Interfacial Behavior of Triblock Copolymers at Hydrophilic Surfaces

Krister Eskilsson[†] **and Fredrik Tiberg***[,‡]

Physical Chemistry 1, Chemical Centre, Lund University, Box 124, S-221 00 Lund, Sweden, and Institute for Surface Chemistry, Box 5607, SE-114 86 Stockholm, Sweden

Received October 23, 1997; Revised Manuscript Received April 8, 1998

ABSTRACT: We report on the adsorption of a series of poly(ethylene oxide)−polytetrahydrofuran−poly(ethylene oxide) copolymers, $EO_{n/2}THF_mEO_{n/2}$, at hydrophilic silica surfaces and relate our findings to the corresponding behavior at hydrophobic surfaces. The adsorption of these copolymers is similar to that of poly(ethylene oxide) homopolymers at low bulk concentrations. However, the copolymer adsorption increases strongly above a certain threshold concentration. This increase, which begins more than 1 order of magnitude below the critical micellar concentration (cmc), is related to the concomitant formation of micellar-like structures at the hydrophilic surfaces. We show in this work that a commercial (ethylene oxide−propylene oxide−ethylene oxide) triblock copolymer, Pluronic F127, exhibits a similar behavior at silica. Due to surface aggregation, much thicker layers are measured on silica than at the hydrophobic surface, where the adsorption results in the formation of a monolayer structure. The adsorbed amount and layer thickness measured on bare silica tend to decrease when the bulk concentration is raised above the cmc. We infer that this is due to changes of the molecular weight distribution and relative block sizes of the copolymers in the surface aggregates, i.e., a polydispersity effect. This study also covers some aspects of the adsorption and desorption kinetics exhibited by the copolymers at silica. As is common for adsorbing polymers, the concentration dependent adsorption process is generally observed to be much faster than the desorption process. The adsorption process is in parts diffusion controlled but overall to a complex to be fully analyzed. During adsorption from solutions with bulk concentrations exceeding the cmc, a clear overshoot of the surface excess is observed after intermediate adsorption times. Again, this is interpreted as being due to polydispersity. Finally, after an initial rapid desorption regime, the surface excess exhibits a logarithmic decay with time during desorption.

Introduction

The use of block copolymers spans a wide range of technical areas. They are used to stabilize particle suspensions and emulsion droplets, obtain protein resistant surfaces, create microenvironments for drug delivery, etc. By varying the chemical nature of the different segments and the architecture of the block copolymers, it is possible to control their behavior at interfaces and thereby the technical applicability. The adsorption behavior of block copolymers has due to its practical importance been subject to a great number of theoretical and experimental studies (cf. current reviews[1−3]).

Most copolymer adsorption studies are performed with the use of diblock copolymers. The adsorption of triblock copolymers has been less extensively studied, but there are some articles dealing with this issue from both experimental and theoretical viewpoints.[4−11] In a recent paper, we presented a study of the behavior of a number of triblock copoly(ethylene oxide−tetrahydrofuran−ethylene oxide), $EO_{n/2}THF_mEO_{n/2}$, at hydrophobized silica.[11] At low surface coverages, it was shown that these copolymers anchor at the surface by both EO and THF units, hence forming a mixed pancake at the surface. However, at higher surface densities, the preferential adsorption of THF segments resulted in a segregation in the interfacial region. At these concentrations, the adsorbed layer comprised an inner region, where the more hydrophobic THF segments preferentially were attached at the surface, and an outer EO rich region of chains extending into solution. This is the classical picture of an adsorbed layer of block copolymers formed in a selective solvent.[4]

The present work deals with the adsorption behavior of the same block copolymers as in the previous study, but the adsorption has now been studied at hydrophilic silica surfaces. Of particular interest in this study is the question: How do the changed surface properties affect the multiscale organization of the block copolymers at the solid−liquid interface? As mentioned, when the solvophobic block interacts favorably with the surface, the adsorbed state is a condensed solvophobic surface layer and a buoy region of extending solvophilic chains. In contrast, if the solvophilic block anchors more favorably with the surface, surface micelles, cylinders, or bilayer type structures are formed. This requires, of course, that the driving force for self-assembly of the hydrophobic groups are sufficiently high. Surface micellar structures have previously been observed for short chain nonionic surfactants adsorbed at silica.[12−18] Their occurrence has also been predicted theoretically for diblock copolymers adsorbing from a selective solvent at solid surfaces.[19] Copolymer−surface interactions and geometrical restrictions imposed by the presence of the two-dimensional surface will most likely modify the bulk self-assembly behavior of the block copolymers to some extent. The critical concentration for self-assembly at the surface may, for instance, be dramatically altered by attractive copolymer−surface interactions. This is a topic addressed in the present work. We also compare the interfacial behavior at hydrophilic silica surfaces with that measured on hydrophobized silica. The copolymer interfacial behavior is also related to the adsorption behavior observed for simple poly(ethylene oxide), PEO, homopolymers. Our

---

[†] Lund University.
[‡] Institute for Surface Chemistry.

S0024-9297(97)01563-5 CCC: $15.00

Table 1. Molecular Weight of the Polymer, Number of Ethylene Oxide Groups, *n*, Number of Tetrahyrdrofuran Groups, *m*, and the Value of the Critical Micellar Concentration, cmc

polymer	MW	*n*	*m*	cmc (wt %)
P224-28	11900	224	28	0.03
P146-28	8400	146	28	0.04
P172-14	8600	178	14	0.2
P128-14	6700	128	14	0.15
P50-14	3200	50	14	0.02

results include adsorption isotherms, layer thicknesses, and data on the kinetics of adsorption and desorption.

Experimental Section

The adsorption measurements were performed by the in situ ellipsometric technique, by which both the surface excess and the adsorbed layer thickness can be determined with a time-resolution of 1−2 s. The technique and the measurement procedure used are thoroughly described in refs 20−23.

Five different ethylene oxide−tetrahydrofuran−ethylene oxide triblock copolymers, $\mathrm{E0}_{n/2}\mathrm{THF}_{m}\mathrm{EO}_{n/2}$, have been studied in this work. Depending on the chemical composition, these are referred to as P224-28, P172-14, P146-28, P128-14 and P50-14, respectively (see Table 1). The first number refers to the number of EO groups, *n*, and the second to the number of THF, *m*, groups of the polymer. The triblock copolymers were produced by Akzo Nobel Surface Chemistry, by ethoxylating PTHF polymers with molecular weights of 1000 and 2000, respectively. The latter were purchased from BASF. The polymer purification procedure and the method used to determine the average n/m ratio (NMR) and cmc's of the copolymers (dye solubilization and absorption measurements) are described in ref 11.

The manufacturers claims that the M_n/M_w value for the polymers is between 1.1 and 1.15. No homopolymers are present in the systems, but there may be small contamination of diblock copolymers. A summary of the properties of the copolymers used is given in Table 1.

