Notes

Kinetics and Equilibria of Adsorption of PEO−PPO−PEO Triblock Copolymers on a Hydrophilic Self-Assembled Monolayer on Gold

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Introduction

Amphiphilic polymers can be exploited to control the properties of solid surfaces. The understanding of the modality of interactions between these macromolecules and a surface therefore has a direct impact on a broad range of technological applications. Pluronics are a series of triblock copolymers, copoly(ethylene oxide−propylene oxide−ethylene oxide) (PEO−PPO−PEO), that exhibit surface-active characteristics at ambient temperature conditions. In addition to finding use in traditional surfactant applications, such as cleaning, detergents, emulsifiers, and colloid stabilizers, Pluronics are of particular interest in biomedical applications because of their low toxicity and lack of immunogenic activity.[1] In our previous work,[2,3] we studied the adsorption−desorption behavior of a family of PEO−PPO−PEO copolymers (we shall use the notation $E_n-P_m-E_n$ for the remainder of the paper) on a model hydrophobic surface consisting of a self-assembled monolayer (SAM) of a methyl-terminated alkanethiolate on gold. We showed that the equilibrium characteristics are complex and that the adsorption process is only partially reversible. Furthermore, it was shown that the relative balance of the hydrophilic and hydrophobic content within a copolymer species determines whether the process is characterized by unimer driven adsorption or whether micelles play a role. Both static and dynamic measurements for adsorption and desorption are analyzed. Similar to our previous work, we use a surface plasmon resonance (SPR) technique with a fast time resolution (0.1 s) and equipped with a parallel plate flow sample holder. By conducting experiments with different flow rates of the polymer solutions, the kinetics of adsorption are obtained.

Experimental Section

Materials. The Pluronic surfactants P123, P103, P105, and F108 were donated by BASF Corp. Deionized water (18 MΩ·cm) from a NanoPure system (Barnstead, Dubuque, IA) was used to prepare the polymer solutions and to run the water rinsing steps in the experiments. All solvents and chemicals were of analytical grade. The ethanol used in thiol solution preparation was absolute 200 proof (Gold Shield Chemical Co., Riverside, CA). 11-Mercaptoundecanoic acid (MUA) used for the formation of monolayers on gold was purchased from Aldrich-Sigma.

Preparation of Gold Slides. We have used high refractive index LaFSN9 glass slides (Schott, Mainz, Germany) as substrates for SPR. Gold of 99.999% purity was used to coat the glass substrates by sputtering. About 50 nm of gold was deposited on the glass slides by heating a gold target in a crucible with an electron beam at a pressure below 5×10^{-6} Torr, with a gold deposition rate of 0.2 Å/s. Finally, the gold slides were annealed at 650 °C for 30 s to minimize the surface roughness of the gold.[4]

Preparation of the MUA Monolayers. Self-assembly of the MUA monolayer was achieved by injecting a 5 mM MUA solution in alcohol into the flow cell containing a freshly prepared gold slide. The solution was allowed to react with the gold for at least 16 h, a time considered to be adequate for SAM formation, and then rinsed with at least 20 mL of ethanol at a flow rate of 5 mL/min and at least 200 mL of water at a flow rate of 10 mL/min to reach complete removal of thiol residue. SPR kinetics experiments showed that more than 99% of MUA SAM formation was complete within 16 h. The solutions used in our experiments were not buffered; they were slightly acidic (pH = 5) due to CO_2 present in the atmosphere. The reported pK_a for surface-bound MUA is about 4.5−4.7.[5,6] At pH = 5 the SAMs are negatively charged. The study of adsorption of all the polymers is done under the same conditions.

