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Adsorption of PEO-PPO-PEO Block Copolymers at Silica

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ABSTRACT: The adsorption at silica of block copolymers of the type PEO-PPO-PEO [PEO and PPO being poly(ethylene oxide) and poly(propylene oxide), respectively], as well as that of PEO, has been studied. For a number of polymers of a total molecular weight of about 15 000, it was found that the adsorbed amount is rather low (0.35–0.40 mg/m²), independent of the PO content in the range 0–30% PO. For a copolymer of a total molecular weight of 4000 and a PO content of 50% the adsorbed amount was about 0.20 mg/m². All polymers investigated formed thin adsorbed layers, with hydrodynamic thicknesses of about 2–5 nm. The pH dependence of the adsorbed amount and the hydrodynamic thickness is similar to that displayed by PEO homopolymers. Ellipsometry experiments on silica surfaces showed good agreement with the experiment on silica dispersions. Furthermore, ellipsometry experiments provided information on both adsorption and desorption kinetics. Both adsorption and desorption are fast processes in these systems, occurring over minutes. Finally, ellipsometry experiments showed that, just prior to solution micellization, an abrupt increase in the adsorbed amount occurred. At temperatures above the critical micellization temperature, the adsorbed amount remained independent of temperature in the temperature range studied. At all temperatures the hydrodynamic thickness was much smaller than the hydrodynamic diameter of the solution micelles. On hydrophobic surfaces, no abrupt increase in the adsorbed amount was observed. The experimental findings were interpreted with a modified mean-field theory.

Introduction

Both bulk and interfacial properties of block copolymers are receiving increasing attention.^{1–15} The reason for this is that it is possible to combine several "incompatible" properties in one molecule, which is of great fundamental interest and which opens vast technological applications of these systems. In particular, block copolymers containing one hydrophobic block and one (or two) hydrophilic block(s) have attracted much attention, both from polymer scientists and scientists working with surfactants. Much of this work has centered around the Pluronics, i.e., block copolymers having PPO as the hydrophobic block and PEO as the hydrophilic block(s) [PPO and PEO being poly(propylene oxide) and poly(ethylene oxide), respectively].

Due to their amphiphilic nature, block copolymers often associate, forming micelles,^{1–6} as well as liquid crystalline phases,^{1,2} in a similar way to low molecular weight surfactants.¹⁶ The self-association is a rather delicate process, which is strongly influenced by, e.g., the total molecular weight, the relative block sizes, and the concentration, as well as by temperature and the presence of cosolutes.

Although the solution properties of the block copolymer systems are of interest, their main utility lays in the fields of polymer adsorption and steric stabilization.^{7–15,17} In order to obtain a good steric stabilization of a dispersion, two fundamental requirements must be fulfilled. First, the adsorbed amount should be high and the adsorbed layer should be firmly attached to the surface. Second, the solvency conditions for the stabilizing polymer should be as good as possible.¹⁷ Naturally, these two requirements are difficult to fulfill simultaneously with homopolymers, since the latter may adsorb poorly under good solvency conditions. One way to overcome this is to chemically graft homopolymers to the surface.⁷ This may, however, be unacceptable in many practical applications. The other

possibility is to use block copolymers, where one block is sparingly soluble and strongly adsorbed, thus providing a good anchor and a reasonably high adsorbed amount, and one (or several) block(s) is(are) nonadsorbing, thus providing steric stabilization.

Although there have been several detailed studies of the adsorption of PEO-PPO-PEO block copolymers at hydrophobic surfaces,^{7–9,11–15} little is known about the behavior of these polymers at hydrophilic surfaces.^{10,15} In particular, one would like to investigate the effects of the total molecular weight and the composition of the copolymers on their adsorption properties. Furthermore, it is of interest to investigate the effects of self-association on the adsorption properties.

Experimental Section

Materials. PEO-PPO-PEO block copolymers were obtained from BASF Wayndotte. The solution properties of F127 will be communicated separately.^{18,19} PEO's of molecular weights of 20 000 and 600 were from Serva, Germany, whereas PPO's of molecular weights of 750 and 400 were obtained from Shell Chemicals, U.K., and Fluka, Switzerland, respectively. All polymers were used without further purification. Silica (Ludox HS40, with a stated average diameter of 12 nm and a specific surface area of 230 m²/g) was obtained from Du Pont, Wilmington, DE, and was dialyzed against Millipore water for 1 week before use. The concentration of the stock solution was determined gravimetrically. The pH was not adjusted, if not stated otherwise. In the cases of pH adjustment, HCl and NaOH were used. Tannic acid was obtained from BDH, England.

Surfaces. Silicon wafers (p-doped, Boron; resistivity 0.01–0.02 ohm cm) were obtained from Ohmetric Ltd., Finland. These wafers were further oxidized thermally with dry oxygen at 920 °C for 65 min followed by annealing and cooling in an argon flow to obtain a thickness of the oxidized layer in the range of 360–370 Å. The slides were then cleaned in a mixture of 25% NH₄OH (pro analysi, Merck), 30% H₂O₂ (pro analysi, Merck), and H₂O (1:1:5, by volume) at 80 °C for 5 min, followed by cleaning in a mixture of 32% HCl (pro analysi, Merck), 30% H₂O₂, and H₂O (1:1:5, by volume) at 80 °C for 5 min. The surfaces were then rinsed in water and ethanol and kept in ethanol until use. Immediately before the experiments, the slides were plasma cleaned in low-pressure residual air, using a radio-frequency glow

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discharge unit (Harrik PDC 3XG, Harrik Scientific Corp., Ossining, NY). After plasma treatment, the substrate was immediately transferred to the ellipsometer cuvette.