Silica surfaces were prepared by the following procedure. Polished silicon test slides (p-type, boron-doped, resistivity 1−20 Ω·cm) were purchased from Okmetic Ltd. The wafers were oxidized thermally in an oxygen atmosphere at 920 °C for ≈1 h, followed by annealing and cooling in an argon flow. This procedure results in a SiO_2 layer thickness of 300 Å. The oxidized wafers were then cut into slides with a width of 12.5 mm and cleaned according to the procedure described in ref 22. Before use, the surfaces were dried under vacuum, 0.001 mbar, and then treated in a plasma cleaner (Harrick Scientific Corp., model PDC-3XG) for 5 min prior to the start of the adsorption measurements. The hydrophilic wafers obtained by this technique are referred to simply as silica surfaces.

Hydrophobized silica (h-silica) surfaces were obtained by placing oxidized, cleaned, and plasma-treated substrates in a reactor, which prior to the injection through a septum of 2 mL of dimethyloctylchlorosilane, was evacuated from air by a water suction pump. The exposure to dimethyloctylchlorosilane was prolonged for about 18 h at 38 °C, and the surfaces were then rinsed with ethanol followed by water, cleaned with surfactants, again rinsed in water and ethanol, and finally stored in ethanol. Before use, the surfaces were dried under vacuum, 0.001 mbar. The advancing and receding water contact angles were 105 ± 5 and 95 ± 5 degrees, respectively. To avoid potential problems associated with an air film sticking to the hydrophobic surface, ethanol was pumped through the cuvette before water was added. Note that reproducible measurements could not be obtained without this intermediate step. The ethanol was then rinsed off by a continuous flow of double-distilled Millipore water, DD-MP, and prior to the start of the adsorption measurements, both silica and h-silica were allowed to stabilize in the aqueous solvent for at least 1 h.

Results and Discussion

The present investigation deals with the behavior of triblock copolymers of the type $\mathrm{E0}_{n/2}\mathrm{THF}_{m}\mathrm{EO}_{n/2}$ at bare hydrophilic silica surfaces. We also compare the adsorption at the hydrophilic silica surface with that measured on hydrophobized silica (h-silica). The polymers are abbreviated P*n*-*m* copolymers, where *n* and *m* indicate the number of EO and THF groups, respectively. Before studying the adsorption behavior, the polymers were characterized in terms of composition, molecular weight, and cmc (see Table 1). These data were discussed in our previous paper.[11] All P*n*-*m* copolymers studied in this investigation form micelles in bulk solution and exhibit fairly distinct cmc values in the concentration range 0.02−0.2 wt %; see Table 1. The present work shows that adsorbed copolymers also tend to associate into micellar-like structures, provided the substrates are hydrophilic. Later in the article, we reveal that the adsorption of a similar commercial triblock copoly(ethylene oxide−propylene oxide−ethylene oxide), Pluronic F127, also results in the formation of micelle-like structures at the interface.

The surface aggregation behavior discussed throughout this article is based on time-resolved ellipsometric measurements of adsorbed amounts and layer thicknesses.

Adsorption Isotherms. The adsorption isotherms of the different P*n*-*m* copolymers studied, i.e., P224-28, P146-28, P172-14, P128-14, and P50-14, as well as that of the P90 homopolymers is presented in Figures 1 and 2. The isotherms were measured on both hydrophilic silica and hydrophobized silica (h-silica).

h-Silica. In our earlier paper, we exclusively discussed the adsorption at h-silica and we refer to that paper for a detailed discussion.[11] Nevertheless, it is of interest to compare the adsorption at the different surfaces. Some details about the behavior on h-silica are, therefore, also included in this presentation.

All P*n*-*m* copolymers were found to form monolayers at h-silica, with the middle tetrahydrofuran block anchoring at the surface and the ethylene oxide groups either anchoring at the surface or protruding into the aqueous phase. The degree of anchoring of the EO chains depended critically on the surface coverage.

Copolymers with relatively long EO chains were observed to exhibit an interfacial behavior that was very similar to that of the P90 homopolymer in the low-coverage region. The difference observed between copolymers with different molecular weights in the low-concentration region was found to be a typical polymer molecular weight effect. It is well-known that long-chain polymers exhibit more high-affinity type isotherms.[1]

Both THF and EO chains tend to form trains on h-silica at low coverages. As the surface coverage increases, however, the EO chains are increasingly forced away from the surface. This is due to the stronger attraction between the surface and THF groups than between the surface and EO groups. The shorter hydrophobic middle PTHF block cause the copolymers to adsorb much more strongly than the PEO homopolymers at higher bulk polymer concentrations. In this concentration regime, the isotherms are generally rather well described by the conventional Langmuir isotherm. Note that the same observation was done earlier for short-chain ethylene oxide-based surfactants.[23] As is further seen in Figures 1 and 2, the plateau surface excess (in mass per unit area) is approximately the same for all P*n*-*m* copolymers at h-silica. Therefore, the plateau surface area per polymer molecule increases

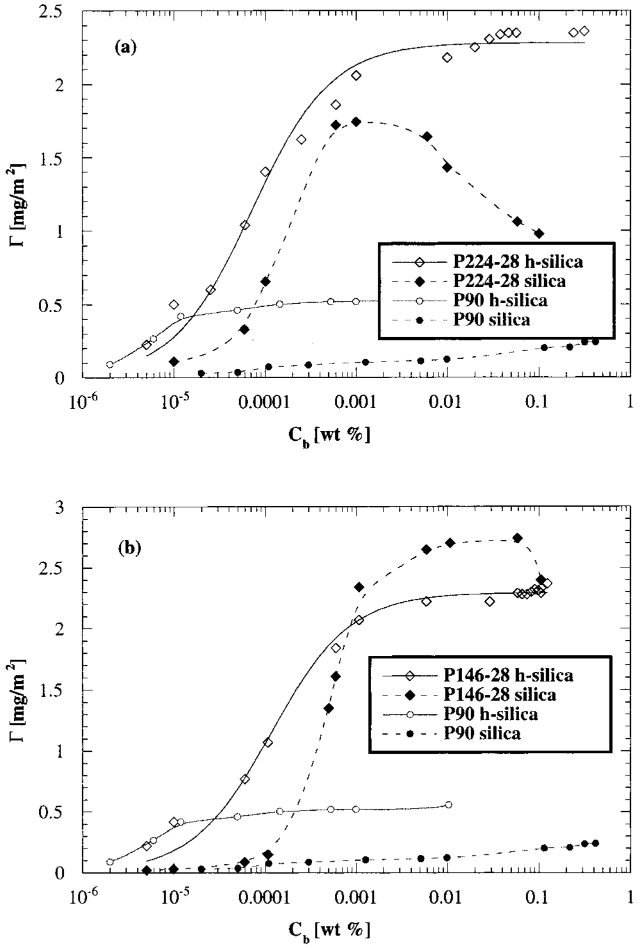

Figure 1. Adsorption isotherms for the homopolymer P90 and the copolymers: (a) P224-28; (b) P146-28. The graphs show the isotherms measured on bare hydrophilic silica as well as on hydrophobized h-silica ($T = 25$ °C). The solid line fit to the copolymer isotherms shows the best fit of the experimental data to the Langmuir equation, whereas the rest are drawn only to guide the eye.