Surface Plasmon Resonance Apparatus. Detailed descriptions of the SPR and flow cell setup have been given in a previous article.[2] Briefly, we have used a SPR setup in the Kretschmann configuration;[7] monitoring the change of reflectivity of the system with time at a fixed angle captured the kinetics. A custom-built rectangular slit flow cell was used to achieve laminar flow conditions. We followed the kinetics by fixing the detector at a given angle and monitoring the reflectivity as a function of time. Typically this angle is chosen 0.5°−2° less than the resonance angle so that changes in reflectivity are linearly related to the shift in resonance angle or, alternatively, to the change in adsorbed layer thickness. For adsorption kinetics the flowing solution in the slit flow cell was changed from distilled water to a Pluronic solution (in water). To determine adsorption kinetics, experiments were conducted with different flow rates of the polymer solutions. For desorption studies the flowing solution in the slit flow cell was changed from a Pluronic solution to distilled water. The sampling times were 0.1 s. Adsorption and desorption kinetics were complemented with full SPR angular scans before and after each kinetic run. By fitting the angular scans with a Fresnel multilayer optical model,[8,9] we were able to extract the thicknesses of the adsorbed layers. These, in turn, can be used to evaluate the excess surface concentrations by the method of De Feijter et al.[10] At higher concentrations of polymer in solution the change of reflectivity for an adsorption or desorption experiment is not only due to the changes in the adsorbed layer, but it is also affected by the concentration related change in refractive index in the bulk solution. We took this concentration effect into account by calculating the extent

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Table 1. Properties of Pluronics Selected for This Study

polymer	M_w	m = #PO	n = #EO	cmc [μM]^a
P123	5750	69	2 × 19	30
P103	4950	60	2 × 17	168
P105	6500	56	2 × 37	385
F108	14600	50	2 × 132	3078

[a] Interpolated cmc data at T = 25 °C from Alexandridis et al.[1]

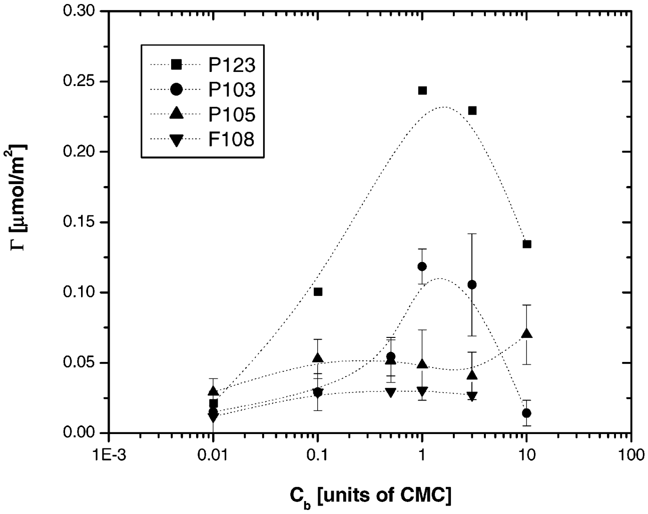

Figure 1. Adsorption isotherms for Pluronics P123 ($E_{19}-P_{69}-E_{19}$), P103 ($E_{17}-P_{60}-E_{17}$), P105 ($E_{37}-P_{56}-E_{37}$), and F108 ($E_{132}-P_{50}-E_{132}$). The dotted lines are drawn as an aid to the eye.

of bulk fluid contribution with the optical model and by subtracting it from the kinetics curves. Finally, all measurements were performed at room temperature.

Results and Discussion

The Pluronics P123 ($E_{19}-P_{69}-E_{19}$), P103 ($E_{17}-P_{60}-E_{17}$), P105 ($E_{37}-P_{56}-E_{37}$), and F108 ($E_{132}-P_{50}-E_{132}$) were selected for the study. Table 1 gives details on the properties of these Pluronics. The compounds in Table 1 are known to be somewhat polydisperse, with a value of M_w/M_n from about 1.1 to 1.2.[11] The first two compounds [P123 ($E_{19}-P_{69}-E_{19}$) and P103 ($E_{17}-P_{60}-E_{17}$)] have a similar EO/PO ratio (EO/PO ~ 0.56) but differing numbers of PO units in the PPO block: 69 vs 60. The P123 with 69 PO units has a significantly lower critical micelle concentration (cmc) than P103 with 60 PO units, and P123 can be considered to be more hydrophobic. Comparison of the three compounds P103 ($E_{17}-P_{60}-E_{17}$), P105 ($E_{37}-P_{56}-E_{37}$), and F108 ($E_{132}-P_{50}-E_{132}$) shows an increasing content of the hydrophilic PEO block and an average content of about 55 PO units per PPO block. The cmc increases as the number of EO units increases from 34 to 264.

