbon (n = 8; m = 14, 16, 18, 20) and fluorocarbon (n = 8, 10, 12; m = 16) block lengths demonstrated that subtle changes in the block length ratio significantly alter the mechanics of two-dimensional gels across one order of magnitude. These findings open perspectives for the fabrication of two-dimensional gels with tuneable viscoelasticity via self-assembly of mesoscale, low-molecular-weight materials.*

Two-dimensional (2D) gels based on low-molecular-weight materials are of interest for stabilizing foams and emulsions in foods and cosmetics, and also for the effective encapsulation and controlled release of drug and gas molecules. The formation of 2D gels has been reported for metal (Au, Ag) and Si nanoparticles coated with surfactant molecules.[1] Naumann et al. reported that monolayers of phospholipids coupled to poly(ethylene glycol) (PEG) chains underwent the "gelation" ($G' > G''$), which was assigned to the lateral condensation of PEG chains.[2] Monolayers of synthetic glycolipids also form networks via hydrogen bonding between the carbohydrate head groups.[3] Recently, some of us reported that monolayers of lipopolysaccharides (LPSs), which are the major constituents of the outer membranes of Gram negative bacteria, form 2D gels in the presence of

Ca^{2+}.[4] Importantly, in all the cases reported so far, the formation of 2D gels was observed only when the monolayers were strongly compressed. The aggregation of "hard" colloidal particles experiencing short-range attractive interactions can lead to the emergence of arrested states at low volume fractions due to the eventual formation of space spanning structures.[5] However, to the best of our knowledge, no 2D gel has ever been described for self-assembled organic molecules at zero surface pressure.

Here, we report that self-assembled mesoscopic surface domains of fluorocarbon/hydrocarbon diblock copolymers, $C_nF_{2n+1}C_mH_{2m+1}$ (*FnHm*, n = 8–10; m = 14–20) can form physical 2D gels even at or near zero surface pressures without chemical cross-links.

Fluorocarbon/hydrocarbon diblock copolymers[6] are known to form discrete, highly monodisperse circular surface domains at the air/water interface with the fluorinated blocks up and the hydrogenated chains down and in contact with water (Scheme 1). Grazing incidence X-ray diffraction
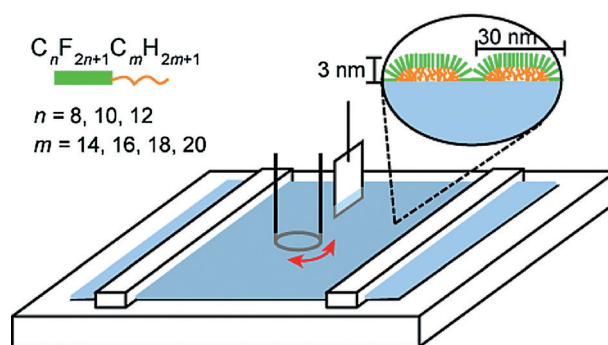
Scheme 1. Investigated *FnHm* diblock copolymers and schematic representation of the experimental setup. *FnHm* molecules form mesoscopic domains on the water subphase even at $\pi \approx 0$ mN m^{-1}.

(GIXD) showed that the fluorocarbon chains are packed in a hexagonal lattice, while the hydrocarbon chains are much poorly ordered.[7] The latter can be attributed to the mismatch in the cross-section of the fluoro- and hydrocarbon blocks.[8] The surface domains organize in quasi-crystalline hexagonal arrays when spread and compressed as Langmuir monolayers at the air/water interface, as shown by grazing incidence small-angle X-ray scattering (GISAXS).[9] The diameter of these domains (ca. 30 nm) is about an order of magnitude

