Structure of Poly(ethylene oxide) Surfactant Polymers at Air−Water and Solid−Water Interfaces

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ABSTRACT: The surface active properties of novel poly(ethylene oxide) (PEO) containing surfactant polymers were investigated at the air−water and graphite−water interfaces. The surfactant polymers are comblike polymers consisting of a poly(vinylamine) backbone with 2 kDa PEO and hexanal side chains. The polymers were prepared with various grafting ratios of the two side chains. Surface pressure isotherms were obtained for spread monolayers for the range of polymer compositions. Two transitions are observed at 5 and 11 mN/m, which are interpreted as stages of desorption for the PEO side chains from the interface into the aqueous subphase. It is demonstrated that it is possible to scale the isotherms quantitatively to provide an accurate determination of the side chain composition. We characterized the adsorption process of two of the surfactant polymers at the water−graphite interface, using tapping mode atomic force microscopy (AFM). With high hexanal:PEO content (e.g., 8:1), the surfactant polymer rapidly forms a compact and complete monolayer 1.2 nm thick. At lower hexanal:PEO content (e.g., 4:1), a disordered layer is formed. After several hours, this layer rearranges into small scattered domains with banded structures. The structure of these layers is interpreted using a model of surface adsorption and the surface pressure isotherms.

Introduction

Stable surface modifications are important in a broad range of applications in biotechnology and materials sciences. This can include passifying surfaces, making them less reactive, or creating surfaces that interact with the environment specifically or nonspecifically. In the area of interface modification and surface assembly, considerable effort has been devoted to studying poly(ethylene oxide) (PEO) as a surface modifying agent, particularly for biomedical applications.[1,2] The attachment of PEO to surfaces has been acheived by utilizing chemical grafting,[3] self-assembled monolayers,[4] and surface adsorption of PEO diblock copolymers.[5]

PEO is an unusual molecule in that it is highly water-soluble yet exhibits surface active properties. In aqueous solution, PEO behaves like a highly dynamic random coil, yet it can readily pack and form a crystallized solid under conditions of high concentration, elevated temperature, or high pressure. The ethylene component is sufficiently hydrophobic to facilitate formation of an absorbed PEO surface layer at an air−water interface and to significantly reduce the surface tension of water.[6] PEO also has been studied extensively in the form of diblock surfactants (e.g., PEO−lipid constructs)[7] and linear block copolymers.[8,9] The interfacial properties of PEO, and PEO when tethered to a more hydrophobic component, have been the subject of numerous studies in which the Langmuir−Blodgett (LB) film balance technique has used to gain insight into the structure−property relations.[6−9]

Recently, novel comblike surfactant polymers have been synthesized as a simple means to quickly modify hydrophobic surfaces.[6,10−12] The molecular structure of the surfactant polymers consists of a poly(vinylamine) backbone with *both* hydrophilic and hydrophobic side chains. The synthetic method allows both the composition and ratio of side chains to be varied to generate any number of surfactant polymers with tailored properties. Functionally, the multiple hydrophobic side chains act to physically bind the polymers to hydrophobic surfaces, while the hydrophilic side chains remain solvated at the interface, generating the desired surface properties. Surface modification is accomplished with a simple one-step dip coating and promises to be an effective means of modifying surfaces quickly for numerous potential applications.

In previous work, oligosaccharide surfactants polymer were synthesized as a means to engineer protein resistant biomaterial surfaces.[11,12] Surfactant polymers having hydrophilic dextran and hydrophobic hexanoyl side chains were shown to modify a graphite surface such that protein adsorption is significantly reduced.[11] In a subsequent report, a series of surfactant polymers were synthesized having various ratios of hydrophilic poly(ethylene oxide) (PEO) and hydrophobic hexanal side chains.[10] These surfactant polymers were shown to create bacterial resistant surfaces when adsorbed to hydrophobic surfaces. Bacterial adhesion was dependent on the ratio of the PEO to hexanal side chains. It was suggested that the conformation of the surface adsorbed surfactant polymer is responsible for the differing bacterial adhesion, but the structure of the adsorbate was not investigated.