Adsorption and Desorption Isotherms. The adsorption isotherms of the polymers are shown in Figure 1 in terms of the amount adsorbed (μmol/m^2) vs units of the cmc. The maximum amount for P105 ($E_{37}-P_{56}-E_{37}$) is 0.05 μmol/m^2, or 0.40 mg/m^2. This amount is of the order of values reported for adsorption of P105 on silica particles by Killmann et al.[12]as well as on flat silica by Malmsten et al.[13] The two species with the higher ratio of hydrophobic to hydrophilic content (P123 ($E_{19}-P_{69}-E_{19}$) and P103 ($E_{17}-P_{60}-E_{17}$)) generally exhibit larger adsorbed amounts than do the species with the longer hydrophilic blocks (P105 ($E_{37}-P_{56}-E_{37}$) and F108 ($E_{132}-P_{50}-E_{132}$)). The maximum adsorption values of the F108 (0.025 ± 0.012 μmol/m^2) are low, and these small amounts is difficult to measure accurately. The low amounts adsorbed for P105 and F108 can be attributed to an entropic effect. The monomers are quite soluble in water, and adsorption of molecules on the surface would lead to less disorder, and hence a decrease in entropy, than when the molecules are dissolved in the bulk.

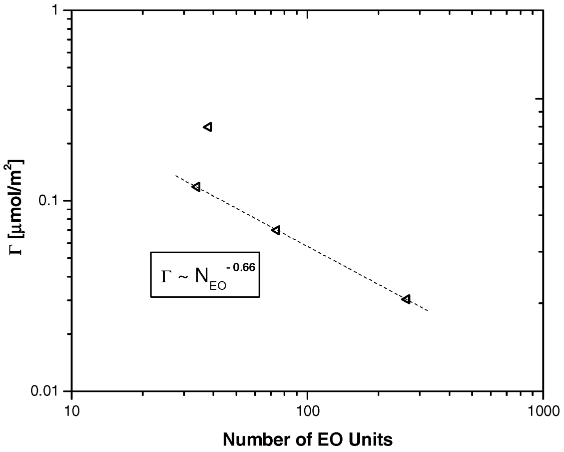

Figure 2. A log–log graph of the adsorbed amount at maximum coverage vs the total number of EO units for Pluronics P123 ($E_{19}-P_{69}-E_{19}$), P103 ($E_{17}-P_{60}-E_{17}$), P105 ($E_{37}-P_{56}-E_{37}$), and F108 ($E_{132}-P_{50}-E_{132}$). The dashed line is a linear fit of the adsorbed amounts for P103, P105, and F108.

We observe in Figure 1 a maximum for the adsorbed amounts of P123 and P103 near the vicinity of the cmc. This behavior can be attributed to the polydispersity.[14] As the bulk concentration of the polymer increases, more surface-active species may displace less surface-active species on the surface.

The P123 maximum is approximately double the value of the P103, and this is probably due to the greater amount of PO units in the P123. The hydrophobic units of the P103 can decrease the interaction with bulk water molecules by forming a bilayer at the hydrophilic SAM surface.

Similar trends were obtained in our previous adsorption studies for a hydrophobic surface. However, in comparison to the hydrophobic surface, the present results indicate much lower amounts of adsorption for the hydrophilic surface. The P123 ($E_{19}-P_{69}-E_{19}$) is lower in the adsorbed amount by a factor of 3 compared to results obtained for the hydrophobic surface.[2,3] The adsorptions are lower by a factor of 10 for the other triblock polymers compared to the hydrophobic surface. This is consistent with the findings of Shar et al. for adsorption of a series of Pluronics, with smaller PPO blocks, on silica[11] and on polystyrene latex.[11]

Figure 2 shows the adsorbed amounts at maximum coverage plotted against the number of EO units in the copolymers.

