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Adsorption of Pluronic F-127 on Surfaces with Different Hydrophobicities Probed by Quartz Crystal Microbalance with Dissipation

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Triblock copolymers of polyethylene oxide (PEO) and polypropylene oxide (PPO), that is, PEO_n-PPO_m-PEO_n, better known as Pluronic can adsorb to surfaces in either a pancake or a brushlike configuration. The brushlike configuration is advantageous in numerous applications, since it constitutes a surface repellent to proteins and microorganisms. The conformation of the adsorbed Pluronic layer depends on the hydrophobicity of the substratum surface, but the hydrophobicity threshold above which a brushlike conformation is adopted is unknown. Therefore, the aim of this study is to investigate Pluronic F-127 adsorption on surfaces with different hydrophobicities using a quartz crystal microbalance with dissipation. Adsorption in a brushlike conformation occurred on surfaces with a water contact angle above 80°, as inferred from the thickness, viscosity, and elasticity of the adsorbed layer. The concentration of Pluronic F-127 in solution affected only the kinetics of adsorption and not the final layer thickness or conformation of adsorbed Pluronic molecules.

Introduction

Triblock copolymers of polyethylene oxide (PEO) and polypropylene oxide (PPO), that is, PEO_n-PPO_m-PEO_n, better known as Pluronic, are used in a variety of industrial and biomedical applications,¹ among others, to discourage protein adsorption and bacterial adhesion.^{2–7} Treatment of hydrophilic silica surfaces with Pluronic F-108 reduced adsorption of proteins by 60%, while treatment of hydrophobic surfaces with Pluronic F-108 completely inhibited protein adsorption,⁸ possibly due to a different conformation of Pluronic F-108 on the different sorbent surfaces. Indeed, Schroen et al.⁸ suggested that the conformation of physically adsorbed triblock copolymers depends on the hydrophobicity of the sorbent surface: on a hydrophilic surface, the two terminal PEO_n blocks attach, resulting in a pancake conformation of the adsorbed triblock copolymer, whereas on a hydrophobic surface the PPO_m block anchors to the surface, leaving the PEO_n chains dangling in the adjacent solution. When the adsorbed number of polymer chains is sufficiently high, a brush conformation is adopted, as has been demonstrated for adsorption of Pluronic molecules on polystyrene films and on hydrophobic dimethyl-dichlorosilane-coated silica.^{5,7} Formation

of a brush coating of PEO chains on a surface creates superior nonadhesive properties. A highly hydrated layer of PEO chains is unfavorably compressed by an approaching particle, causing a repulsive osmotic force and a reduced mobility of the polymer chains. Both discourage close contact of the particle with the surface and, consequently, suppress adhesion. A brush coating of Pluronic F-127 on silicone rubber reduced the adhesion of bacteria by 1 order of magnitude and was stable against high shear stresses for more than 20 h.^{6,9}

It is crucial to be able to establish the conformation of adsorbed Pluronic molecules on different surfaces in order to engineer a surface that meets the requirements for a particular application and to determine the threshold hydrophobicity above which PEO blocks adopt a brushlike conformation. Most techniques, unfortunately, only yield limited information on the conformation of adsorbed Pluronic. A quartz crystal microbalance with dissipation (QCM-D) is highly sensitive for studying the adsorption processes in real time,¹⁰ while it gives insight into the characteristics and conformation of the polymer chains in the adsorbed layer.^{11,12}

The aim of this study is to determine the threshold hydrophobicity above which the pancake structure of adsorbed Pluronic F-127 changes into a stable brushlike conformation, employing a QCM-D probe.

Materials and Methods

Pluronic F-127 (polyethylene oxide (PEO)-polypropylene oxide (PPO)-polyethylene oxide block copolymer with an average molecular structure of PEO₉₉PPO₆₅PEO₉₉ and a molecular weight of 12 600), 1-octadecanethiol (HS(CH₂)₁₇CH₃), and