A model has been proposed for the adsorption of oligosaccharide surfactant polymers onto a graphite

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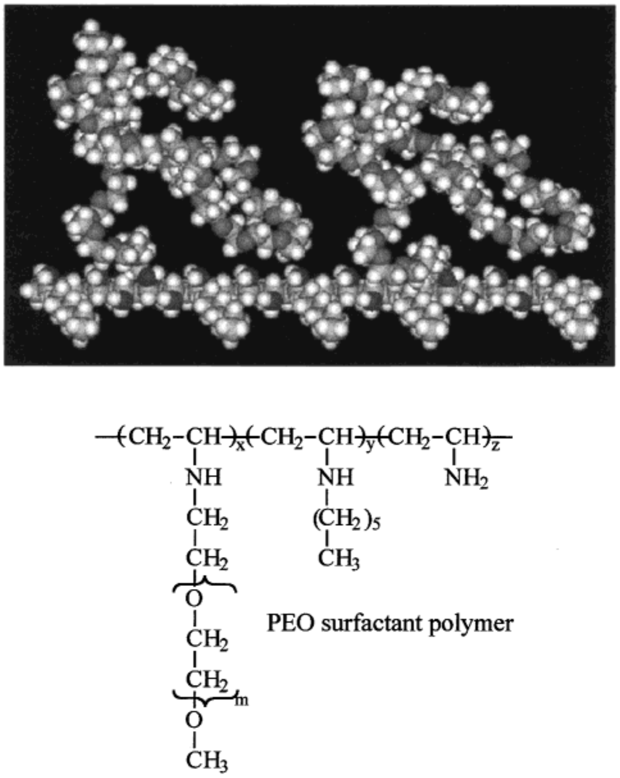

$-(CH_2-CH)_x(CH_2-CH)_y(CH_2-CH)_z-$ with side groups $NH-CH_2-CH_2-(O-CH_2-CH_2)_m-O-CH_3$, $NH-(CH_2)_5-CH_3$ and NH_2

Figure 1. Molecular model and chemical composition of poly(ethylene oxide)−hexanal surfactant polymers (PEO-hex). The surfactant polymer consists of a poly(vinylamine) backbone with 2 kDa PEO and hexanal side chains. (A) The molecular model of a 1:2.5 PEO-hex shows a portion of the surfactant polymer in a surface adsorbed conformation.[17] (B) The chemical composition of PEO-hex where $m = 45$.

substrate based on atomic force microscopy (AFM) data.[11] The alkanoyl side chains adsorb epitaxially to the graphite, confining the polymer backbone to the surface, while the oligosaccharide side chains extend into the aqueous solution. Direct application of this model to PEO surfactant polymer adsorption is complicated by the fact that, although PEO is soluble in water in all concentrations, it has surface active properties. Therefore, the PEO and hexanal side chains will adsorb competitively to the substrate, resulting in potentially complex surface structures.

In this report, we utilize surface pressure isotherms of spread layers and atomic force microscopy (AFM) of adsorbed polymer to characterize the surface adsorbed structures of the PEO−hexanal surfactant polymers. The surface pressure data are interpreted on the basis of isotherms of PEO and PEO lipopolymers,[6] while the AFM data are considered in the light of the surface pressure data and the previously reported model of surfactant polymer adsorption.[11]

Experimental Section

Polymers. Poly(*N*-vinyl monomethoxy poly(ethylene oxide) ethylamine) and poly(*N*-vinyl monomethoxy poly(ethylene oxide) ethylamine-*co*-*N*-hexanamine) (PEO-hex) were synthesized as previously reported: synthesizing poly(vinylamine) (PVAm) and subsequently attaching to the reactive amine sites the two types of branches, hydrophilic and hydrophobic chains (Figure 1).[10,12] The molar feed ratios of side chains were varied to produce different ratios of the hydrophobic (hexanal) to hydrophilic (PEO, DP ∼45, $M_n = 2.0$ kDa) branches on the PVAm backbone ($M_n = 32$ kDa). The resulting polymers were characterized by Fourier transform infrared (FTIR) and ^{1}H NMR spectroscopies. Polymers were produced with four different PEO to hexanal feed ratios: 1:0, 1:2, 1:4, and 1:8. Based on NMR and XPS analysis, the PEO-to-hexanal ratio of the three hexanal containing polymers range from 1:1.4 to 1:11.