We see that the molar adsorbed amount, or, equivalently, the number of adsorbed chains per unit area, for the series P103, P105, F108 decreases with increasing length of the outer PEO blocks. This observation is consistent with the results of a Monte Carlo simulation by Balazs et al.,[15] who found a decrease of the number of bound chains for triblock copolymers with longer outer anchoring blocks. In Figure 3, we recast the same adsorbed amount data against the molecular weight of the copolymers. We see that the maximum coverage is a weak function of molecular weight for P103, P105, and F108. This behavior is similar to that of low molecular

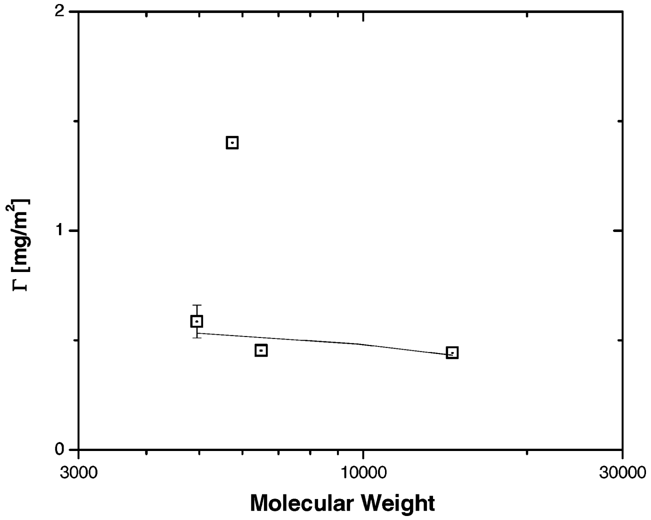

Figure 3. Semilog graph of the adsorbed amount at maximum coverage vs molecular weight for Pluronics P123 ($E_{19}-P_{69}-E_{19}$), P103 ($E_{17}-P_{60}-E_{17}$), P105 ($E_{37}-P_{56}-E_{37}$), and F108 ($E_{132}-P_{50}-E_{132}$). The line is a fit of the points for P103, P105, and F108.

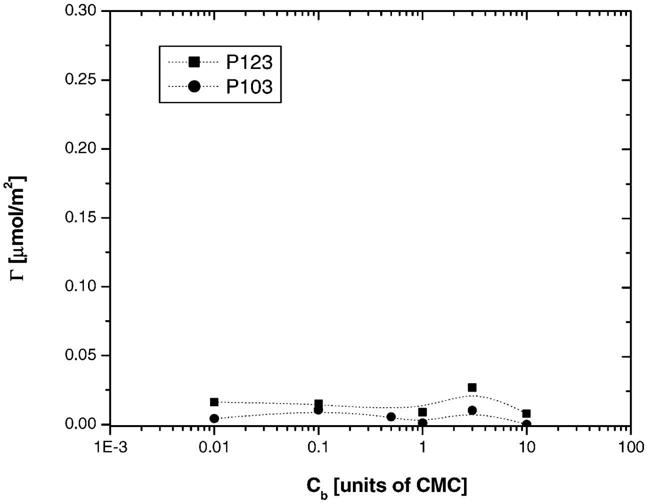

Figure 4. Residual amount left on surface at the end of desorption experiment; for Pluronics P123 ($E_{19}-P_{69}-E_{19}$) and P103 ($E_{17}-P_{60}-E_{17}$).

weight homopolymers, and from the kinetics, we infer that these samples adopt a monolayer structure at the surface.

For Pluronic adsorption on silica it has been inferred that that hydrogen bonding between the ether groups in the EO units and the silanol groups at the silica surface is responsible for the adsorption.[13,16] It is unlikely that hydrogen bonding plays a dominant role in the adsorption on the hydrophilic SAM here. The adsorption of the Pluronics P123 ($E_{19}-P_{69}-E_{19}$), P103 ($E_{17}-P_{60}-E_{17}$), P105 ($E_{37}-P_{56}-E_{37}$), and F108 ($E_{132}-P_{50}-E_{132}$) shows a decrease with an increase in the number of EO units.

The P123 copolymer, on the other hand, exhibits an enhanced adsorption behavior compared to the rest of the series. As mentioned previously, this result is probably due to the formation of a bilayer, and we will discuss this further in the kinetics section.