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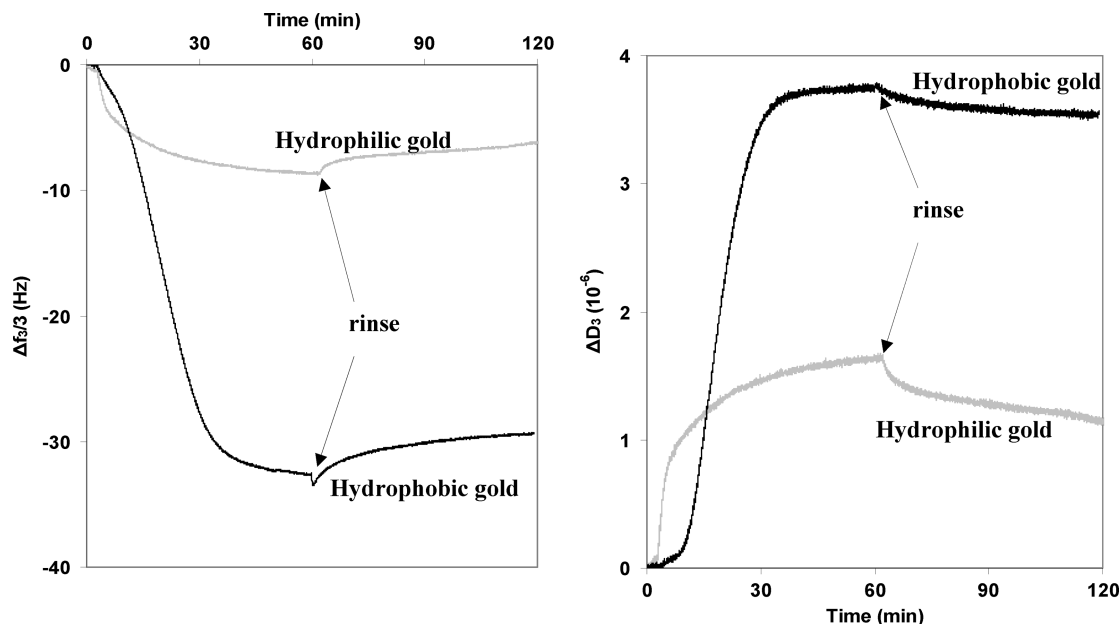


Figure 1. Example of the frequency shift and dissipation change for the 3rd overtone as a function of time during adsorption of Pluronic F-127 from 0.0005 g L^{-1} solution on hydrophobic (black line) and hydrophilic (gray line) gold surfaces. Arrows indicate the point in time at which the flow chamber was rinsed with water.

11-mercapto-1-undecanol ($\text{HSCH}_2(\text{CH}_2)_9\text{CH}_2\text{OH}$) were purchased from Sigma-Aldrich, USA. Ethanol, ammonia, and hydrogen peroxide were of analytical grade and purchased from Merck, Darmstadt, Germany.

Preparation of Crystal Surfaces. Quartz crystals coated with gold and titanium were purchased from Q-Sense AB, Sweden. Prior to use, all crystals were rinsed thoroughly with ultrapure water and dried under a flow of nitrogen. Cleaned, hydrophobic gold-coated crystals were made hydrophilic by exposure to UV/ozone treatment for 10 min followed by immersion into a 3:1:1 mixture of ultrapure water, ammonia solution, and H_2O_2 maintained at $70\text{--}80^\circ\text{C}$ for at least 10 min and a final rinse with water and UV/ozone treatment for another 10 min. To further vary the hydrophobicity of the gold-coated crystals, hydrophilic gold-coated crystals were coated with a self-assembled monolayer (SAM) by immersion of the crystals into a 1 mM solution of $\text{HS}(\text{CH}_2)_{17}\text{CH}_3$ (1-octadecanethiol) or $\text{HSCH}_2(\text{CH}_2)_9\text{CH}_2\text{OH}$ (11-mercapto-1-undecanol) dissolved in ethanol for 18 h while shaking moderately to create a hydrophobic or hydrophilic SAM, respectively.

Contact Angle Measurements. Prior to adsorption experiments, water contact angles of $1 \mu\text{L}$ sessile droplets were measured on all surfaces using a homemade contour monitor. On each sample, three droplets were placed on different spots; their average contact angles are reported.

Adsorption Experiments. Adsorption of block copolymers to crystal surfaces with various coatings was investigated using a QCM-D model Q-sense E1 (Q-Sense AB, Gothenburg, Sweden), which allows monitoring of changes in both resonance frequency of the quartz crystal and dissipation of its energy as a function of time. The crystal is excited to oscillate at its fundamental resonance frequency (4.95 MHz) and its 3rd, 5th, 7th, 9th, 11th, and 13th overtones. Addition of mass to the crystal surface is registered as a decrease in resonance frequency (Δf), whereas the change in dissipation (ΔD) depends on the viscoelastic properties of the adsorbed film and its interaction with the surroundings. The crystal is fixed in a closed chamber that allows flow of liquids over the crystal surface while the signals are recorded.