Hydrophobic slides were prepared by treating hydrophilic slides with a 0.1% v/v solution of $\text{Cl}_2(\text{CH}_3)_2\text{Si}$ (Merck, Germany) in trichloroethylene (pro analysi, Merck, Germany) for 90 min. They were then rinsed in trichloroethylene and absolute ethanol, whereafter they were kept in absolute ethanol until immediately prior to use. The surfaces obtained were hydrophobic, with a critical surface tension of about 27 mN/m.²⁰ Before use, they were rinsed in distilled water, placed in the ellipsometer cuvette, and allowed to stabilize for 5 h prior to experiment.

The ellipsometer used was a modified automated Rudolph thin film ellipsometer, Type 43603-200E, controlled by a personal computer, and with a xenon lamp, filtered to give 400 nm, as the light source. Throughout, in situ experiments were made.

Methods. The adsorption isotherms were determined by the following procedure: a mixture of 10 wt % silica, water, and a suitable amount of polymer was prepared. The mixture was then thoroughly equilibrated by end-to-end rotation for at least 24 h to obtain equilibrium adsorption. The dispersions were then centrifuged at 15 000 rpm for 30 min, whereafter the supernatant was carefully removed. The equilibrium polymer concentration was determined by precipitation with tannic acid, followed turbidometrically at 400 nm.²¹ The temperature used was 25 °C throughout.

The ellipsometry measurements involved two steps, viz., (i) determination of the complex refractive index of the substrate and (ii) addition of the polymer solution, followed by a standard evaluation of the adsorbed amount according to de Feijter,²² with $dn/dc = 0.150 \text{ cm}^3/\text{g}$,⁶ as a function of time, with a time resolution of a few seconds. Four-zone corrections were used throughout, in order to eliminate, e.g., effects of component imperfections.²³ The adsorption temperature was 25 °C, if not stated otherwise. Stirring was performed by a magnetic stirrer. Rinsing was achieved with a continuous flow of water through the cuvette. A constant bulk polymer concentration of 1000 ppm was used throughout.

The hydrodynamic thickness of the adsorbed layers was obtained with photon correlation spectroscopy (PCS). In these measurements, a Malvern 7027 correlator system (Malvern Instruments Ltd.) was used, together with a Coherent CR 2000K super graphite krypton-ion laser, except for the temperature experiment, where a 35-mW He-Ne laser (Spectra Physics, Houston, TX) was used. The PCS measurements were performed at a solids concentration of 0.10 wt % and 0.9 mM NaCl. No dependence of the diffusion coefficient on the solids concentration or on salinity was found at these concentrations. Moreover, no angular dependence was observed. The PCS measurements presented were all performed at a measuring angle of 90°. The hydrodynamic radii were calculated according to the Stokes-Einstein equation, and the hydrodynamic thickness of the adsorbed layer was obtained as the difference between the hydrodynamic radii in the presence and absence of adsorbed polymer. The temperature used was 25 °C, if not stated otherwise.

Model Calculations

In order to gain some further information on the adsorption of PEO-PPO-PEO block copolymers at silica, some model calculations were performed. The model used is a modified mean-field theory, which extends the theory of Evers et al.^{24,25} to the case where the adsorbed polymers may have internal degrees of freedom.^{26,27} The use of internal states results in effective segment-segment interaction parameters which are temperature and concentration dependent. This model, which was originally devised for describing the existence of a lower consolute temperature occurring in some aqueous polymer solutions and for predicting the conformational equilibrium of poly(ethylene oxide) in homogenous solution,²⁸ has now been extended to heterogeneous systems and has previously been used successfully for describing the adsorption properties of PEO-PPO-PEO block copolymers on hy-

Table I
Internal State parameters U_{AB} (Energy) and g_{AB} (Statistical Weight), Surface Interaction Parameters $\chi_{B,\text{surface}}$, and State-State Flory-Huggins Interaction Parameters $\chi_{BB'}$ (Energies in kJ mol^{-1})

species	state	state no.	U_{AB}	g_{AB}	$kT\chi_{B,\text{surface}}^a$
water		1	0	1	3.3
EO	polar	2	0 ^b	1 ^b	0
	nonpolar	3	5.086 ^b	8 ^b	3.2
PO	polar	4	0 ^c	1 ^c	2.5
	nonpolar	5	11.5 ^c	60 ^c	5.7

$kT\chi_{BB'}$				
state no.	2	3	4	5
1	0.6508 ^b	5.568 ^b	1.7 ^c	8.5 ^c
2		1.266 ^b	0 ^d	1.3 ^e
3			1.3 ^e	0 ^d
4				1.4 ^c

^a The adsorption parameter χ_s is related to the interaction parameters by $\chi_s = -\lambda_{10}(\chi_{\text{segment,surface}} - \chi_{\text{solvent,surface}})$ where $\lambda_{10} = 1/4$ (hexagonal lattice). See also ref 27. ^b From the fit to the experimental PEO-water phase diagram.^{27,28} ^c From the fit to the experimental PPO-water phase diagram.²⁷ ^d Taken to be equal. ^e Taken to be equal.

drophobized silica.⁸ From quantum mechanical calculations,²⁹ the conformations of the -OCCO- segments are divided into two classes of states, one being polar and having the lowest energy, but a low statistical weight, and one being less polar (or nonpolar) and having the higher energy, but a higher statistical weight. This subdivision is further supported by, e.g., ¹³C chemical shift measurements.³⁰ At low temperatures, the former state dominates, thus providing a more favorable polymer-solvent interaction, whereas at higher temperatures, the latter state becomes progressively more important, which results in a more unfavorable polymer-solvent interaction.