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larger than their height (3 nm), which corresponds to the molecular length of the diblock.[10] The cohesion between diblock copolymers within the domains would be caused by van der Waals attractions, while the repulsion that prevents coalescence of domains would originate from the dipoles of the terminal CF_3 group and the CF_2-CH_2 junction.[11] Recently, using GISAXS we demonstrated that increasing the hydrocarbon block length led to a monotonic increase in the diameter of the surface domains from $\Phi \approx 28$ nm ($F8H14$) to $\Phi \approx 36$ nm ($F8H20$), which is attributed to higher van der Waals attractions.[12] Theoretical studies have suggested that the monolayer of $FnHm$ diblock copolymers consists of surface domains in a liquid condensed state dispersed and in equilibrium with $FnHm$ diblock copolymers that form a continuous liquid expanded phase.[13] In fact, pressure–area isotherms revealed compressibilities of $\kappa^{-1} \approx 10$ mN m^{-1} measured at $\pi = 5$ mN m^{-1}, which were similar to compressibilities of fatty acid monolayers in a liquid condensed state.[12]

Although the highly uniform, regular lattice of $FnHm$ surface domains suggests strong lateral correlation, there has been little investigation of the viscoelasticity of $FnHm$ monolayers. Previously, Klein et al. studied the viscoelasticity of $F12H12$ and $F12H20$ monolayers using an interface stress rheometer based on a gliding magnetic needle under oscillating magnetic fields. They reported that the $F12H12$ monolayer was predominantly elastic, showing the characteristic fingerprint of a "colloidal glass".[14] In contrast, $F12H20$ and diblock copolymers in which the $F12$ and $H12$ segments are connected by a phenyl group form elongated micelles and show an elastic response that was, in the latter case, assigned to classical π-π-driven entanglement of these elongated micelles.[14] However, the physical mechanism by which each block contributes to modulate the interfacial viscoelasticity is largely unknown.

In our study, we used an interfacial shear rheometer based on a rotating ring in combination with a Langmuir film balance (Scheme 1).[4] We simultaneously measured the frequency-dependent dynamic surface elastic modulus $G'(\omega)$ and viscous modulus $G''(\omega)$ at different surface pressures without disrupting the mesoscopic $FnHm$ domains. The investigation of homologous series of $FnHm$ diblock copolymers with various hydrocarbon ($n = 8$; $m = 14$–20) and fluorocarbon ($n = 8$–12; $m = 16$) block lengths (Scheme 1) enabled us to clarify the basic molecular parameters that modulate the film mechanics at the air/water interface.

Interfacial shear rheometry allows the quantitative determination of dynamic elastic and viscous properties of monolayers of amphiphilic compounds deposited on liquid surfaces.[15] As compared to the conventional rotating disk devices, this instrument can achieve approximately one order of magnitude higher sensitivity.[15a] The ring and the pressure sensor were of similar size (ca. 10^{-3} m) and approximately five orders of magnitude larger than a single surface domain (ca. 10^{-8} m) and thus insensitive to small local inhomogeneities in the film. In order to compare the dynamic surface modulus of $FnHm$ monolayers, we first verified that the systems exhibit a linear response to the applied stimuli (Figure S1a and b in the Supporting Information). Unless stated otherwise, the

frequency $f = 3$ Hz and strain amplitude $\gamma = 1.5$ mrad were applied throughout the study.

Figure 1 represents the elastic (G') and viscous (G'') modulus of a $F8H16$ monolayer plotted as a function of area
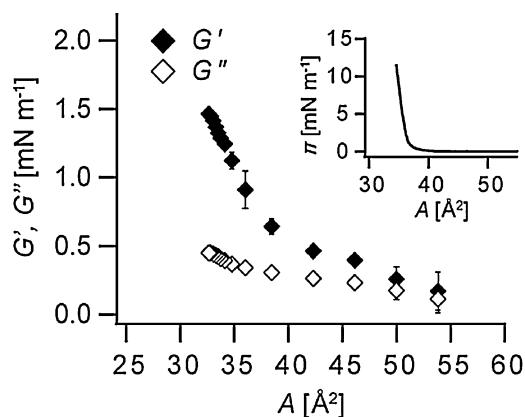
Figure 1. Elastic G' and viscous G'' moduli of a $F8H16$ monolayer measured at $\gamma = 1.5$ mrad and $f = 3$ Hz as a function of molecular area. The corresponding π/A isotherm is shown in the inset.