Spread Monolayers. The samples were dissolved in chloroform (HPLC grade, Aldrich) and spread onto a substrate of pure water (18.2 MΩ·cm) in a 12×70 cm^2 Langmuir−Blodgett (LB) trough (KSV5000, KSV Instrument Ltd., Finland) on an antivibration table in a class 100 clean room. The trough was cleaned carefully with precision wipe paper dipped in distilled chloroform and rinsed twice with pure water. The subphase used was pure water, maintained at 21 ± 1 °C. Solutions of the polymers were spread on the water subphase, and the chloroform was allowed to evaporate for at least 10 min, allowing for the stabilization of the initial surface pressure. The surface tension was measured by the Wilhelmy plate method at 21 ± 1 °C. Symmetric compression at a constant rate was employed to produce the pressure vs surface area isotherms. Multiple measurements were performed for each polymer. To more accurately measure surface tension over a large range of surface concentrations, the amount of polymer added to the trough for different experiments was varied between 0.02 and 0.2 mg. These data, coming from different experiments, overlap and are displayed in the results as continuous curves.

AFM Imaging. Surfactant samples were imaged using a Nanoscope III Multimode AFM equipped with a fluid cell attachment and triangular silicon nitride cantilevers with a nominal spring constant 0.58 N/m (Digital Instruments, Santa Barbara, CA). Highly oriented pyrolytic graphite (ZYB grade) was freshly cleaved and imaged in water, prior to the addition of surfactant solution. Surfactant polymer solutions were prepared with ultrapure (18.2 MΩ·cm) water, filtered with 0.45 μm filter membranes, and diluted to appropriate concentrations (0.1−0.5 mg/mL) for adsorption. Aqueous solutions of surfactant were flowed into the fluid cell and imaged in the presence of the surfactant solutions.

The samples were imaged by AFM in tapping mode at ambient temperatures. The imaging set point was set so that the decrease in the RMS amplitude during imaging was between 5 and 15 nm. The integral and proportional gains and the scan rate were optimized to minimize hysteresis in the forward and backward scans. AFM data were not filtered, although the topographic image data were flattened using a first- or second-order line fit to eliminate sample tilt and/or piezo bow. For long adsorption times (>10 h) it was necessary to turn the AFM laser off to prevent excessive heating and evaporation of the solution from the fluid cell.

Results and Discussion

Surface Pressure. The surfactant polymers provide surface pressure isotherms rich in information. For the polymers with both hexanal and PEO side chains, two transitions are observed. The two transitions occur at surface pressures of around 5.5 and 11 mN/m, as can be seen in the isotherm of PEO-hex 1:8 (Figure 2). At large surface areas, a gradual rise in pressure is observed before the low-pressure transition. The transition is relatively broad, and the pressure continues to rise slightly throughout the transition, suggesting it is not a true transition but rather a gradual conformational change. After the low-pressure transition, the pressure begins to rise again, until the high-pressure transition, which occurs over a significantly smaller area than the low-pressure transition. After the high-pressure transition, the pressure quickly rises upon further compression. Isotherms for each of the surfactant polymers are qualitatively alike, except for the one containing only PEO side chains and no hexanals. For this polymer, the low-pressure transition occurs, while instead of a high-pressure transition, the film collapses into the substrate and so does not exhibit a rapid

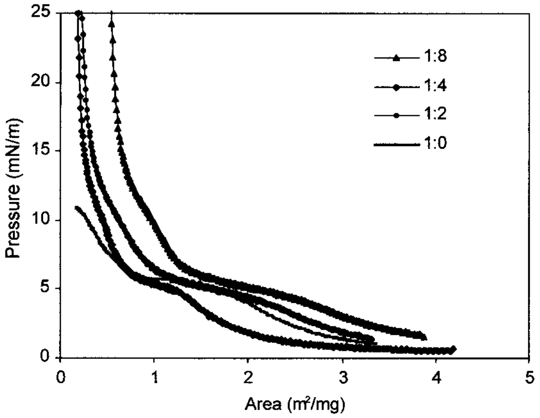

Figure 2. Surface pressure isotherms of PEO-hex surfactant polymers. Two plateaus are observed, near 5 and 11 mN/m, for each of the hexanal-containing surfactant polymers. The hexanal-free exhibits the low-pressure transition but collapses into the substrate at 11 mN/m.

Table 1. Transition Pressures (mN/m) for PEO Surfactant Polymers

sample	low-press. transition	high-press. transition
PEO-hex 1:8	5.0	10.6
PEO-hex 1:4	5.2	10.7
PEO-hex 1:2	5.2	10.1
PEO-hex 1:0	5.6	10.9
PEO(2 kDa)	5.0	
PEO(400 kDa)		10.0
DSPE-EO_{45}		11.1

pressure increase at low areas. The pressures of the transitions were quantified as the pressures at which a minimum in the compressibility of the film occur (Table 1).