On the basis of the molecular weight and the fraction of ethylene oxide, F127, F98, and P75 are modeled as (EO)₉₉(PO)₆₅(EO)₉₉, (EO)₁₂₅(PO)₄₇(EO)₁₂₅, and (EO)₂₄(PO)₃₅(EO)₂₄, respectively. Since aqueous solutions of both PEO and PPO displayed a lower consolute point,³¹ both EO and PO segments are modeled with two internal states, one polar and one nonpolar. The interaction parameters are given in Table I and are the same as those used in a previous study of the adsorption of similar block copolymers at hydrophobic surfaces,⁸ except that the surface interaction parameters were changed in order to be representative of a hydrophilic surface. Moreover, in contrast to the previous model calculations, it was found that separate EO-surface and PO-surface interaction parameters were essential to describe the experimental results (vide infra). A difference between EO-surface and PO-surface interaction parameters of 2.5 kJ/mol was found to give a fair representation of the experimental results. This value compares reasonably well with the free energy change of transferring a CH₂ group of normal alkanes from a hydrocarbon to an aqueous medium (3.7 kJ/mol) and the corresponding quantity from the variation of the critical micellization concentration (cmc) for nonionic surfactants (3.0 kJ/mol).¹⁶

The calculation involves a self-consistent determination of the volume fractions of all species (EO and PO segments and water molecules) and state distributions of the EO and PO segments in each layer of the heterogeneous system. Further aspects of the calculations are given in ref 27.

Throughout, the theoretically determined adsorbed amounts and hydrodynamic thicknesses are presented in an equivalent number of monolayers and layer numbers, respectively, whereas the experimentally determined ad-

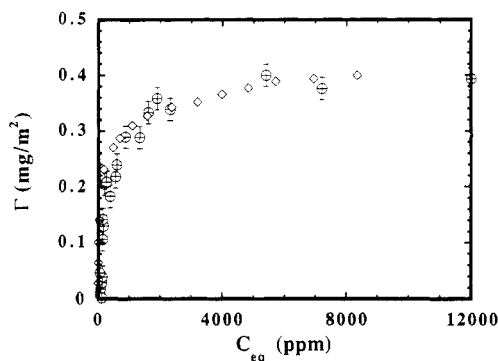


Figure 1. Adsorption isotherms for PEO ($M_w = 20\,000$, open diamonds)³⁵ and F127 (crossed circles) at silica.

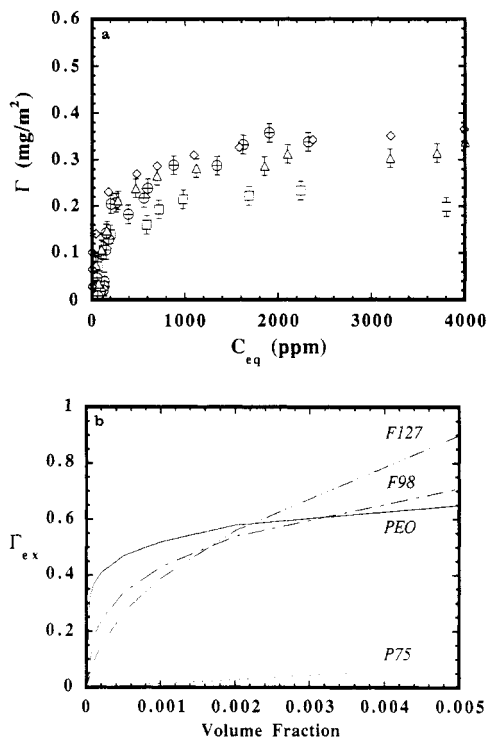


Figure 2. (a) Adsorption isotherms obtained at silica for PEO ($M_w = 20\,000$, open diamonds),³⁵ F127 (crossed circles), F98 (open triangles), and P75 (open squares). (b) Adsorption isotherms from model calculations.

sorbed amounts and hydrodynamic thicknesses are given in mg/m^2 and nm, respectively. It is interesting to note, however, that taking a reasonable lattice size (0.4 nm) results in a fair agreement between model calculations and experimental findings.

Results

As can be seen in Figure 1, the adsorption of F127 at silica closely resembles that of PEO of a comparable molecular weight. In both cases, plateau adsorption is reached at ~ 1000 – 2000 ppm. Moreover, the saturation value of the adsorbed amount is low in both cases (about 0.4 mg/m^2). Different PEO–PPO–PEO block copolymers behave rather similar at silica, as shown in Figures 2–4. Hence, both the adsorbed amount and the hydrodynamic thickness were roughly independent of the relative composition of the copolymer at a fixed total polymer molecular weight of about $15\,000$. For P75, having a total molecular weight of 4000 and a PO content of about 50% , however, the adsorbed amount was significantly lower (about 0.2 mg/m^2), although the hydrodynamic thickness was the same within experimental uncertainty. Hence, the adsorbed

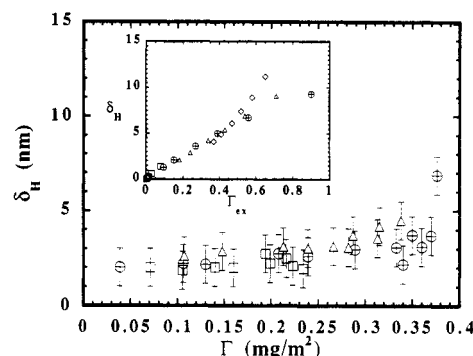


Figure 3. Hydrodynamic thickness at silica of PEO (open diamonds), F127 (crossed circles), F98 (open triangles), and P75 (open squares) versus the adsorbed amount. The inset shows data obtained from model calculations.

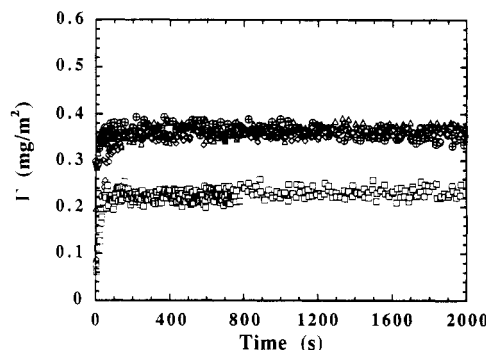


Figure 4. Ellipsometrically determined adsorbed amount of F127 (crossed circles), F98 (open triangles), PEO ($M_w = 20\,000$, open diamonds), and P75 (open squares) at silica versus time. (The data from F127, F98, and PEO coalesce into the upper group of data points.)

layer is thin in all cases (only a few nanometers), and roughly independent of the adsorbed amount. Only at very high equilibrium concentrations for F127 is there a slight increase in the adsorbed layer thickness (Figure 3).