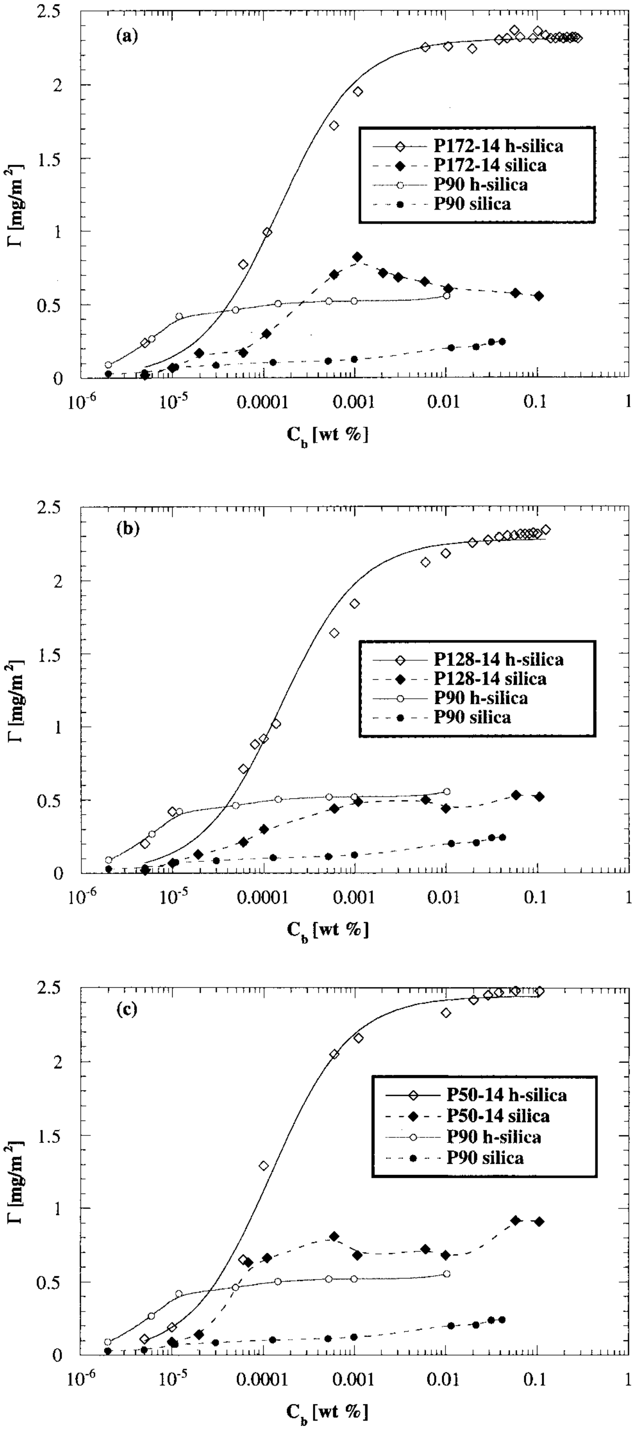

Figure 2. Adsorption isotherms for the homopolymer P90 and the copolymers: (a) P172-14; (b) P128-14; (c) P50-14. For further details, see Figure 1.

linearly with the molecular weight of the copolymer. This fact also smears out possible polydispersity effects during adsorption at hydrophobic surfaces.

Silica. The adsorption plateau value of the P90 homopolymer at the silica surface is about 0.25 mg/m^2 (see Figure 1). This value agrees well with the data by Trens et al.,[24] who determined the isotherms for a large number of poly(ethylene oxide) homopolymers (ranging from 2 to 90 900 segments) by the solution depletion method. Interestingly, the adsorption on silica is much smaller than that on h-silica. A speculative interpretation of this observation is that hydrophobic interactions are responsible for the poly(ethylene oxide) adsorption at both surfaces, i.e., if the silica surface is not fully hydrated and partially hydrophobic on the nanometer scale. Further studies of the EO−silica interactions need to be executed for obtaining a better understanding of the driving force for adsorption of ethoxy-based surfactants and polymers on silica.

Figures 1a,b and 2a−c show that the adsorption isotherms of the P*n*-*m* copolymers at silica exhibit features that are quite different depending on the sizes of the different blocks. These variations were not observed on h-silica. The copolymer adsorption is further much smaller in the low-concentration region on silica compared to on h-silica. This is in agreement with a smaller interaction energy between copolymer segments and silica than between the copolymer segments and h-silica.

The surface excess measured at low bulk concentrations is almost the same for the copolymers and the homopolymer at silica. As the concentration is increased, however, a pronounced increase of the adsorption is observed for the P*n*-*m* copolymers, but not for the P90 homopolymer. This effect is particularly clear for the P*n*-28 copolymers, which exhibit a strong cooperative adsorption increase more than 1 order of magnitude below the cmc. We infer that this increase is caused by the association of block copolymers into

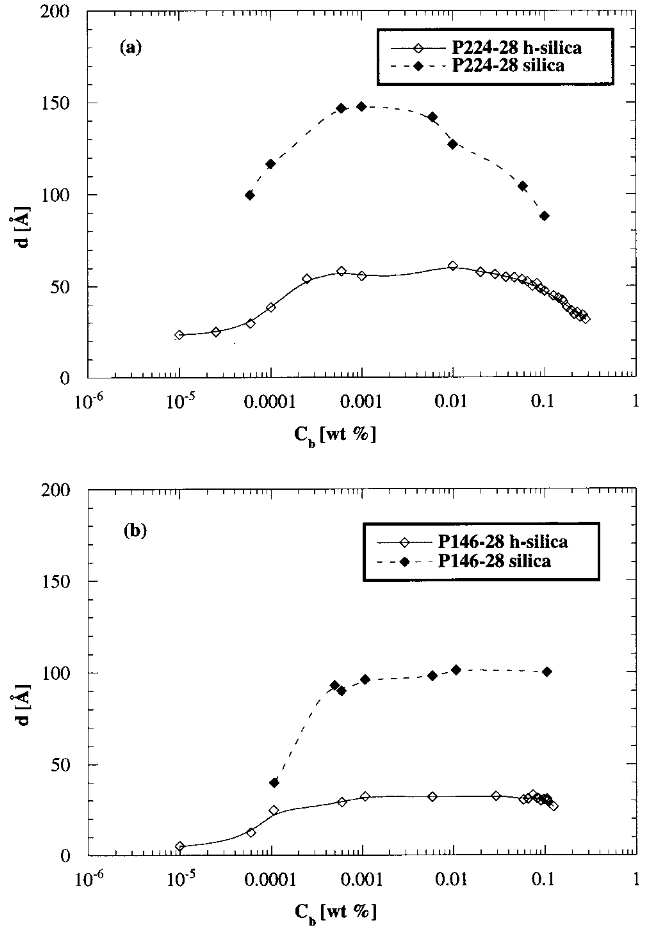

Figure 3. Adsorbed layer thickness as a function of bulk copolymer concentration for the copolymers: (a) P224-28; (b) P146-28. The graphs show the thicknesses measured on bare hydrophilic silica as well as on hydrophobized h-silica ($T = 25$ °C).