Measurements were conducted at a flow rate of 0.2 mL min^{-1} , corresponding with an approximate shear rate of 24 s^{-1} at 20°C . After a stable baseline of the QCM-D signal was obtained while flowing with ultrapure water, polymers were allowed to attach

to a crystal surface from a flowing low (0.0005 g L^{-1}) or high (0.5 g L^{-1}) concentration Pluronic solution for 1 h, followed by rinsing with ultrapure water for another 1 h.

Data Modeling. In the case of hydrated adsorbed films, calculation of the layer properties solely based on frequency shift is inaccurate, and therefore, a viscoelastic model must be used.¹³ We applied the Kelvin–Voigt model to the frequency and dissipation data of all overtones in order to extract information on the viscoelastic properties and thickness of the adsorbed layer, using the QCM-D accompanying software package (Q-Sense, Sweden).¹⁴ The model consists of a viscous damper (dash-pot) and an elastic spring connected in parallel. Assuming the density of the adsorbed layer to be equal to the density of water (1000 kg m^{-3}) and the viscosity of water to be $0.001 \text{ Pa}\cdot\text{s}$ at 20°C , the software program allows calculation of the thickness, viscosity, and elasticity of the adsorbed layer.

Results

Analyses of frequency shifts and dissipation changes revealed that all overtones exhibit similar trends which only differed in magnitude. Therefore, in all figures, we solely present the behavior of third overtone.

Figure 1 shows representative QCM-D graphs for adsorbed Pluronic F-127 molecules on a hydrophilic and hydrophobic gold-coated crystal (see Table 1 for water contact angles). Both frequency shifts and dissipation changes are larger on the hydrophobic gold surface than on the hydrophilic gold surface. The larger frequency shift indicates a greater adsorbed mass at the hydrophobic surface. Note that Pluronic adsorption proceeds at a more or less constant rate until saturation is reached, which is typical for polymer adsorption.¹⁵ Rinsing with water causes a small decrease in frequency shift and dissipation change.

Figure 2 shows the dissipation change versus the frequency shifts during Pluronic adsorption to the different surfaces. On the

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Table 1. Water Contact Angles of Substratum Surfaces, Together with the Viscoelastic Properties of Adsorbed Layer of Pluronic F-127 on Substrata with Different Hydrophobicities^a

substratum	water contact angle (deg)	viscosity (10^{-3} Pa·s)	elasticity (10^5 Pa)
hydrophobic SAM	100 ± 2	2.6 ± 0.0	4.0 ± 0.0
hydrophobic gold	86 ± 2	2.2 ± 0.0	2.8 ± 0.2
titanium oxide	61 ± 1	1.2 ± 0.1	0.7 ± 0.2
hydrophilic SAM	27 ± 1	1.4 ± 0.1	1.3 ± 0.2
hydrophilic gold	16 ± 6	1.6 ± 0.2	1.1 ± 0.6

^a Contact angles represent averages \pm standard deviations for six measurements over two separately prepared surfaces. The viscosities and elasticities represent averages \pm ranges for two separate measurements over two separately prepared surfaces.