The desorption characteristics of the triblock polymers are given in Figure 4. The figure shows the residual amount of polymer left on the surface upon completion of a pure solvent (water) rinse. The desorption process is complete (within the accuracy of the measurements), making the overall adsorption–desorption process reversible. Only the results for Pluronic P123 and P103 are shown. The P105 and F108 desorption results are practically zero and are not shown. The differences between adsorbed and desorbed amounts are small and influenced by the experimental accuracy (±0.012 μmol/m^2) so that no conclusion about reversibility can be made for P105 and F108. The results for P123 and P103 are in contrast to the adsorption of the same triblock polymers on a hydrophobic surface. In that case the adsorption–desorption process was not reversible.[2,3] Since the hydrophilic SAMs show low affinities for adsorption, it suggests that the Pluronics readily detach and disperse into water when the bulk concentration of the polymer is dropped to zero.

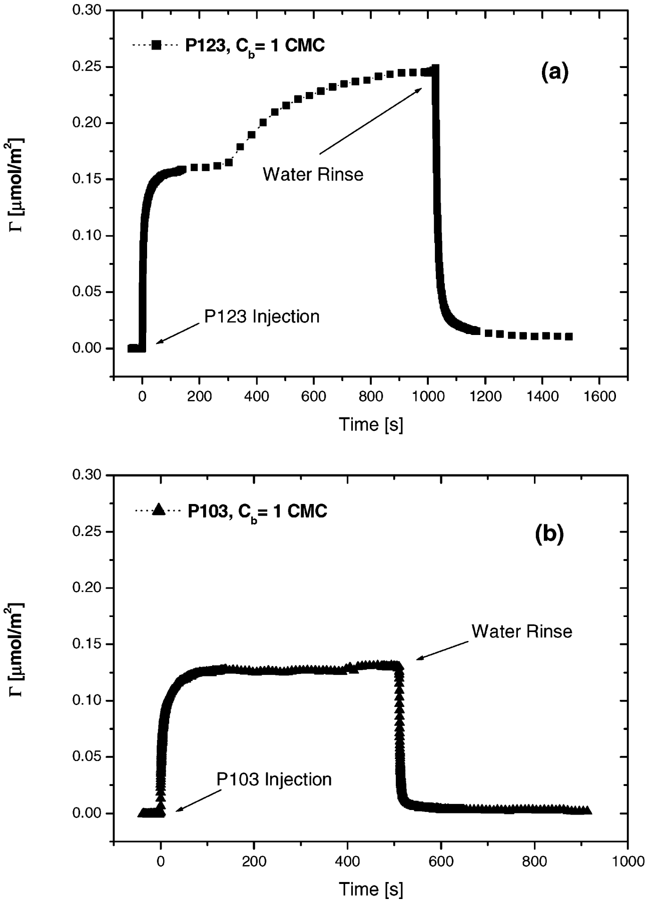

Figure 5. Typical adsorption–desorption kinetics experiment. (a) P123 ($E_{19}-P_{69}-E_{19}$) at 1 cmc: note that following saturation at about 300 [s] it appears that a second layer starts to build up. (b) P103 ($E_{17}-P_{60}-E_{17}$) at 1 cmc: a monolayer is formed. In both experiments no polymer residue is left on the surface after completing the rinsing step.

Adsorption and Desorption Kinetics. In general, the adsorption–desorption kinetics curves have Langmuirian-like behavior, with the notable exception of P123 ($E_{19}-P_{69}-E_{19}$). As can be seen in Figure 5a, an additional shoulder is present. Similar shoulders appear for the kinetics at concentrations above 0.1 cmc. This phenomenon is indicative of the formation of an additional layer or possibly admicelle formation. Another possible explanation is that the polydisperse sample has a higher affinity fraction, with a higher molecular weight, but slower in kinetics that exchanges with another fraction already adsorbed at the surface.[17] However, the latter hypothesis appears very unlikely