micellar-like aggregates in the interfacial region. This statement is supported by, e.g., (i) the shape of the isotherms observed for the different P*n*-*m* polymers at silica (see discussion below), (ii) the maximum observed at higher bulk concentrations, which is indicative of surface self-assembly of polydisperse systems (see discussion below), (iii) the thicknesses obtained in this region, which are much larger on silica than on h-silica (see Figures 3 and 4), and (iv) the adsorption kinetics, which show resemblance to the corresponding time dependencies observed for nonionic surfactants on silica, which have been proven to form surface micellar (and bilayer) type structures at this surface (see discussion below).

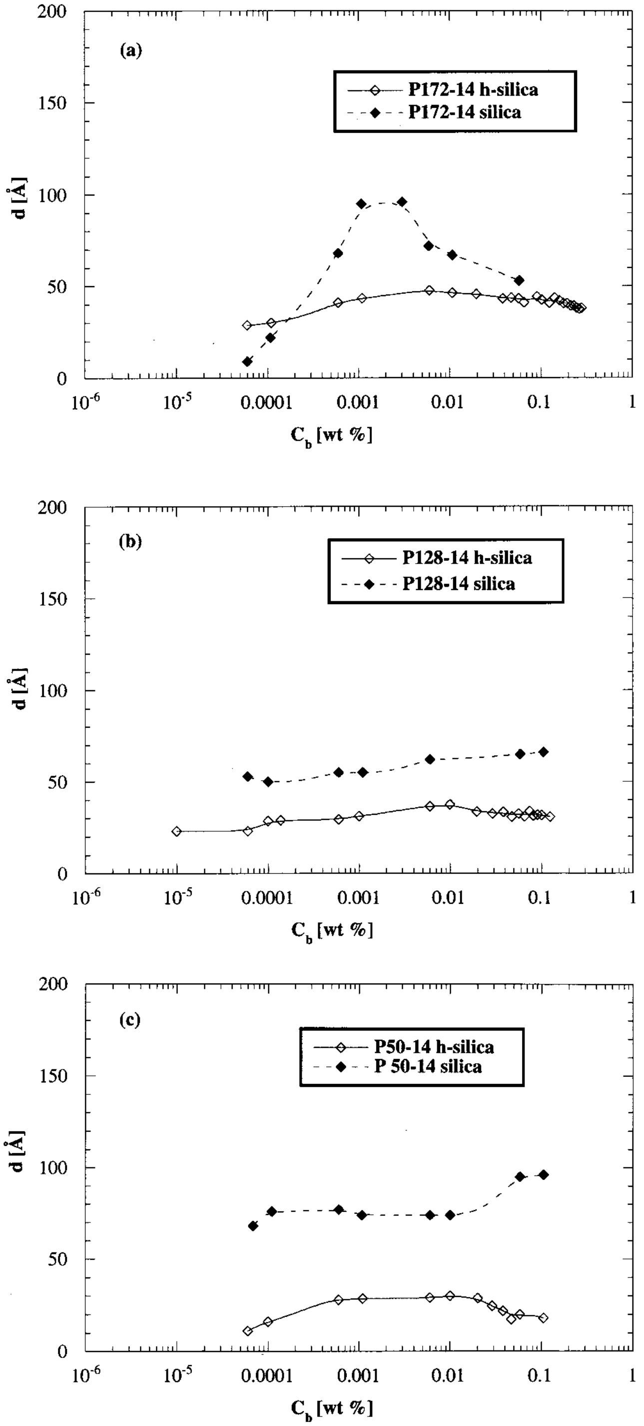

Figure 4. Adsorbed layer thickness as a function of bulk copolymer concentration for the copolymers: (a) P172-14; (b) P128-14; (c) P50-14. For further details, see Figure 3.

The interfacial behavior of the P*n*-*m* copolymers on both silica and h-silica is indeed very similar to that of short-chain poly(ethylene glycol) monoalkyl ethers. Short-chain surfactants clearly associate into surface micelles or bilayer structures just below the cmc at silica.[13,14,22,25−28] Furthermore, binary poly(ethylene glycol) monoalkyl ether, C_nE_m, systems also exhibit an adsorption maximum in the region of the cmc of the mixed system.[17,29] The maximum is explained by the increasing presence of more hydrophilic surfactants in the surface aggregates with increasing concentration, a trend that can be easily calculated by ideal solution theory. The increased presence of surfactants with larger EO headgroups and/or shorter hydrocarbon chains changes the packing conditions in favor of more spherical aggregates with smaller aggregation numbers. This also results in a less efficient packing at the interface. A similar reasoning can also be applied to the copolymer systems studied in this work. Note that the surface aggregate and bulk micellar compositions determined for nonionic surfactants appeared to be almost identical.[17] It is, however, not clear from our measurements to what extent the compositions of the block copolymer surface aggregates correlate with those of the corresponding bulk structures. A striking difference between the surfactant behavior and the behavior exhibited by the copolymers is the concentration relative to the cmc where surface aggregates are first present. This difference is indicative of the adsorption energy. For C_nE_m surfactants with relatively short ethylene oxide chains ($m < 10$), surface aggregation starts approximately between 0.5 and 0.9 cmc. The adsorption increase beyond this concentration is very cooperative. The adsorption energy per surfactant is about 0.5 kT.[17] However, for the copolymers, this process starts more than 2 orders of magnitude below the cmc. This implies that the adsorption energy is much higher for the copolymers. The much stronger collective interactions between the copolymer segments and the surface than between the short chain surfactants and the surface may in the former case lead to a larger compositional discrepancy between bulk and surface aggregates. This is an issue that deserves some further experimental and theoretical work.