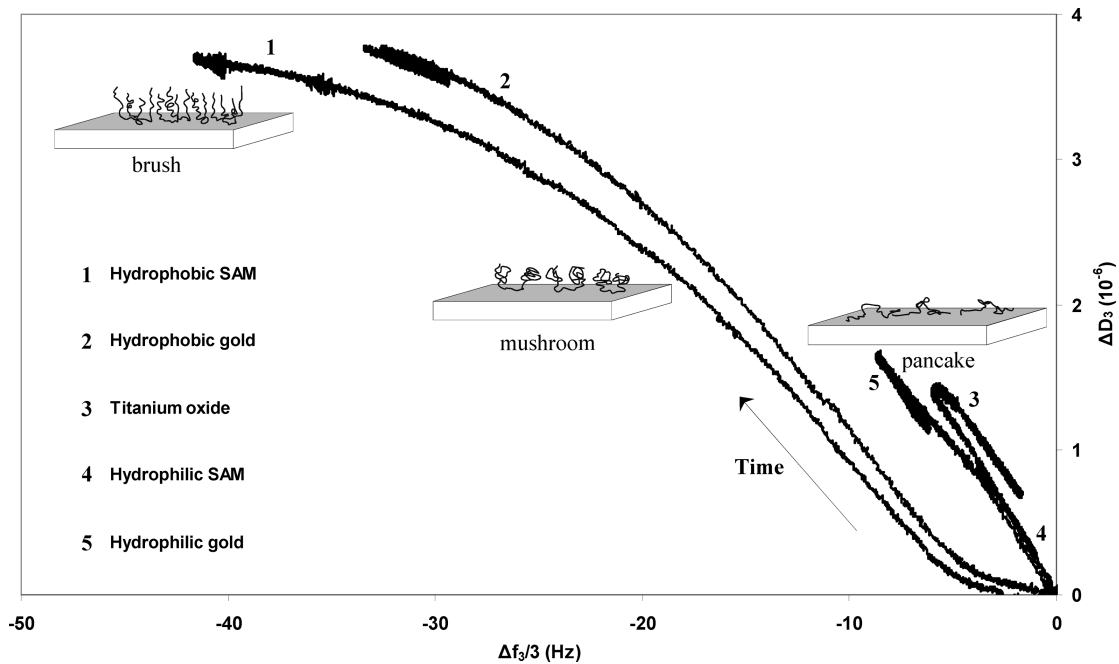


Figure 2. Examples of frequency shifts versus dissipation changes for the 3rd overtone during adsorption of Pluronic F-127 on different substrates.

hydrophilic gold surface, the hydrophilic SAM, and the titanium-coated surfaces, the dissipation change increases linearly with increasing frequency shift, and these curves are overlapping to a major extent. On hydrophobic surfaces, however, two distinct transitions are observed, and the curves level off toward higher frequency shifts.

Figure 3 illustrates the effect of Pluronic concentration on its adsorption to a hydrophobic gold surface. A higher concentration of Pluronic clearly causes faster and more extensive frequency shifts and dissipation changes than a lower concentration. Yet, the amount adsorbed in steady-state is not influenced by the Pluronic concentration, as both frequency shift and dissipation change reach the same value after rinsing with water.

The viscosity and elasticity of the adsorbed layer on various surfaces after rinsing and calculated from the Kelvin–Voigt model are shown in Table 1. The viscosity of the adsorbed layer is above 2.2×10^{-3} Pa·s on hydrophobic surfaces, whereas the viscosity does not exceed 1.6×10^{-3} Pa·s on hydrophilic ones. The elasticity of the adsorbed Pluronic layer is also hydrophobicity dependent, exceeding 2.8×10^5 Pa on hydrophobic surfaces and decreasing toward more hydrophilic surfaces.

Figure 4 shows the thickness of the adsorbed layer versus the water contact angle of the substratum surfaces. The thickness remains below 2 nm until the substratum hydrophobicity exceeds 80° , above which the adsorbed layer strongly increases to almost 9 nm.

Discussion

Although different types of surfaces have been coated with Pluronic F-127 for a range of applications, the characteristics of Pluronic adsorption are not yet fully understood. In this study, we show that the thickness of the adsorbed layer exceeds a certain value, only if the substratum surface is sufficiently hydrophobic with a water contact angle of above 80° , while also the viscosity and elasticity of the adsorbed layer are higher when adsorbed on hydrophobic surfaces, possibly indicative of different molecular conformations in the adsorbed Pluronic layer.

The relation between the change in dissipation and the frequency shift upon adsorption of small amounts of Pluronic molecules to surfaces with a water contact angle up to 80° is essentially linear and similar (see Figure 2), which indicates that adsorbed triblock copolymers on these surfaces adopt the same structure. It has been argued that such copolymers are adsorbed at hydrophilic surfaces in a so-called pancake structure in which the two PEO_n segments are attached to the surface. On the two most hydrophobic surfaces, however, Pluronic adsorption takes place in three different phases. In the first phase, the frequency increases with little or no change in dissipation (see Figure 2), suggesting molecules find ample sites at the surface to interact with, which leads to a stretched conformation of the polymer chains along the surface. Dissipation is a measure of energy transfer from the system to the surroundings. Clearly, the oscillating crystal loses less energy when it interacts less with the