Ellipsometry measurements on macroscopic silica surfaces showed good agreement with those on colloidal silica. Thus, adsorbed amounts of $0.40 \pm 0.05\text{ mg/m}^2$ were obtained for the polymers of a total molecular weight of about $15\,000$, independent of the PO content in the range of 0 – 30% PO (Figure 4). As in the case of colloidal silica, P75 showed a significantly lower adsorbed amount ($0.23 \pm 0.05\text{ mg/m}^2$). Furthermore, the thicknesses obtained from ellipsometry, using four-zone averaging and treating the system with a four-film model²³ (about 2 – 6 nm ; results not shown), agree reasonably well with those obtained with PCS. The time-resolved ellipsometry measurements further showed that both adsorption and desorption kinetics are fast, on the order of a few minutes (Figures 4 and 5). Furthermore, dilution of the polymer solution results in a decrease in the adsorbed amount, although the desorption is far from complete. On reinjecting the original polymer concentration, the adsorbed amount increases to its value prior to rinsing.

At higher pH, both the adsorbed amount and the hydrodynamic thickness decrease until, at $\text{pH} \approx 10.6$ – 10.8 , complete desorption occurs (Figure 6). Again, good agreement was found between solution depletion and ellipsometry measurements. Thus, adding NaOH to a pH of 11 results in an instant desorption of the polymer, as shown in Figure 7.

Although the silica dispersion in the presence of F127 was stable at room temperature and at elevated temperatures following plateau adsorption, this was not the case

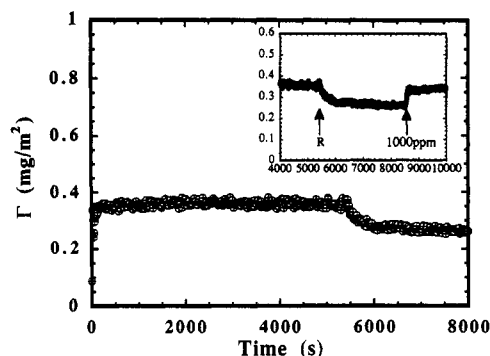


Figure 5. Ellipsometrically determined adsorbed amount of F127 (at $C_{eq} = 1000$ ppm) at silica versus time. R indicates rinsing with water. The inset shows the effect of reinjection of 1000 ppm of F127 after rinsing.

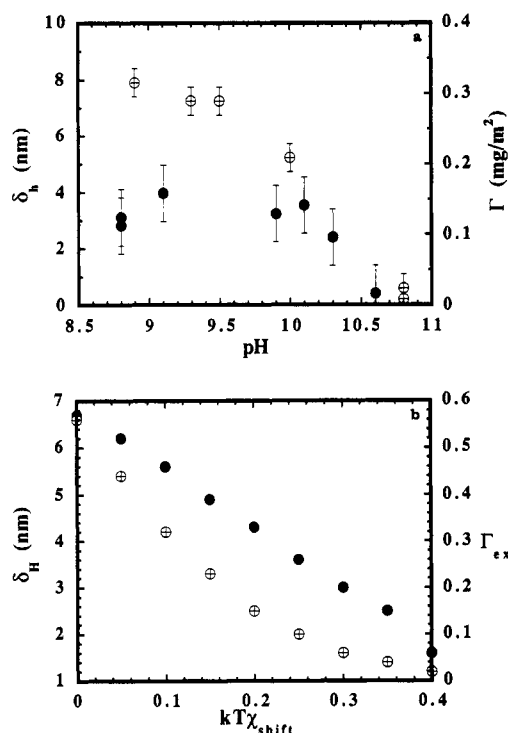


Figure 6. (a) Adsorbed amount (crossed circles) and hydrodynamic thickness (filled circles) of F127 at silica versus pH. (b) Adsorbed amount (crossed circles) and hydrodynamic thickness (filled circles) of F127 obtained from model calculations. The species-surface interaction parameters were modified in order to model an increasingly hydrophilic surface according to $\chi_{B,surface}^{(modified)} = \chi_{B,surface} \pm \chi_{shift}$, $\chi_{B,surface}$ being the parameters given in Table I. The negative sign is applied for water, whereas the positive sign is applied for EO and PO segments, irrespective of state.

at partially saturated surfaces. Thus, adsorption measurements at elevated temperatures were precluded due to flocculation of the silica particles. (The origin of this flocculation is unknown at present, but a similar effect has previously been observed also for nonionic surfactants.^{32,33} Further studies on this seem important but are out of the scope of the present investigation). Hence, only measurements of the hydrodynamic thickness at full coverage could be made as a function of temperature, and the corresponding adsorption measurements could not be carried out in a meaningful way. Instead, therefore, we used ellipsometry for the studies of the temperature dependence of the adsorbed amount. As can be seen in Figures 8–11, the adsorbed amount increases dramatically just prior to the critical micellization temperature (cmt), whereafter it levels off. (The data points of Figures 8, 10,

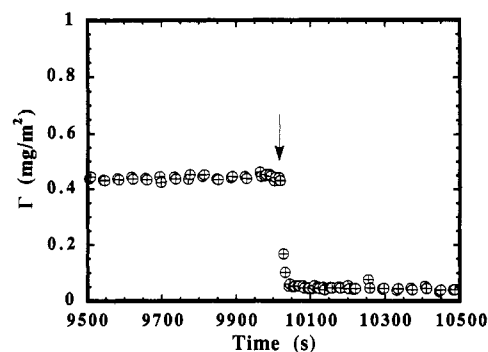


Figure 7. Ellipsometrically determined adsorbed amount of F127 at silica at 25 °C. The arrow indicates injection of NaOH to a final pH of 11.