To understand the nature of the surface pressure isotherms of the PEO surfactant polymers, it is important to first appreciate the surface active behavior of PEO. This knowledge can then help interpret how numerous PEO molecules tethered together on a polymer backbone respond to increasing lateral pressure. The fact that PEO has surface active properties has been known for many years.[13] This is highly unusual behavior considering that PEO is soluble in water in all proportions.[14] The structure of the polymer layer at air−water interfaces has been characterized by forming spread layers[15] and by examining surface layers formed from solution.[16] The structure of the polymer layer is inferred from the isotherms, and thermodynamics of the layers have been measured by varying the temperature.[17] The structure of the layer has been further probed by surface potential, ellipsometry, surface light scattering, and wave damping. No differences between spread layers and layers formed from solution are observed until high bulk solution concentrations are reached.[6,18,19]

The compression of spread layers has demonstrated that PEO with a molecular weight above 100 kDa will compress to a surface pressure around 10 mN/m when the surface concentration reaches ~1.4 mg/m^2, independent of molecular weight.[17] Above this concentration, the polymer layer becomes unstable, leading to polymer desorption into the solution. For PEO below 100 kDa, the film collapses at lower surface pressures.[17] The collapse pressure for 2 kDa PEO was measured to be 5 mN/m.[6]

When a hydrophobic tail is attached to the PEO, the behavior changes significantly. Kim and Cao observed an increase in the surface pressure for PEO, with two 16-carbon hexadecyl tails attached. They attribute the increase to the dehydration of the PEO layer near the interface with a reduction in the hydrogen bonding of the PEO molecules, creating a more hydrophobic layer.[19] Studies on PEO lipopolymers provide a basis for understanding such increases in surface pressure upon film compression.[6,20−22] For lipopolymers consisting of PEO (M_n = 2 kDa) headgroups linked to DSPE (an 18-carbon, two-tailed lipid) two transitions are observed: one around 10 mN/m and another around 20 mN/m. The onset of a transition was observed as a maximum in compressibility at 7.8 mN/m. Prior to the first transition, the polymer layer has been shown to form a spread surface layer, termed a pancake conformation.[6] Upon compression, the PEO desorbs from the interface to form a dense layer in the subphase (so-called pancake to mushroom transition),[23] observed as the first transition. It is of note that when 2 kDa PEO is bound to the interface at one end (as by the lipid tail), it no longer behaves like free 2 kDa PEO, which collapses at 5 mN/m, but rather like high molecular weight PEO. The second transition, which was originally interpreted as a mushroom to brush conformational transition,[20] has been more recently shown to be a special feature of PEO lipids corresponding to a dehydration of the PEO driven by lipid condensation, based on surface tension[6] and IRRAS measurements.[21]

We now propose a physical description of the compression of the surfactant polymers based on the above discussion. We begin with the polymer with no hexanal side chains. Since the polymer backbone exhibits no significant surface activity, this polymer is considered as simply a number of 2 kDa PEO molecules tethered to each other. At low surface concentrations, we observe a gradual surface pressure increase before the first transition, characteristic of the compression of a PEO pancake layer (Figure 3A). The transition occurs at a pressure between 5 and 6 mN/m, slightly higher than the characteristic collapse of free 2 kDa PEO. This suggests that individual PEO side chains are desorbing from the air−water interface; however, in constrast to the free PEO which are free to diffuse into the substrate, the desorbing PEO are held in the proximity of the surface via the PVAm backbone attached to surface bound PEO (Figure 3B). This results in a change in the chemical potential of the solution to which the surface layer is exposed. We attribute the slight increase in the collapse pressure between the tethered and untethered PEO to this local concentration increase. With further compression, the local concentration of desorbed PEO increases, eventually resulting in a continued increase in surface pressure up to the collapse of the monolayer around 11 mN/m (Figure 3C). This collapse pressure is characteristic of high molecular weight PEO and the transition pressure of PEO lipopolymers. The PEO side chains transition from behaving like individual low molecular weight PEO chains to tethered or high molecular weight PEO. This is not observed for the tightly tethered 2 kDa PEO lipopolymers and so is considered a unique property of the loosely tethered PEO.