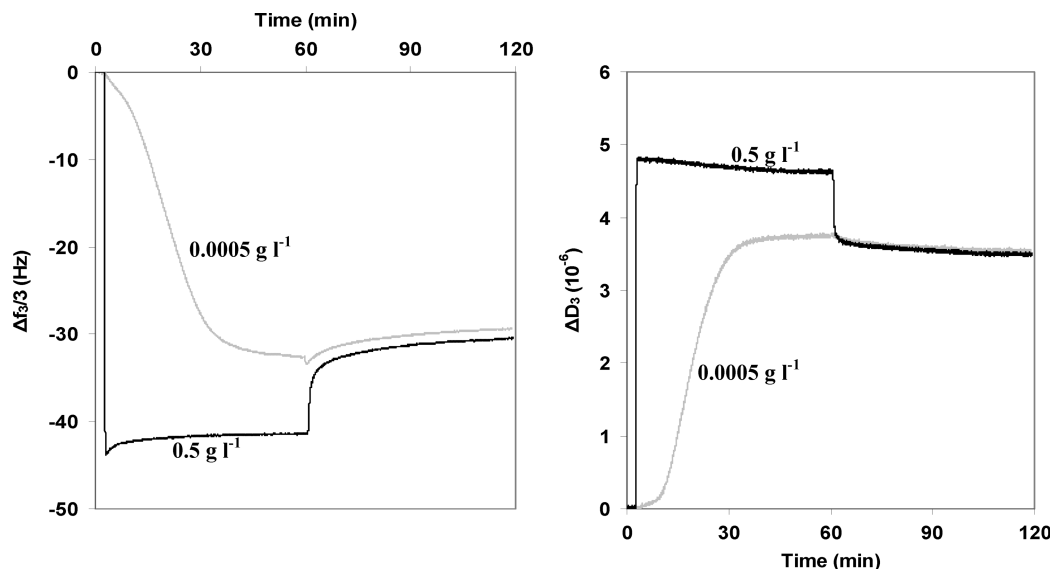


Figure 3. Example of the frequency shift and dissipation change for the 3rd overtone as a function of time during Pluronic F-127 adsorption from a low (0.0005 g L^{-1} , gray line) and high (0.5 g L^{-1} , black line) concentration solution on a hydrophobic gold surface.

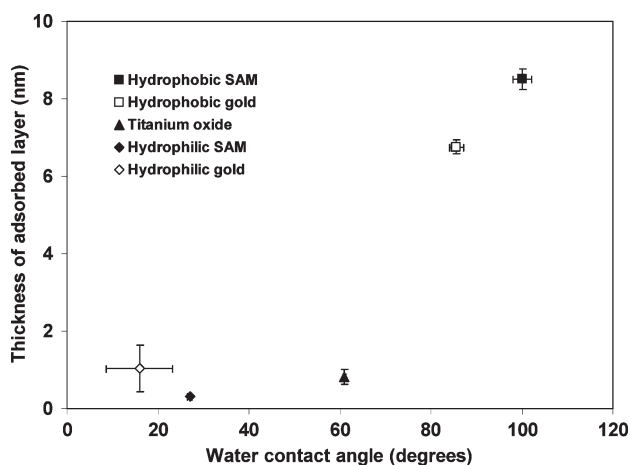


Figure 4. Thickness of adsorbed Pluronic layer as a function of the water contact angle on the underlying substratum surface. Error bars represent the standard deviations for contact angle measurements (over six spots on two independently prepared surfaces) and ranges for thicknesses of adsorbed layer (duplicate experiments on separately prepared surfaces).

surrounding water, and this is the case when the polymers are stretched along the surface. During further adsorption, hydrophobic interaction between the surface and PPO blocks of newly arriving molecules causes displacement of PEO blocks of pre-adsorbed molecules from the surface and the space available for PEO blocks to stretch on the surface gradually decreases, forcing the adsorbed molecules to adopt a mushroomlike structure. This increases the interaction of the adsorbed layer with surrounding water and alters the ratio between dissipation change and frequency shift. Adsorption of more PPO blocks leads to increased packing density of the PEO chains until they are forced to stretch away from the surface and form a brushlike conformation. Further adsorption increases the frequency shift, with little effect on the dissipation change, as also observed for a chemically grown brush.¹⁶ At its steady-state, the adsorbed layer on a hydrophobic surface is less dissipative (smaller $-\Delta D/\Delta f$), that is, more rigid, compared to the soft one on a hydrophilic surface.

It has been shown that for chemically grafted brushes an increase in the initiator density leads to an increase in the elasticity of the brush layer.¹⁷ Accordingly, Lubarsky et al.¹⁸ reported that the elasticity of adsorbed protein layers decreases by increasing the level of hydration of the proteins (decreasing the packing density of polymeric chains in the layer). This indicates that for a given system the elasticity of an adsorbed layer is related to the packing density of the polymers in that layer. Therefore, our observation of the higher elasticity of the adsorbed layer on hydrophobic surfaces compared to hydrophilic ones (see Table 1) supports the suggestion that the packing density of polymer chains is higher in the adsorbed layer on a hydrophobic surface. This, in turn, supports that on hydrophobic surfaces the adsorbed triblock copolymers are in a brushlike conformation. Moreover, the viscosities measured for adsorbed layers on hydrophobic surfaces are in good agreement with values found by Fu et al.¹⁷ for chemically grafted brushes. This is understandable because a higher volume density of PEO chains in the brushlike layer suggests a more hydrogel-like structure with a higher viscosity.