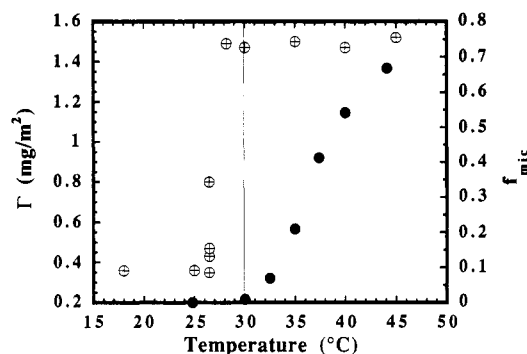


Figure 8. Ellipsometrically determined adsorbed amount of F127 at silica (cross circles) and fraction of micellar polymer molecules (filled circles)¹⁸ versus temperature. The solid line represents the cmt.

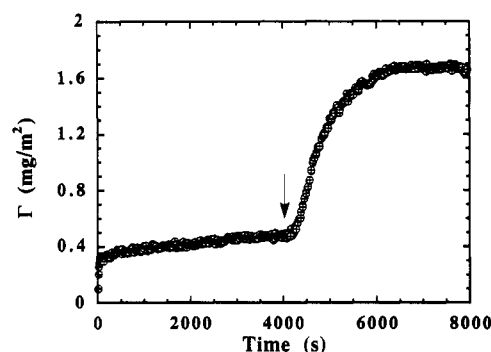


Figure 9. Ellipsometrically determined amount of F127 adsorbed at silica. The arrow indicates raising the temperature from 26.5 to 28.2 °C.

and 11 were obtained by separate experiments at each temperature. However, the same results were obtained from adsorption at low temperature, with a subsequent increase in temperature.) At temperatures higher than cmt, the adsorbed amount remains constant. The ellipsometry experiments further showed that the extent of desorption on rinsing is larger at higher temperatures and that the desorption is slower. Hence, at 45 °C, rinsing results in a decrease in the adsorbed amount from about 1.5 to 0.5–0.6 mg/m² (results not shown), whereas the corresponding values at 25 °C are 0.40 and 0.25 mg/m², respectively. Note that the effects of approaching the cloud point (CP) per se are very small, since CP is very high (CP \approx 110 °C¹⁸). This can clearly be seen from the invariance with temperature of the adsorbed amount of PEO (Figure 10), despite the CP's of F127 and PEO being essentially the same.¹⁸ Note further that no abrupt increase of the adsorbed amount just prior to the cmt was observed for hydrophobized silica surfaces (Figure 11), although the adsorbed amount at hydrophobized silica

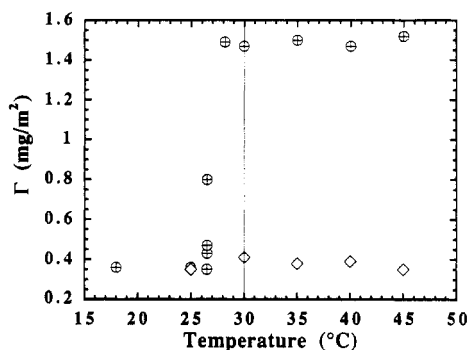


Figure 10. Ellipsometrically determined adsorbed amount of F127 (crossed circles) and PEO ($M_w = 20\,000$, open diamonds) at silica versus temperature. The solid line represents the cmc.¹⁸

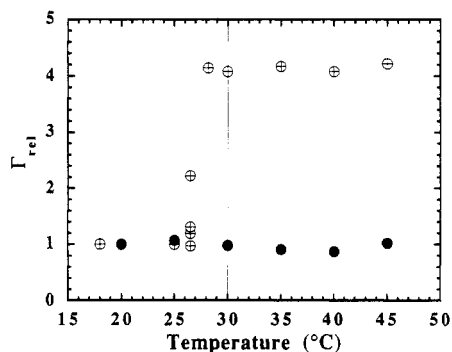


Figure 11. Ellipsometrically determined temperature-dependent relative adsorbed amount ($\Gamma_{rel,T} = \Gamma_T/\Gamma_{20^\circ\text{C}}$) of F127 at silica (crossed circles) and hydrophobized silica (filled circles). The solid line represents the cmc.¹⁸

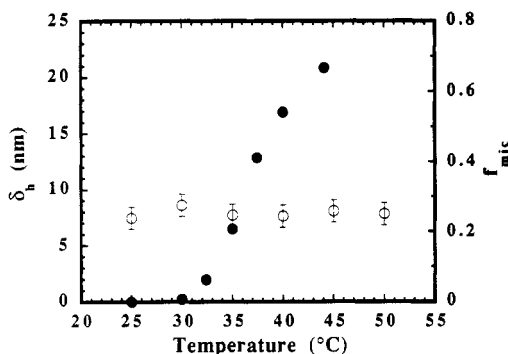


Figure 12. Hydrodynamic thickness at silica of F127 ($C_{eq} = 6000$ ppm) versus temperature (open circles). Shown also is the fraction of micellar polymer molecules (filled circles).¹⁸

(2.1 ± 0.2 mg/m²) was significantly larger than that at untreated silica surfaces at all temperatures.

Despite the dramatic increase in the adsorbed amount, the hydrodynamic thickness is essentially unaffected by the increase in temperature (Figure 12). Hence, even at high temperatures, the adsorbed layer thickness is significantly smaller (about 8 nm at $C_{eq} = 6000$ ppm) than twice the hydrodynamic radius of the micelles formed in solution (about 22 nm^{3,4,18}).

Discussion

Particle Size. Before discussing the adsorption properties of the polymers under investigation, it is important to discuss the particles by themselves. According to the manufacturer, these particles have a surface area of 230 m²/g and an average particle diameter of 12 nm. From electron microscopy we obtained a diameter of about 15 nm, i.e., a slightly larger value (results not shown). From SANS we obtained an average particle size of 11 nm (results

not shown). Hence, the agreement between different methods is reasonable. Furthermore, since the adsorbed amounts found in this study agree reasonably well with previous ones, using both Ludox³⁵ and other silica dispersions,^{10,36,37} and since the agreement between experiments using silica particles and macroscopic silica surfaces is good, we use the surface area stated.