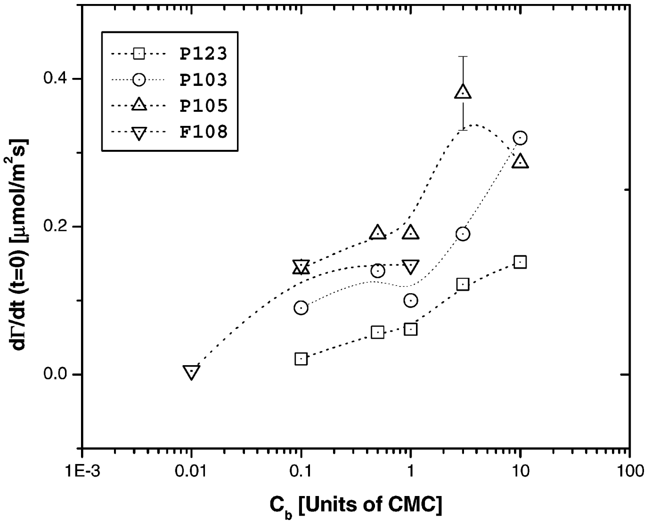

Figure 6. Intrinsic initial rates of adsorption for Pluronics P103 ($E_{17}-P_{60}-E_{17}$), P123 ($E_{19}-P_{69}-E_{19}$), P105 ($E_{37}-P_{56}-E_{37}$), and F108 ($E_{132}-P_{50}-E_{132}$); values extracted from convective−diffusive model described in ref 6. Lines are drawn to aid the eye.

since, although both PEO and PPO segments are known to adsorb,[4,18] we did not observe this effect for a hydrophobic surface.[2] Furthermore, we note that enhanced adsorption of similar magnitude has been reported for F127 by Eskilsson et al.[14] (F127 ($E_{97}-P_{69}-E_{97}$) has the same length of the PPO block as P123 ($E_{19}-P_{69}-E_{19}$)). They showed, by ellipsometric measurements, that the thickness of the adsorbed layer at saturation was comparable to twice the radius of the F127 micelles in solution.

Figure 5b gives the analogous adsorption/desorption kinetic experiment for P103 ($E_{17}-P_{60}-E_{17}$) as a comparison. We observe the formation of only one layer.

In Figure 6, we show the intrinsic initial rates of adsorption obtained from the experimental data using a convective−diffusive model.[3]

With the exception of F108 (limited data points), all the copolymers exhibit enhanced rates of adsorption past the cmc, and thus the micelles are likely to play a role in the adsorption process. Micelles often contain many multiple monomers, but the increase in adsorption beyond the cmc is modest, so it does not appear that whole micelles directly adsorb onto the surface. Apparently, the micelle presence near the surface modifies the kinetics of polymer adsorption. The micelle plays a role in releasing monomers at the surface in a preferred orientation. Below the cmc, the monomer molecules should arrive at the surface in random, three-dimensional conformations. Above the cmc, a micelle present at the SAM surface should release the monomers (unto the surface) with a preferred orientation leading to an increase in the kinetics of adsorption on the surface. Monomers have certain conformations in a micelle, with the more hydrophobic PO units inside and the hydrophilic EO units outside the micelle. The monomers in the micelle have the EO units orientated to the surface when the micelle arrives at the surface, facilitating an increase in the adsorption process.

Conclusions

In summary, we have investigated the adsorption and desorption behavior of a family of PEO−PPO−PEO triblock copolymers on a gold surface modified by a carboxyl-terminated SAM of a long-chain mercaptoalkanoic acid. We find that the adsorbed amounts go through a maximum near the critical micelle concentration (cmc). The adsorption process is fully reversible. We observe enhanced adsorption rates past the cmc regardless of the relative balance of the hydrophilic and hydrophobic content within the copolymer. The adsorbed amount at saturation is generally independent of molecular weight, but in the case of copolymer P123, the copolymer with the highest degree of hydrophobicity in the series studied, we observe a marked enhancement, possibly due to the formation of a bilayer. We have compared the results of this work with results of our previous study for the same system on a model hydrophobic surface. Overall, the rates and adsorbed amounts for the hydrophilic surface are an order of magnitude lower than in the case of the hydrophobic surface.

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