The suggestion that adsorbed Pluronic molecules adopt a brushlike conformation on hydrophobic surfaces can be evaluated by theoretical calculations. The condition for having a polymer brush coating is¹⁹

$$1/D < R_{\text{FI}}^2 \quad (1)$$

where D is the grating density of polymer chains to the surface and R_{FI} is the Flory radius of a chain in a good solvent ($R_{\text{FI}} \approx aN^{3/5}$, where a is the monomer size and N is the degree of polymerization). The Flory version of the Alexander model for a brush relates the thickness (T_c) and density of a brush as:

$$T_c \approx aN(a^2D)^{1/3} \quad (2)$$

Using eq 1, the minimum value for D is calculated to be approximately 0.033 nm^{-2} (taking the size of a PEO monomer,

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0.35 nm^{20}), which corresponds to a layer thickness of 5.5 nm, as can be calculated using eq 2. Thus, a layer thickness well above 5.5 nm would reflect a brush conformation. A thickness above 5.5 is measured only for the hydrophobic gold and SAM surfaces (see Figure 4). This is in line with our interpretation of experimental observations that on the two most hydrophobic surfaces a brushlike conformation is adopted. Based on our QCM data, the threshold water contact angle beyond which Pluronic F-127 adopts a brushlike conformation is around 80° . However, it has to be realized that the density of the brush obtained by adsorption of triblock copolymers is low as compared to the density that could be reached by chemical grafting. This is because further increase in loss of conformational entropy of the PEO chains with increasing packing density will stop further adsorption of Pluronic from the solution.

At this stage, it must be noted that experiments were also done on silicon-dioxide-coated crystals, with a water contact angle of $49 \pm 3^\circ$, yielding a layer thickness of less than 2 nm, as expected for a relatively hydrophilic surface, but with a viscosity ($2.4 \pm 0.1 \times 10^{-3} \text{ Pa}\cdot\text{s}$) and elasticity ($3.4 \pm 0.5 \times 10^5 \text{ Pa}$) that are both higher than expected for hydrophilic surfaces. It has been shown that acidic oxides such as silicon dioxide adsorb PEO chains from the solution via an acid–base reaction.²¹ Silicon-dioxide-coated surfaces are also known to yield unexpected interactions with vesicles. For instance, using QCM-D, Reimhult et al.²² indicated that adsorbed vesicles are more flattened on the silicon-dioxide-coated surface than on titanium-coated or hydrophilic gold-coated crystals. Similarly, a possibly strong attraction of Pluronic molecules toward the silicon-dioxide-coated surface leads to an increase in density of polymer chains in the film, at the expense of

the film thickness, which in turn may give rise to an elevated elasticity of the adsorbed layer.

The frequency shifts and dissipation changes after adsorption of Pluronic F-127 on surfaces (see Figure 1) decrease only slightly upon rinsing with water, suggesting that its adsorption is irreversible. The high affinity of Pluronic for hydrophobic surfaces is furthermore suggested by the observation that the steady-state adsorption is independent of the concentration of Pluronic in solution over a wide concentration range, that is $0.0005\text{--}0.5 \text{ g L}^{-1}$ (see Figure 3). The concentration, however, considerably influences the kinetics of adsorption, and adsorption reaches its maximum in less than 5 min for the higher concentration of 0.5 g L^{-1} , while it takes more than 30 min for a 1000 times lower concentration. Prior to rinsing, the highest frequency shifts and dissipation changes are observed for adsorption from the 0.5 g L^{-1} Pluronic solution, probably because a high concentration of Pluronic may cause adsorption of multiple molecular layers, that interact loosely with the substratum surface and are washed away during rinsing.

Conclusions

The thickness of an adsorbed Pluronic layer and the conformation of the molecules in the layer strongly depend on the hydrophobicity of the underlying surface and not on the Pluronic concentration in the adjacent phase. Adsorption of Pluronic F-127 on hydrophobic surfaces with a water contact angle above 80° yields a brushlike conformation with a thickness between 6 and 9 nm. The viscosity and elasticity of an adsorbed Pluronic layer in a brushlike conformation are higher than those in a pancake conformation.

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