However, there is an ambiguity as to the interpretation of the hydrodynamic thicknesses. As described in the Experimental Section these are obtained as the difference of the hydrodynamic radii in the presence and absence of adsorbed polymer. However, the particle diameter, in the absence of adsorbed polymer, was found by PCS to be 39 nm, also at particle and electrolyte concentrations where interactions are insignificant. Hence, it seems that these particles are very big hydrodynamically, which may be due to their slightly irregular shape (as inferred from electron microscopy; results not shown). We do not, however, believe that there are any particle aggregates present, based on both electron microscopy and the absence of angular dependence in the diffusion coefficient. Note that similar effects have been observed previously, although to a smaller extent.³⁴ In any case, this uncertainty of the size of the particles makes the interpretation of the hydrodynamic thicknesses difficult. However, considering that good agreement was found between our findings and those by Killmann et al.,¹⁰ this, surprisingly enough, seems to be of minor importance for the present investigation as well.

State of Adsorption. It is previously well-known that PEO,^{7,10,35–39} as well as surfactants and block copolymers containing EO groups,^{40–45} adsorb onto silica. It has been shown that silanol groups are essential for the adsorption to occur at all, and it has therefore been inferred that hydrogen bonding between the ether oxygens in PEO and the silanol groups at the silica surface is responsible for the adsorption.³⁷

If the adsorption of PEO is comparably easy to study, the adsorption of PPO is more difficult, since PPO is insoluble in water at intermediate and high molecular weights.³¹ Only at very low molecular weights is PPO soluble in water in experimentally convenient concentrations. Hence, PPO fractions of molecular weights of 750 and 400 were used to study the adsorption of PPO. As a first attempt, we tried the solution depletion method, which showed, within experimental uncertainty, the same solution polymer concentration before and after adsorption (results not shown). This could indicate that PPO does not adsorb at silica. However, it is equally likely that adsorbed polymer molecules desorb on centrifugation, which is especially likely, considering the very small silica particles used. However, also ellipsometry measurements showed no detectable adsorption of PPO, which means that the tendency for PPO to adsorb at silica is small ($\Gamma \leq 0.05$ mg/m²) or even nonexistent. PEO with a similar molecular weight, on the other hand, showed a detectable adsorption at silica ($\Gamma \approx 0.10$ mg/m²; results not shown). Hence, we conclude that PEO has the stronger tendency to adsorb at silica surfaces. This is not an unexpected result. Although the solubility of PPO is lower than that of PEO, the charge of the silica surfaces gives rise to image charge effects between the adsorbing polymer and the surface, which counteracts adsorption. (Only to some extent is the surface charge reduced on adsorption of, e.g., PEO.⁴⁶) These effects are expected to be more pronounced in the case of PPO.

Having discussed the adsorption of both PEO and PPO, we are now ready to proceed to block copolymers of PEO

and PPO. As can be seen in Figures 1, 2, and 4, the adsorption of a PEO-PPO-PEO block copolymer ($M_{w, \text{total}} \approx 15\,000$) containing 20 and 30% PO is essentially identical to that of a PEO homopolymer of a comparable molecular weight. In all cases, the adsorption isotherm is of a rather low-affinity type, with a plateau value of about 0.4 mg/m^2 .

At all total molecular weights and at all polymer compositions used in the present investigation, the extension of the adsorbed layer is quite small. Hence, the hydrodynamic adsorbed layer thickness is only a few nanometers and only weakly dependent on the adsorbed amount. The most important reason for the low values of the hydrodynamic thickness is undoubtedly the low adsorbed amounts. Thus, the surface is unsaturated with respect to the polymer, which reduces the tendency for especially tail formation. This gives rise to a low hydrodynamic thickness, since the tails to a large extent determine the hydrodynamic thickness.⁴⁷

The results presented above agree very well with those found by Killmann et al. in a previous study.¹⁰ Hence, these authors found that the adsorbed layer thickness was only about 2 nm, independent of the total molecular weight within experimental uncertainty, although only a limited molecular weight range and just one equilibrium concentration was investigated. Furthermore, the adsorbed amount obtained for Pluronic P105 in the previous investigation (about 0.4 mg/m^2) agrees reasonably well with those obtained in the present investigation, considering the uncertainty in available surface area.

In order to obtain some further understanding of these systems, we performed some model calculations, the principles of which have been outlined previously. As can be seen in Figure 2b and Figure 3 (inset), the model calculations agree reasonably well with the experimental results. Furthermore, the importance of the low surface coverage for the hydrodynamic thickness is illustrated by the inset of Figure 3, showing that the hydrodynamic thickness (calculated from the segment density distribution according to ref 47) depends on the adsorbed amount only and not on polymer composition and molecular weight. In fact, using a lattice size of 0.4 nm, a quantitative agreement of the adsorbed amount is obtained (one layer corresponds to 0.5 mg/m^2). The only exception from this is the adsorbed amount of P75, where the model predicts a much lower value than that observed experimentally. By a different set of interaction parameters (i.e., equal EO-surface and PO-surface interaction parameters), this difference is eliminated. The cost of this, however, is a larger spread of the adsorbed amounts of PEO, F98, and F127. Considering the absence of unambiguous literature data on the surface interactions, we present the results obtained using a reasonable set of parameters, rather than pursuing the search for an optimal set.

Looking in more detail (Figure 13) into the state of adsorption of these polymers at silica, we see that the segment density profiles of PEO, F98, and F127 are essentially similar, whereas the overall segment density at a given distance from the surface is significantly lower for P75, a consequence of the lower adsorbed amount in the latter case. As was found previously with hydrophobic surfaces,⁸ the fraction of polar states of both PO and EO decreases on approaching the surface (results not shown), which is due to the increasing polymer concentration.