Adsorbed Layer Thickness. The evolution of the adsorbed copolymer layer thickness as a function of bulk copolymer concentration is presented in Figures 3a,b and 4a–c. The curves show the thicknesses obtained at both silica and h-silica.

h-Silica. The adsorbed layer thicknesses at low surface coverage when THF and EO chains tend to form trains at the hydrophobic surface are generally found to be small. However, for all P*n*-*m* copolymers studied, the thickness increases monotonically with the concentration until a pseudoplateau is reached. The ellipsometric thickness at the semiplateau, d_p, scales with the number of EO groups according to the approximate relation $d_p \propto n$, with the exception of the smallest P50-14 polymer. The apparent decrease of the adsorbed layer thickness observed above approximately 0.1 wt % is most likely due to the existence of a depletion layer located outside the adsorbed layer. Above about 0.1 wt %, the optical contrast between the depletion layer and the bulk solution, is large enough to cause the apparent decrease of the layer thickness presented in Figures 3 and 4. For a more extensive discussion see our previous paper.[11]

Silica. The adsorbed layer thickness versus concentration curves follow similar trends on increasing the concentration as the surface excess. At small surface coverages (<0.3 mg m^{-2}), the thickness cannot be determined by the ellipsometric technique with an adequate accuracy.[30] Therefore, the data points are not presented in Figures 3a,b and 4a–c, only data with less than ±10% error are shown. Nevertheless, the copolymers appear to adopt a relatively flat configuration relative to the surface at low surface coverages. The thicknesses are scattered around 30 Å. This value corresponds quite well with measured layer thicknesses of poly(ethylene oxide) homopolymers and poly(ethylene oxide)-based triblock copolymers on silica spheres.[7]

At higher bulk concentrations, where the cooperative increase of the surface excess is observed, a concomitant large increase of the adsorbed layer thickness is also detected. This behavior is particularly clear for P*n*-28 and P172-14 copolymers. The maximum thickness is for all copolymers more than 2 times larger on silica than on h-silica. This result is good evidence for the fact that these copolymers form some type of surface micellar structures on silica with the EO chains attaching at the surface as well as extending into the aqueous phase. Thereby, they efficiently shield the more hydrophobic THF chains from extensive contact with the water solvent. The THF groups must, therefore, be primarily located in the middle part of the adsorbed layer. The fact that the layer thickness of, for instance, P224-28 is about 50 Å larger than that observed for P146-28, while the surface excess is smaller, indicates that the latter molecules form surface aggregates with a more spherical shape and smaller aggregation numbers. The same effect of increasing the EO chain length has previously been observed for nonionic surfactants adsorbed on silica.[17]

The mean thickness and the adsorbed amount measured for the P224-28 and P172-14 copolymers reaches a maximum in the region close to the cmc. At higher concentrations, we observe a decrease of the layer thickness and adsorbed amount with increasing bulk concentrations (see Figures 1–4). We interpret this as being due to polydispersity. With increasing copolymer concentration, bulk and surface aggregates incorporate an increased fraction of more hydrophilic block copolymers which in relative terms have larger ethylene oxide segments. This leads to an increased curvature of the aggregates and possibly also to increased effective copolymer–surface interaction relative to the forces governing self-assembly.[17] A fraction of the observed decrease of the ellipsometric thickness observed above 0.1 wt % may, however, also be attributed to the presence of a depletion layer, which is located between the adsorbed layer and the bulk solution.[11]

Most of the published work on the surface self-assembly and adsorption of block copolymers concern triblock ethylene oxide–propylene oxide–ethylene oxide copolymers ($EO_{n/2}PO_mEO_{n/2}$) adsorbed at silica surfaces. These copolymers are generally referred to by the trade name Pluronics. They differ from the P*n*-*m* ($EO_{n/2}$-$THF_mEO_{n/2}$) copolymer used most extensively in our study in the fact that each PO monomer has one less hydrocarbon compared to the THF monomer. The middle block in a Pluronic copolymer is, therefore, effectively less hydrophobic than that in a P*n*-*m* copolymer.

Killman et al.[7] measured the adsorption of different Pluronics and pure PEO on dispersed silica particles. The adsorbed amount was in this study determined by the solution depletion method and the adsorbed layer thickness was measured by both photon correlation spectrometry (PCS) and ultracentrifugation (UC). Silica particles with a diameter of 212 nm were used as substrates in this work. For a PEO homopolymer (MW = 18 000 g mol^{-1}), they obtained a thickness of 3 nm at the adsorption plateau. The corresponding value for Pluronic P105 copolymer ($n = 148$; $m = 56$) was only found to be slightly larger, ≈0.40 mg m^{-2}, whereas the hydrodynamic layer thicknesses measured for a number of different Pluronics were all under 3 nm, i.e., substantially smaller than the values of the mean layer thicknesses obtained in this study. Malmsten et al.[8] also measured adsorption isotherms of different Pluronics, i.e., F127 ($n = 198$, $m = 65$), F98 ($n = 250$, $m = 47$), and P75 ($n = 48$, $m = 35$), and the pure PEO homopolymer (MW = 20 000) on silica particles by the solution depletion method. The silica particles used in this work had a hydrodynamic diameter of 39 nm. Thicknesses of the adsorbed layers were in this work also estimated by photon correlation spectroscopy (PCS). The plateau adsorption values obtained from isotherm measurements for the different Pluronics and the PEO homopolymer were also in this work observed to be rather small (≈0.3–0.4 mg m^{-2}) and, therefore, in agreement with previous findings by Killman and co-

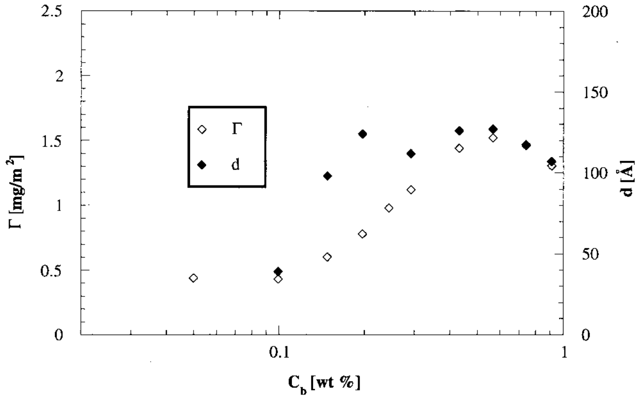

Figure 5. Surface excess and adsorbed layer thickness versus bulk copolymer concentration of Pluronics F127 at bare hydrophilic silica ($T = 25$ °C).