per molecule. For each data point, the measurement was performed over 90 s, confirming that the system reached the thermodynamic equilibrium (Figure S1c). The corresponding surface pressure-area (π-A) isotherm is displayed in the inset. The onset of the increase in G' and G'' appears around $A = 50$ Å^2, while the surface pressure still remains $\pi \approx 0$ mN m^{-1}. It is notable that G' is always larger than G'', indicating that the $F8H16$ monolayer is predominantly elastic, thus forming a 2D gel even in the diluted phase. This behavior is clearly different from the gelation of other surfactant monolayers, which emerges only at high surface pressures.[3,11] When the monolayer is compressed to reach the onset of the increase in π ($A \approx 35$ Å^2), the dynamic moduli already reach $G' = (0.9 \pm 0.1)$ mN m^{-1} and $G'' = (0.34 \pm 0.02)$ mN m^{-1}. Such a predominantly elastic response of the $FnHm$ monolayers can be attributed to the strong dipole repulsion between CF_3-chain termini and CF_2-CH_2 junctions, which prevent the coalescence of surface domains.[11]

To confirm that other $FnHm$ diblock copolymers can also form 2D gels near zero surface pressure, we systematically varied the length of hydrocarbon and fluorocarbon blocks. The viscoelastic response of other $F8Hm$ monolayers implies that these monolayers are also predominantly elastic at $\pi \approx 0$ mN m^{-1} (Figure S2). These results suggest that the surface domains are already laterally correlated at such low surface pressures. Indeed, GISAXS experiments showed the presence of ordered structures at $\pi \approx 0$ mN m^{-1} for $F8H14$ (Figure S3). Variations of G' and G'' with Fn and Hm block length provide some insight on the relative impact of each block on the mechanics of the film (Figure 2; see Table S1 for exact values). First, G'' exhibits a monotonic increase when Hm increases from 14 to 20, which can be attributed to the increase in size of the surface domains due to increasing van
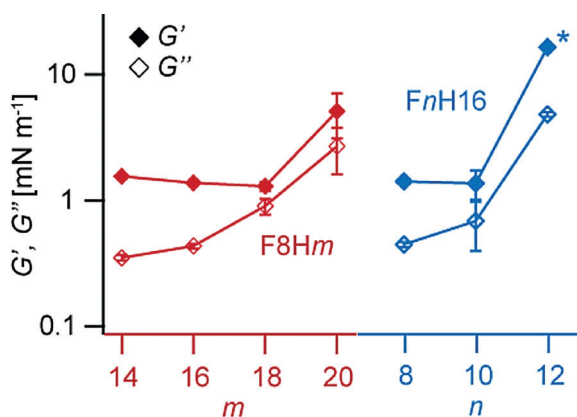
Figure 2. Elastic (G') and viscous (G'') moduli of $FnHm$ monolayers measured at $\pi = 5$ mN m^{-1}, $\gamma = 1.5$ mrad and $f = 3$ Hz plotted as a function of hydrocarbon chain length m for $F8Hm$ (red) and fluorocarbon chain length n for $FnH16$ (blue). *G' still exhibited a continuous increase even after 90 s (Figure S5a).

der Waals attractions between hydrocarbon chains.[7b,12,16] G' remains almost constant for $m = 14$, 16, and 18, but a significant 3-fold increase is observed for $m = 20$.[17]

Next, we investigated how the fluorocarbon block length influences the interfacial viscoelasticity of $FnH16$ monolayers (Figure S4). Figure 2 represents G' and G'' at $\pi = 5$ mN m^{-1} plotted as a function of n. The increase from 8 to 10 causes no significant increase of G' and G''. In contrast, $F12H16$ shows significantly higher moduli. Note that G' of $F12H16$ did not reach the full equilibrium at $\gamma = 1.5$ mrad and $f = 3$ Hz, showing a continuous increase even after 90 s (Figure S5a). However, the observed tendency was further confirmed by repeating the measurements at $\gamma = 3$ mrad and $f = 5$ Hz, where the system reached the thermodynamic equilibrium (Figure S5b). Interestingly, the change in G' caused by the elongation of the Fn block from 8 to 12 is almost by one order of magnitude, which is much more pronounced than that caused by the elongation of the Hm segment.