An interesting question still to be answered is the distribution of different segments within the adsorbed layer. As can be seen in Figure 14, using the interaction parameters of Table I, the EO segments are preferentially

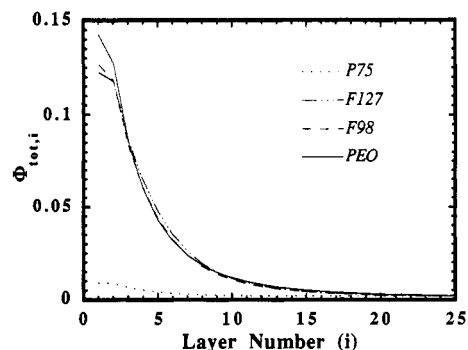


Figure 13. Total volume fraction ($\phi_{\text{tot},i}$) of PEO, F98, F127, and P75 versus layer number (i). Parameters used are shown in Table I. The bulk volume fraction was 2×10^{-3} .

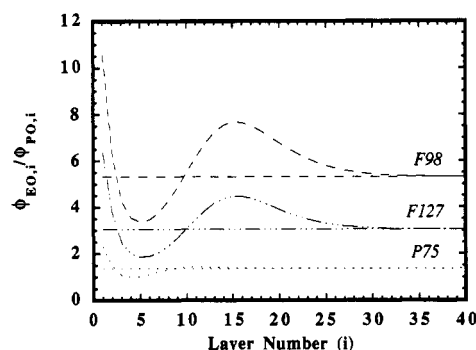


Figure 14. Calculated EO-PO volume fraction ratio ($\phi_{\text{EO},i}/\phi_{\text{PO},i}$) for F127, F98, and P75 versus layer number (i). The lines indicate the corresponding ratios in the bulk solution. Parameters used are shown in Table I. The bulk volume fraction was 2×10^{-3} .

adsorbed and located in the proximity of the surface. Furthermore, since EO is more soluble than PO, the EO segments are also preferentially located in the outer part of the adsorbed layer. The PO segments, on the other hand, interacting poorly as they do with both solvent and surface, are preferentially located in the middle part of the adsorbed layer.

Effects of pH. It is rather well-known that the amount of an adsorbed polymer can be reduced by the addition of a low molecular weight substance (displacer),³⁵ having a higher affinity for the surface than that of the polymer. In the case of silica, this is most readily accomplished by increasing the pH.^{35,37,41} Thus, at higher pH, the silica surface becomes increasingly (negatively) charged,⁴⁶ thus increasing the affinity of cations for the surface, as well as decreasing the affinity of the polymer for the surface. As the adsorption/desorption process is rather subtle, the desorption occurs at a rather well-defined pH, the actual value of which depends on the relative "strength" of adsorption of the polymer and the displacer. For PEO the critical desorption pH is about 10.4–10.8.^{35,41} As can be seen in Figure 6a, essentially the same value was obtained with F127 (containing 30% PPO), which was further supported by PCS measurements. These findings could in principle indicate that PO and EO segments adsorb equally strongly at silica surfaces and that they are equally sensitive to the silica surface charge. However, considering the extra methyl group of PO, probably reducing the polarity of the latter, this seems less likely. Instead, it seems plausible that these results indicate that EO segments are primarily responsible for the anchoring of the block copolymers at silica surfaces, which is indicated by theoretical calculations as well (Figure 14).

Although the effects of electrostatics are difficult to treat within the model used here, due to the long range of these

interactions, a qualitative agreement with experimental results can still be reached. This is achieved by, instead of explicitly taking electrostatics into account, modeling the increasing surface charge by making the surface more hydrophilic. As can be seen in Figure 6b, both the adsorbed amount and the hydrodynamic thickness of F127 decrease monotonically, in agreement with experimental observations, and at a sufficiently hydrophilic surface, a depletion zone is formed ($\Gamma_{\text{ex}} < 0$).

Effects of Temperature. An interesting property of the block copolymers is their ability to form aggregates of different shapes and sizes. In analogy with low molecular weight EO-containing surfactants,¹⁶ the tendency to associate increases (i.e., the cmc decreases) with increasing temperature.^{3-5,18} This, in turn, is mainly related to the decreasing solubility of the PPO block at higher temperature (PPO has a lower consolute temperature of about 50 °C at $M_w = 400$).³¹ Naturally, it is of major interest to investigate the impact of such solution properties on the adsorption of these polymers (note that for uncharged low molecular weight surfactants, the adsorbed amount often remains essentially constant at equilibrium concentrations above the cmc⁴⁰⁻⁴⁵).

From the temperature dependence of the adsorbed amount and, especially, from the "cooperativity" found in the increase of the adsorbed amount, it seems not too far-fetched to infer that a surface association takes place just prior to solution micellization, giving rise to the strong increase in the adsorbed amount. However, even at temperatures higher than cmt, the adsorbed layer thickness (≤ 8 nm, obtained by adsorbing under plateau conditions at low temperature for 24 h, followed by a subsequent increase in temperature) is considerably less than twice the hydrodynamic radius of the solution micelles (22 nm), clearly showing the absence of intact micelles at the surface (the possibility of very sparse adsorption of intact micelles is discounted, since this is inconsistent with the adsorbed amount).