workers. The hydrodynamic layer thicknesses were found to be in the range between 3 and 8 nm for all copolymers. However, Malmsten and co-workers also made measurements on flat silica substrates by ellipsometry. As the temperature was raised at a fix bulk concentration of the F127 copolymer, they observed a strong adsorption increase from 0.4 to 1.6 mg m^{-2}. This increase was observed close to the critical micellization temperature, cmt. This was claimed to be due to the cooperative formation of surface aggregates. However, the hydrodynamic thicknesses presented in the same study did not increase with increasing temperature and surface coverage. Therefore, it was concluded that intact micelles were clearly absent at the surface, but it was nevertheless claimed that some sort of surface aggregation took place. To get a better picture of this Pluronic system and to be able to see if surface aggregation is a common feature for different types of copolymers, we decided to investigate the same F127 systems using ellipsometry. Both the surface excess and the layer thickness were determined in our work. The data obtained are shown in Figure 5. As can be seen, the layer thicknesses indeed increase strongly as the surface excess begins to increase just prior to the bulk cmc (=0.7−1 wt %[31,32]). The mean thickness goes from about 40 Å to values between 120 and 140 Å. The latter value can be compared to twice the hydrodynamic radii of a F127 micelle, $2r_h \approx 220$ Å. De Gennes showed theoretically that the ellipsometric thickness, d, for adsorbed homopolymers in a good solvent can be related to the hydrodynamic thickness, d_h, by the relation: $d \approx d_h^{0.67}$.[33] In the region where surface micelles are expected, we find that $d \approx 2r_h^{0.87-0.90}$. This is of course dependent on the segment density profile, which we have no exact knowledge about. We can nevertheless conclude that adsorbed F127 copolymers tend to form micellar-like aggregates at the silica surface. These structures are first observed in the concentration region 0.2−0.4 cmc. The surface excess and the thickness does also for the F127 system appear to decrease when the cmc is exceeded.

The results by Malmsten and co-workers show that intact micelles do not form on nanoparticles, but we show here that such structures are present at the flat silica surface used in this study.[8] This finding is further supported by the self-consistent mean-field calculations.[8] We thereby point out that adsorption results obtained at flat surfaces cannot be compared to results obtained on particles with radii that are of the same order of magnitude as the copolymer micelles in solution. However, the adsorption results obtained below the surface aggregation concentration appear to be similar at the particle and the flat surfaces, respectively.

To summarize, it is clear that the P*n*-*m* copolymers behave in a similar fashion as Pluronics, but the formation of surface aggregates starts closer to the cmc for the Pluronics. The difference is believed to be due to the more hydrophobic character of the PTHF block compared to the PPO block. Moreover, as discussed previously, there are many similarities between the adsorption behavior of EO-based copolymers presented here and that of short-chain nonionic surfactants. This is observed at both hydrophobic and hydrophilic surfaces.

Adsorption and Desorption Kinetics. The kinetic data presented in this part feature the copolymer P224-28 at bare hydrophilic silica. The corresponding adsorption and desorption kinetics observed at hydrophobic surfaces was discussed in our previous paper.[11] Basically, three kinetic regimes are encountered during adsorption on h-silica: In the first regime (low surface coverage), the adsorption was found to be diffusion controlled, with rates that were proportional to the concentration difference between the bulk solution and the subsurface located just outside the adsorbed layer. The bulk concentration, C_b, is constant due to the large volume-to-surface ratio used in the experiment. The subsurface concentration, C_s, can be calculated from the isotherm.[34] In the diffusion-controlled regime, we have fast equilibration in the surface region. Under these conditions, we know that the subsurface concentration at a particular surface excess value, $C_s(\Gamma)$, equals the corresponding inverse isotherm value, $C_b(\Gamma)$. The experimental adsorption kinetics for P224-28 on h-silica could in the diffusion-controlled regime be modeled using a stagnant layer (which separates bulk solution from the subsurface) of $\delta \approx 10^{-4}$ m.[11] In the second regime (intermediate coverages and adsorption times), the kinetics are governed by the rate of displacement of anchored EO chains by THF chains of adsorbing copolymers. Finally, in the third regime (high surface coverages), the adsorption slows down markedly due to the energy barrier caused by the presence of the relatively dense brush of adsorbed EO chains. In this regime, the surface excess varies proportionally with log t. A similar log t dependence was also observed during the major part of the desorption process.

At the hydrophilic bare silica surface, we observe some similarities in the time dependence, but also substantial differences. Figures 6a,b shows the adsorption kinetics for P224-28 measured at long and short times, respectively. We see the following clear trends: A region of constant adsorption rate is entered, i.e., $\Gamma \sim t$, a short while after the adsorption process has been initiated The rate in the linear adsorption regime scales with the concentration according to the relation $d\Gamma/dt \sim C_b$. The adsorption rate under steady-state conditions is given by

$$\frac{d\Gamma}{dt} = \frac{D_p}{\delta}(C_b - C_s(\Gamma))$$

In the very beginning of the adsorption process, $C_s(\Gamma)$ increases rapidly with increasing coverage ($C_s(\Gamma) = C_b(\Gamma)$ from the isotherm in Figure 1). This may to some extent explain the decaying adsorption rate observed at short times. However, this may also have a more complex origin related to the initial surface aggregation process. The adsorption rate depends on a large number of parameters, such as the polymer characteristics (e.g., the critical surface aggregation and micelle concentrations (csac and cmc), polydispersity, diffusion constants, micellar association and dissociation constants, and hydrodynamic properties of the system (influencing the size of the stagnant layer). This makes it difficult to interpret the adsorption kinetics in a simple way. However, the linear adsorption regime appears relatively easy to understand. This constant adsorption rate regime is entered at surface coverages where the cooperative increase of the surface excess is first seen in the isotherm. Therefore, $C_b - C_s(\Gamma)$ in eq 1 will only change slowly in this region when $C_b > C_s(\Gamma)$. Hence, as previously has been observed for nonionic surfactants on silica, cooperative isotherms give rise to constant adsorption rates. Note that the number of measured surface excess values in the isotherm in Figure 1 are rather few. Therefore, the copolymer isotherm may very well exhibit stronger cooperative features than is apparent in the figure. In the previous study of the adsorption kinetics at hydrophobic silica we also observed a linear adsorption regime at intermediate coverages and adsorption rates. The origin of this was claimed to be substitution of PEO segments at the surface by PTHF segments. We do not believe that this is the case in the present system, since the concentration dependence is different and agrees with that expected in the diffusion-controlled regime. Furthermore, the adsorption kinetics exhibit features very similar to those observed for short-chain nonionic surfactants at hydrophilic silica. These surfactants adsorb at bare silica with a contstant rate during the majority of the adsorption process due to the fact that the adsorption isotherm is almost step-shaped. The adsorption kinetics of these systems have further been successfully accounted for by theory.[16,23,35]

Another interesting effect seen in Figure 6 is the overshoot of the surface excess observed for the P224-28 polymer at intermediate adsorption times and concentrations larger than the cmc. This shows that back-diffusion of a fraction of the already adsorbed polymers must take place at long times. The fact that the surface excess at the maximum in the Γ−*t* curve does not reach the same maximum value as is observed in the isotherm shows, however, that local equilibrium conditions do not prevail at the subsurface or indeed throughout the stagnant layer region during the whole adsorption process. However, there is clearly a continuous adjustment toward equilibrium conditions, which is rapid enough to cause an overshoot of the surface excess at short times. This creates an outward chemical potential gradient, causing desorption of a fraction of the polydisperse polymers, most likely of smaller copolymers with relatively short EO chains. A final comment about adsorption kinetics is displayed in Figure 6a,b. The slow substitution adsorption regime seen at the h-silica surface is not observed at the hydrophilic silica surface.[11]