The elastic modulus of $FnHm$ monolayers is determined by repulsive interactions between surface domains that are confined in a 2D system at the air/water interface.[18] The net dipole moment per domain is determined by 1) the domain size and 2) the alignment of molecular dipoles. Recently, we reported that the domain size increases from $\Phi_{F8H18} \approx 32$ nm to $\Phi_{F8H20} \approx 36$ nm by using grazing-incidence X-ray scattering (GISAXS).[12] In general, the elongation of hydrocarbon chains increases the lateral chain ordering, as widely reported in self-assembled monolayers.[17] In our experimental system, the increase from $m = 18$ to 20 leads to an increase in the ordered chain fractions.[17a] However, due to the mismatch in cross-sectional areas between fluorocarbon chains (ca. 30 Å^2) and hydrocarbon chains (ca. 20 Å^2),[8] the lateral ordering of fluorocarbon chains is disturbed.[19] This results in the poorer alignment of molecular dipoles (Figure S6). Thus, it is plausible that these counteracting effects cause a moderate increase in G' by a factor of 3–4. The elongation of Fn block from $n = 8$ to 12 also results in an increase in the domain size from $\Phi_{F8H16} \approx 29$ nm to Φ_{F12H16}

≈ 33 nm.[12] Different from H-blocks, the increase in "bulkier" fluorocarbon chain ordering by elongation from $n = 10$ to 12[20] does not disturb the lateral packing of hydrocarbon chains. Therefore, a pronounced increase in G' by a factor of approximately 20 can be explained by the combination of the increase in the domain size and the higher alignment of molecular dipoles.[11a]

The formation of 2D gels by $FnHm$ found in this study at $\pi \approx 0$ mN m^{-1} is clearly different from the gelation of organic monolayers reported in previous accounts: the formation of gel occurs only when films are compressed to high surface pressures or cross-linked via entanglement as for denatured proteins.[2b,21]

To further shed light on the influence of the area per molecules on the mechanics of the film, we compared the frequency dispersion ($f = 2$–10 Hz; $\gamma = 1.5$ mrad) of G' and G'' of $F8H18$ monolayers at four different surface pressures (Figures 3a and b). At $\pi = 0$ mN m^{-1} ($A \geq 40$ Å^2), the power law exponent (slope) was approximately 1 for both G' and G'', which is characteristic for soft glassy materials.[22] A slight compression of the film to $\pi = 1$ mN m^{-1} ($A = 33$ Å^2) is sufficient to change the exponent of G' to approximately 0. In contrast, the exponent of G'' remains almost constant at 1. Such a frequency dispersion, $G' \propto f^0$ and $G'' \propto f^1$, is a typical fingerprint of Kelvin–Voigt solids (Figure S7, see the Supporting Information for more information).[23]

Figure 3c shows the relationship between G'' and G' at $f = 2$–10 Hz, collected at different surface pressures. At $\pi = 0$ mN m^{-1} (solid circles), the film behaves predominantly elastic over the whole frequency window, and the phase shift (loss angle) δ remains constant at $\delta = \tan^{-1}(G''/G') \approx 0.6$ (inset). In contrast, when the film was slightly compressed to $\pi = 0.5$ mN m^{-1} (open triangles), the loss angle exhibits a clear increase by increasing frequency, $\delta \approx 0.4$ at $f = 2.3$ Hz to $\delta \approx 0.9$ at $f = 10$ Hz (inset). As a result, δ exceeds $\pi/2$ beyond a critical frequency $f = 6$ Hz, indicating that the film becomes predominantly viscous (shaded region in Figure 3c). The observed tendency is even more pronounced at higher surface pressures. The extremely high sensitivity of loss angle to the change in area per molecule suggests that the film is already in the close proximity of the rheological transition at $\pi \approx 0$ mN m^{-1}.