An analogous kind of associative adsorption, often involving large interfacial aggregates, has previously been suggested for nonionic surfactants, e.g., of the type C_nE_m and $C_n\phi E_m$, based on the strong cooperativity, correlated to the solution cmc, observed in the adsorption displayed by these surfactants.⁴⁰⁻⁴⁵ Indeed, it has been shown directly by fluorescence quenching that just prior to cmc (infinite) interfacial aggregates are formed in these systems.^{44,45} Furthermore, this behavior has been successfully treated theoretically.^{24,48,49}

It is interesting to note that, although there is a pre-micellar associative adsorption at untreated silica surfaces, this is not the case with hydrophobic surfaces (Figure 11). Clearly, this difference has to do with the segment density distribution and the location of the PO groups in the adsorbed layer. In the case of hydrophobic surfaces, PO segments are clearly enriched in the proximity of the surface, whereas the EO segments are located in the outer parts of the adsorbed layer, as has been demonstrated previously.⁸ Furthermore, the PEO tails are rather extended, and rather thick adsorbed layers are formed.¹⁰ In the case of hydrophilic surfaces, on the other hand, thin adsorbed layers are formed. Furthermore, the tendency for PO groups to be located close to the surface decreases. In fact, with reasonable parameters, the EO groups are preferentially adsorbed, whereas the PO groups are preferentially located in the middle region of the adsorbed layer (vide supra). It is rather clear that these differences of the segment density distributions will give rise to different behavior as regards interfacial aggregation.

An example of similar effects is the adsorption of nonionic, EO-containing surfactants. At hydrophobic surfaces, these surfactants adsorb with their hydrophobic tail toward the surface, resulting in monolayer adsorption and one-step adsorption isotherms. On hydrophilic surfaces, on the other hand, these surfactants adsorb with their hydrophilic tail toward the surface, resulting in double-layer adsorption and, at least occasionally, in two-step adsorption isotherms. Although the adsorption of PEO-PPO-PEO block copolymers cannot be expected to be identical to that of these surfactants, analogous effects are still expected to occur, although to different degrees.

Similar conclusions have further been reached in several previous theoretical investigations. Hence, van Lent et al.²⁴ found that for A_xB_y block copolymers and a B solvent, preferential adsorption of the A segments resulted in a "monolayer", whereas, in the case of preferentially adsorbing B segments, the adsorbed layer was found to be a "double layer", much in accordance with our results. Furthermore, Böhmer and Koopal⁴⁸ studied the adsorption of nonionic flexible chain surfactants and came to the conclusion that, in the case of hydrophilic surfaces, a bilayer was formed provided that the surfactant is balanced, whereas, in the case of hydrophobic surfaces, only monolayer formation was predicted. Furthermore, at hydrophilic surfaces, association effects are of great importance and saturation adsorption is obtained close to the cmc. On hydrophobic surfaces, on the other hand, steric hindrance of the hydrophilic blocks is the limiting factor and the correlation with the cmc is lost. Finally, Levitz⁴⁹ modeled the aggregative adsorption of nonionic surfactants onto hydrophilic surfaces from water and related this to the bulk micellization. The author found that, in accordance with experimental observations, the rising part of the isotherm is always located below, but close to, the cmc and that plateau adsorption is due to the constant chemical potential slightly above the cmc. He also found that the aggregation number of the interfacial aggregates is a strongly increasing function close to the cmc, which is in good agreement with experimental observations.^{44,45}

Although the micellization of the PEO-PPO-PEO block copolymers is well-known, actual values of cmc's appear to be less well-defined than those of, e.g., surfactants of the type C_mE_n , and reported values often differ by several orders of magnitude, depending on the method of investigation. However, it is also well-known that the degree of association is a strongly increasing function of the temperature,^{3-5,18} and here reasonably good agreement is obtained between different methods. Hence, instead of looking at the concentration dependence at a fixed temperature, we decided to investigate the temperature dependence at a fixed total polymer concentration. However, the two approaches are very similar, since in one case we approach the cmc by increasing the equilibrium concentration, whereas in the other, a fixed equilibrium concentration is approached by increasing the temperature, i.e., decreasing the cmc. Hence, similar effects are expected in the two cases, and the reasoning of the previous section is transferable to the present case.

Previously, van de Steeg and Gölander investigated the adsorption of, inter alia, Pluronic F127 at hydrophobicity gradient surfaces.¹⁵ Although some qualitative trends agree between our studies, some differences remain. For example, the adsorbed amount in the hydrophilic end of the surface (1.23 ± 0.15 mg/m² at 23 °C, using $dn/dc = 0.150$ cm³/g) is substantially higher than that obtained in the present investigation (0.40 ± 0.05 mg/m² at 20 and 25 °C). Also in the case of hydrophobic surfaces, the ad-

sorbed amounts obtained by van de Steeg and Gölander $[(3.0-3.3) \pm 0.4 \text{ mg/m}^2]$, using $dn/dc = 0.150 \text{ cm}^3/\text{g}$ are significantly higher than those found in the present investigation $(2.1 \pm 0.2 \text{ mg/m}^2)$. These differences are most likely due to differences in surface preparation procedures in the two studies. Hence, the procedure of van de Steeg and Gölander resulted in surfaces more hydrophobic ($\theta_A = 110^\circ$) than those prepared by us ($\theta_A = 90^\circ$),²⁰ which result in a higher adsorbed amount.¹⁵ Upon comparison of the adsorbed amounts obtained at a comparable surface hydrophobicity, a good agreement is obtained. In the case of hydrophilic surfaces, no plasma treatment was used in the previous investigation, which usually results in higher adsorbed amounts. Interestingly, the adsorbed amounts obtained by van de Steeg and Gölander on hydrophilic surfaces agree well with those obtained by us at temperatures above cmt, which may indicate that the cmt in the previous investigation was some 5 °C lower than that in the present investigation. Batch differences of this kind have previously been observed for these rather poorly characterized polymer systems.^{3-5,18}

Summary

Block copolymers of the PEO-PPO-PEO type adsorb at silica in much the same way as a PEO homopolymer of a comparable molecular weight, independent of the PO content in the range 0-30% PO. Furthermore, the pH dependence is similar to that displayed by PEO. Good agreement was found between the ellipsometry experiments and the experiments on colloidal silica particles. Furthermore, a qualitative agreement was found between experimental findings and model calculations. In particular, the model calculations showed that the PO segments are preferentially located in the middle region of the adsorbed layer. Finally, the effect of solution micellization was found to markedly affect the adsorption at hydrophilic surfaces, whereas that at hydrophobic surfaces is independent of solution micellization.

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