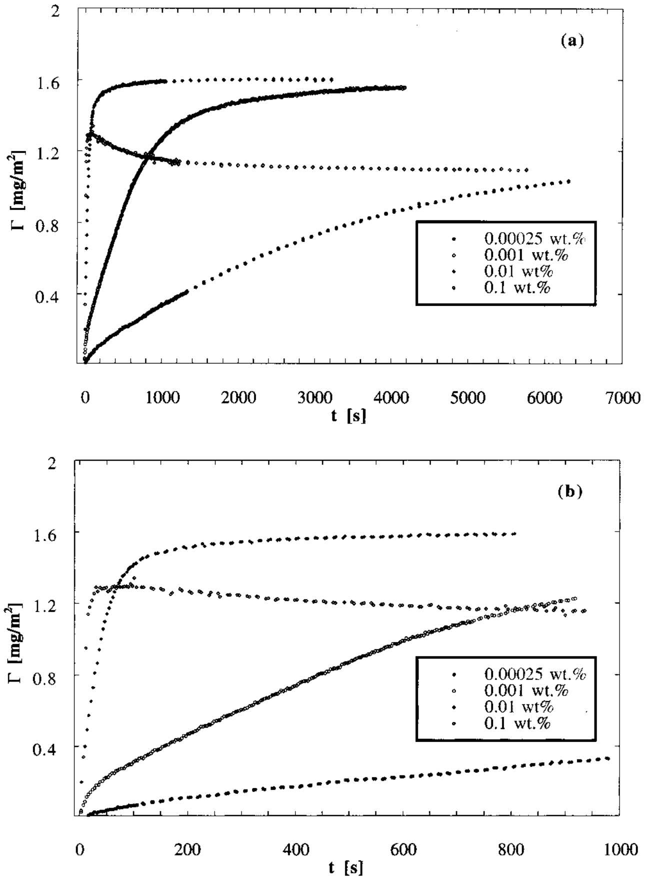

Figure 6. Evolution at (a) long and (b) short times of the adsorbed amount with time during adsorption of P224-28 from solutions with different bulk concentrations ranging from 2.5 × 10^{-4} to 0.1 wt %.

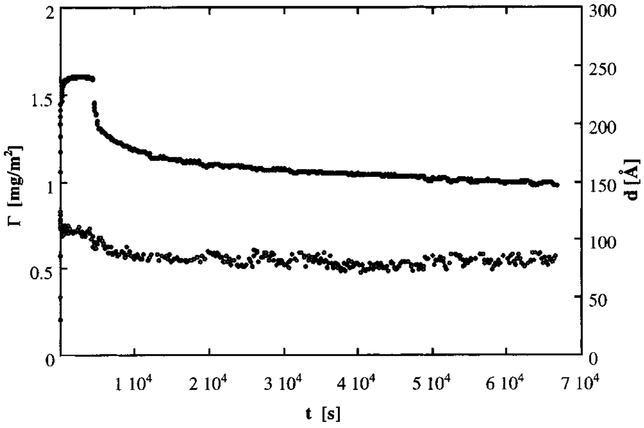

Figure 7. Time dependence of the surface excess and the adsorbed layer thickness during adsorption and desorption of P224-28. The copolymer was injected at $t \approx 0$ ($C_b = 0.01$ wt %), and rinsing with pure water was initiated at $t \approx 4200$ s.

Figure 7 shows the evolution of both the adsorbed amount and the thickness of the adsorbed layer when polymer was injected at $t \approx 0$ ($C_b = 0.01$ wt %) and the buildup of the adsorbed layer from this moment was monitored as a function of time. The initial adsorption rate is fast at this rather high copolymer concentration. Steady-state conditions are, indeed, reached within a relatively short period of about 10 min. Rinsing with pure water is then initiated at $t \approx 4200$ s. The desorption is initially relatively fast during this step, but the rate slows down markedly as time goes by. We observe that the desorption proceeds proportionally to log *t* after the initial rapid desorption period. The same relation is observed during desorption from the h-silica surface. The most pronounced difference is that initial desorption is observed to be somewhat faster at silica compared to at h-silica. The total faction of polymers desorbed during the first 20 h is about 35% at silica

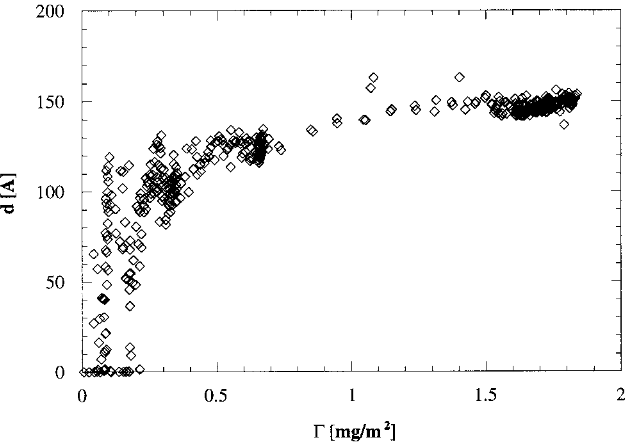

Figure 8. Mean thickness versus the surface excess for the copolymer P224-28. The data are collected from adsorption measurement where d and Γ were monitored as a function of time and C_b was increased from 5×10^{-5} to 5×10^{-3} wt % to cover the entire range of surface coverages.

compared to around 25% at h-silica. Again, since surface aggregates are present at the silica surface, dissociation kinetics of these entities may play an important role for the desorption kinetics. It has earlier been shown that the micellar lifetime of these block copolymers is long, i.e., of the order of hours.[36] It is hence likely that both the micellar dissociation kinetics and detachment rates of copolymers from the surface limit the subsurface concentration and, hence, the desorption kinetics. We note further that polydispersity complicates the interpretation of kinetic data in these copolymer systems. Finally, we see that no maximum is observed during rinsing, which would be expected if local equilibrium conditions were kept at the subsurface during the process. Note, however, that the stagnant layer volume is small and that a very small reservoir for back-diffusion exists during desorption. This is different from the situation during adsorption. The observation that no maximum is observed during desorption is opposite to that observed for binary nonionic surfactant systems, for which a clear maximum was seen. However, in this case, the concentration of the counter diffusing component in the stagnant layer was high enough to keep local equilibrium conditions at the subsurface.