The obtained results demonstrate that mesoscopic domains of $FnHm$ diblock copolymers form 2D physical gels even at $\pi = 0$ mN m^{-1}, which has, to our knowledge, never been reported for other organic compounds. The gelation of self-assembled domains of $FnHm$ at zero surface pressure shares common features with gels formed by "hard" particles, while the other 2D gels of self-assembled organic molecules reported so far underwent gelation only at high surface pressures. These unique rheological properties can be attributed to the strong dipole repulsions between $FnHm$ domains. The fact that G' and G'' can be modulated by one order of magnitude by a subtle change in the molecular structure suggests a large potential of $FnHm$ diblock copolymers in stabilizing microbubbles, emulsions and gels against a wide range of compression and expansion.

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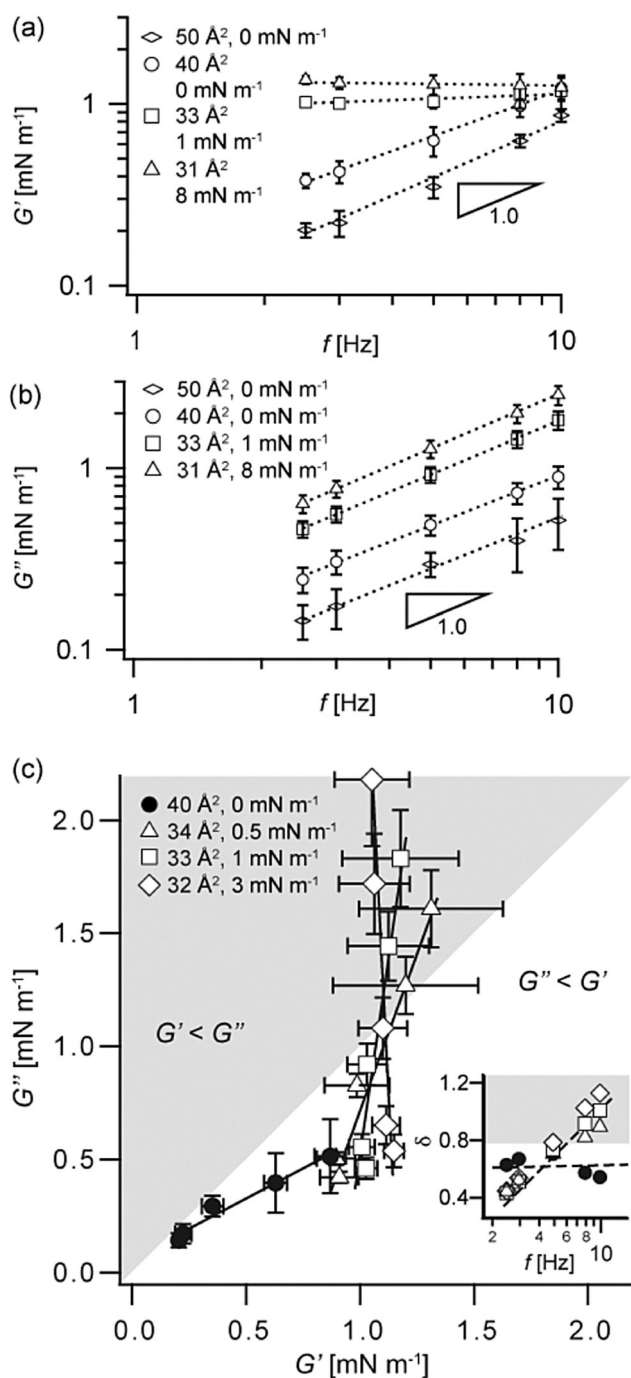
Figure 3. Frequency sweep of *F*8*H*18 monolayer at different surface pressures/ molecular areas. a) Elastic modulus *G′* and b) viscous modulus *G″* as a function of oscillation frequencies at $\gamma = 1.5$ mrad. The dotted lines are linear fits. c) Viscous modulus *G″* vs. elastic modulus *G′* of *F*8*H*18 monolayer measured at different surface pressures/molecular areas. The inset displays the frequency dispersion of the phase shift δ. The shaded regions indicate the predominantly viscous regime where $G′ < G″$, thus $\delta > \pi/2$. The black lines are guides for the eyes.

Conflict of interest

The authors declare no conflict of interest.

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