We observe similar transition pressures for the polymers that have additional hexanal side chains, but instead of the film collapsing around 11 mN/m, the hexanal prevents the polymer from desorbing, resulting in a steep increase in surface pressure after the transi-

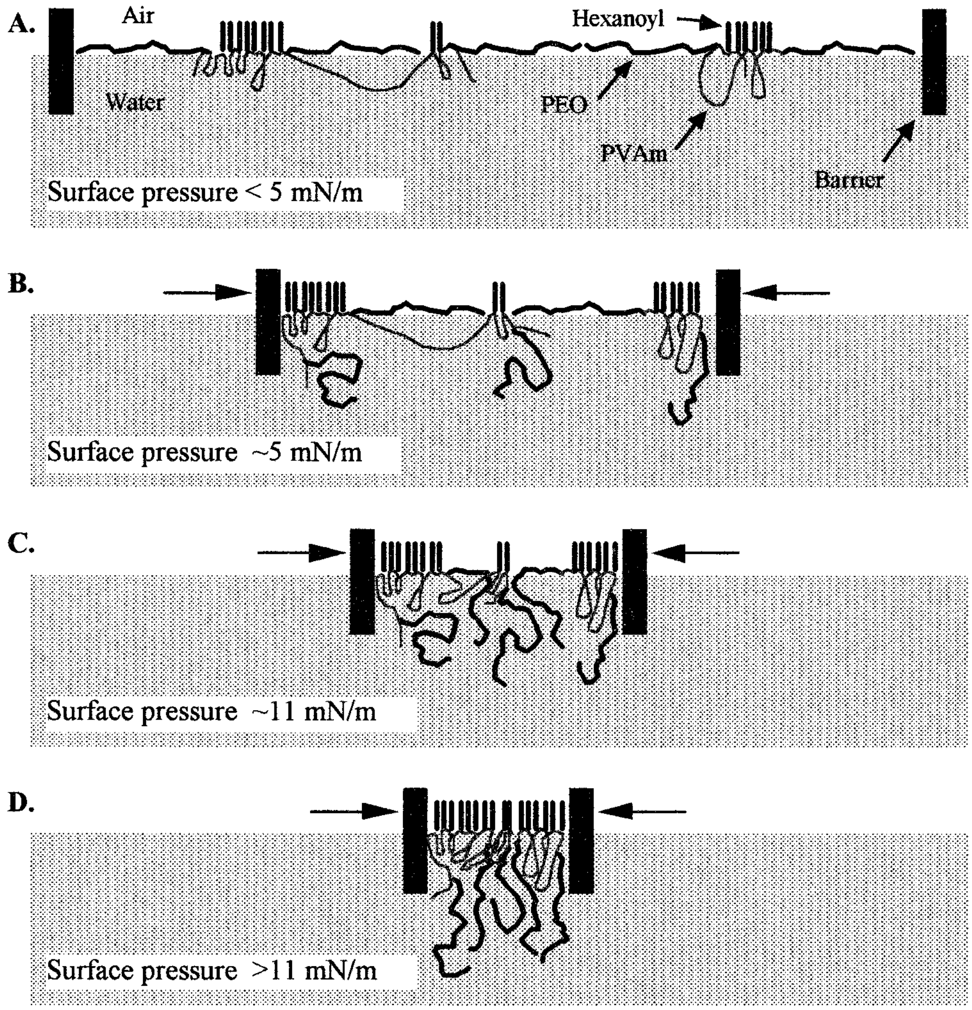

Figure 3. Schematic drawing of possible PEO side chain conformations leading to formation of 11 nm bands as observed in AFM images. The PEO side chains are presumed to force the separation of the polymer backbone by adsorption to the graphite substrate. If the PEO side chains adsorb in a compact conformation (B), the linear extent of each chain would be about 5 nm as determined from surface pressure data. The 11 nm separation of the polymer backbone is created by PEO chains on each side However, the PEO chains adsorbing in a more extended conformation could account for the 11 nm of separation (C). The extended length of the PEO side chains is ~17 nm, which results in reduced separation by an indirect path. On the basis of the low number of PEO side chains per polymer, the conformation in (C) is more likely than (B).

tion. At this point, the PEO is forced into a subsurface layer with the hexanal at the interface (Figure 3D).

To lend support to this interpretation, we scaled the isotherms based on two assumptions: (1) that the area at high pressures is not affected by the PEO content and is due solely to the packing of the hexanal side chains and (2) that below the first transition the area is the result of the addition of the area of the PEO pancake layer and the hexanal side chains.

The first assumption is only appropriate when the number of hexanal chains is large compared to the number of PEO side chains. From data on mixed monolayers of lipids and lipopolymers, it is evident that the PEO can contribute to the molecular area; at a ratio of 1 PEO to 2.5 alkane chains, there is a 10% increase in molecular area at 30 mN/m. In our case, the assumption is valid since the surfactant polymers have many hexanals per PEO, and since the PEO is only loosely packed, it should have a small effect on the area at the interface. We take the ratio of the area/mass of the surfactant polymers and of pure hydrocarbons (based on 0.225 nm^2/hexanal) at 30 mN/m. The result is a value for the mass fraction of the hydrocarbon side chains in each surfactant polymer.