Finally, the dependence during adsorption of the mean layer thickness, d, on the surface excess, Γ, during adsorption is shown in Figure 8. The data are collected during time-resolved ellipsometric measurements of d and Γ during which the bulk concentration has been changed in six consecutive steps from 5×10^{-5} to 5×10^{-3} wt %. The majority of the data shown are collected during slow adsorption and are, hence, likely to be representative also for the relation between Γ and d close to equilibrium. The most interesting feature seen in Figure 8 is the fact that the thickness increases very rapidly up to about 100 Å with increasing adsorption. The thickness is almost twice as large as that observed at the hydrophobic silica surface already at an adsorbed amount of about 0.3 mg m^{-2} (i.e., the value where the cooperative increase appears in the isotherm). Above ca. 0.3 mg m^{-2}, the surface excess increases slowly with the adsorbed amount. This further increase of the adsorbed amount is probably due to increased stretching of chains due to both interactions between chains in the aggregates and aggregate–aggregate interactions. It is interesting to note that the $d-\Gamma$ curves at silica and h-silica, respectively, exhibit completely different behaviors. In the h-silica case, two clear linear regions of increasing Γ with d were observed. In this case, the surface copolymer conformation at the surface developed according to a mixed pancake–loop–brush scheme.[11] At the silica surface, we appear to go directly from a mixed pancake to surface micelles.

Conclusions

The adsorption behavior of triblock copoly(ethylene oxide–tetrahydrofuran–ethylene oxide) at silica have been studied and analyzed. Our findings have been compared to those obtained for a similar triblock copolymer with a propylene oxide segment replacing the middle polytetrahydrofuran chain. Both types of copolymer systems appear to adsorb much like a PEO homopolymer of a comparable molecular weight at low bulk concentrations. However, we find that all triblock copolymers studied form surface micellar structures at silica at higher bulk concentrations. These surface aggregates appear to form at the interface when a critical surface aggregation concentration is exceeded. The formation of surface aggregates is cooperative and starts 2 orders of magnitude below the cmc for the tetrahydrofuran-based copolymers. The propylene oxide-based copolymers form aggregates much closer to the bulk cmc. A maximum in layer thickness and adsorbed amount is observed in the region of the bulk cmc. We infer that this reflects the polydispersity of the copolymer samples. The same behavior has previously been observed for binary C_nE_m surfactant systems at silica. Adsorption and desorption kinetics is complicated by the multitude of subprocesses occurring during these processes as well as due to the polydispersity. We note, however, that the cooperative features of the isotherm result in a large region where the adsorption rate is more or less constant.

Most observations at the silica surface contrast those at the hydrophobized silica surface. In particular, surface micelles are formed at silica whereas a monolayer structure is adopted on h-silica. The different behaviors at the two surfaces have a large influence on equilibrium values of the adsorbed amount, the adsorbed layer thickness and the adsorption kinetics.

Acknowledgment. We thank Professor Martin Hellsten (Akzo-Nobel Surface Chemistry AB) for providing us with the polymer samples used in this study. The Swedish National Board for Industrial and Technical Development (NUTEK) and the Swedish Research Council for Engineering Sciences (TFR) are acknowledged for financial support.

References and Notes

(1) Fleer, G. J.; Scheutjens, J. M. H. M. *Colloids Surf.* **1990**, *51*, 281–298.
(2) Halperin, A.; Tirell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31–72.
(3) Milner, S. T. *Science* **1991**, *21*, 905–914.
(4) Marques, C.; Joanny, J. F.; Leibler, L. *Macromolecules* **1988**, *21*, 1051–1059.
(5) Balazs, A. C.; Lewandowski, S. *Macromolecules* **1990**, *23*, 839–848.
(6) Balazs, A. C.; Gempe, M. *Macromolecules* **1991**, *24*, 168–176.
(7) Killmann, E.; Maier, H.; Baker, J. A. *Colloids Surf.* **1988**, *31*, 51–71.
(8) Malmsten, M.; Linse, P.; Cosgrove, T. *Macromolecules* **1992**, *25*, 2474–2481.
(9) Tiberg, F.; Malmsten, M.; Linse, P.; Lindman, B. *Langmuir* **1991**, *7*, 2723.

(10) Ou-Yang, D. H.; Zihao, G. *J. Phys.* **1991**, 1375−1385.
(11) Eskilsson, K.; Tiberg, F. *Macromolecules* **1997**, *30*, 6323.
(12) Cummins, P. G.; Staples, E.; Penfold, J. *J. Phys. Chem.* **1990**, *94*, 3740.
(13) Levitz, P.; Van Damme, H.; Keravis, D. *J. Phys. Chem.* **1984**, *88*, 2228.
(14) Levitz, P. *Langmuir* **1992**, *7*, 1595.
(15) McDermott, D. C.; Lu, J. R.; Lee, E. M.; Thomas, R. K.; Rennie, A. R. *Langmuir* **1992**, *8*, 1204.
(16) Tiberg, F.; Jönsson, B.; Lindman, B. *Langmuir* **1994**, *10*, 3714.
(17) Tiberg, F.; Jönsson, B.; Tang, J.; Lindman, B. *Langmuir* **1994**, *10*, 2294.
(18) Grant, L. M.; Tiberg, F.; Ducker, W. *J. Phys. Chem.*, in press.
(19) Ligouire, C. *Macromolecules* **1991**, *24*, 2968.
(20) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland: Amsterdam, 1989.
(21) Landgren, M.; Jönsson, B. *J. Phys. Chem.* **1993**, *97*, 1656.
(22) Tiberg, F.; Landgren, M. *Langmuir* **1993**, *9*, 927.
(23) Tiberg, F. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 531.
(24) Trens, P.; Denoyel, R. *Langmuir* **1993**, *9*, 519.
(25) Gellan, A.; Rochester, C. H. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 2235.
(26) Böhmer, M. R.; Koopal, L. K. *Langmuir* **1990**, *6*, 1478.
(27) Clunie, J. S.; Ingram, B. T. In *Adsorption from Solution at the Solid/Liquid Interface*; Parfitt, G. D., Rochester, C. H., Eds.; Academic Press: New York, 1983; pp 105−152.
(28) Tiberg, F. Ph.D., Lund University, 1994.
(29) Brinck, J.; Tiberg, F. *Langmuir* **1996**, *12*, 5042.
(30) Tiberg, F.; Brink, J. In *Surfactant Adsorption and Surface Solubilization*; Sharma, R., Ed.; American Chemical Society: Washington, DC, 1995; Vol. 615; pp 231−240.
(31) Linse, P.; Malmsten, M. *Macromolecules* **1992**, *25*, 5434.
(32) Alexandridis, P.; Athanassiou, V.; Fukuda, S.; Hatton, T. A. *Langmuir* **1994**, *10*, 2604−2612.
(33) de Gennes, P. G. *Adv. Colloid Interface Sci.* **1987**, *27*, 189.
(34) Ward, A. F. H.; Tordai, L. J. *J. Chem. Phys.* **1946**, *14*, 453.
(35) Brinck, J.; Jönsson, B.; Tiberg, F. *Langmuir* **1998**, *14*, 1058.
(36) Holmqvist, P.; Nilsson, S.; Tiberg, F. *Colloid Polym. Sci.* **1997**, *275*, 467.

MA9715637