The second assumption is based on previous results showing that, for PEO lipopolymers at low surface pressure, the area of the PEO in the pancake conformation is additive with the area occupied by the hydrocarbon chains.[6] The surface area below the first transition is simply the sum of the areas of the PEO and the hexanal side chains. The contribution to the area from the hexanal is determined from the area at high surface pressure and subtracted from the isotherm, based on the area of saturated alkyl chains at 2.5 mN/m. The isotherm is then proportionately scaled based on the area at 2.5 mN/m for 2 kDa PEO. The resulting isotherms are presented in Figure 4. The scaled isotherms overlay within experimental error, giving confidence that the assumptions are appropriate. The validity of the scaling suggests that, through the first transition, the PEO is partially responsible for the area of the isotherm, whereas beyond the second transition, it plays a diminishing role. Therefore, the transition depends on the proportion of PEO side chains desorbed from the interface, while the collapse is dependent on the number of hexanal side chains present.

From the scaling factors, the mass fractions of PEO and hexanal chains were determined. On the basis of

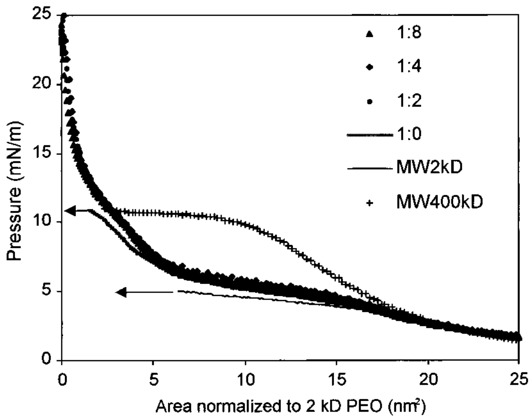

Figure 4. Scaled surface pressure isotherms of PEO-hex surfactant polymers. The isotherms from Figure 2 were scaled to 2 kDa PEO at 2.5 mN/m after the hexanal contribution (based on the area at 35 mN/m) was subtracted. Note that the three hexanal-containing isotherms overlay each other over the full range of the measurement. The hexanal-free polymer deviates from the others at the high-pressure transition, when it collapses into the solution. The isotherm for 2 kDa PEO and scaled high molecular weight PEO (from ref 6) are shown for comparison.

Table 2. Surfactant Polymer Composition Calculated from Surface Pressure Isotherms

sample	M_n (kDa)	side chains/polymer PEO	side chains/polymer hexanal	PEO-to-hexanal ratio from surface press.	PEO-to-hexanal ratio from NMR[a]
PEO-hex 1:8	121	26	435	1:16	1:11
PEO-hex 1:4	49	6	58	1:10	1:5
PEO-hex 1:2	65	13	85	1:7	1:3
PEO-hex 1:0	52	10			

[a] From ref 10.

the known molecular weight of the PVAm backbone and these mass fractions, the total molecular weight, the side chain ratio, and the number of PEO and hexanal side chains are calculated for each polymer (Table 2). These values are in qualitative agreement but significantly different than the values measured by NMR and XPS.[10] The values from NMR and XPS are prone to large errors for calculations based on small signals and for NMR by possible shielding of portions of the molecule by unimolecular micellation. Therefore, the values presented here are considered to be more accurate.

Summarizing the surface pressure behavior, the PEO surfactant polymers at high surface areas act like a spread monolayer of PEO. As the layer is compressed, the pressure increases to above 5 mN/m, at which pressure individual 2 kDa PEO side chains begin to desorb from the surface but remain near the surface since they are tethered by the PVAm backbone. When the surface has been compressed so that much of the PEO has desorbed, the pressure begins to rise again. When the pressure reaches 11 mN/m, the final PEO is squeezed from the interface. If there are hexanal side chains, the pressure will continue to rise; if not, the polymer collapses into the solution.

Atomic Force Microscopy. The adsorption of two different PEO-hex surfactant polymers (1:4 and 1:8 feed ratios) were characterized using atomic force microscopy (AFM). The more hydrophobic 1:8 PEO-hex is slightly soluble in water and was adsorbed at a nominal concentration of 100 μg/mL. The solution was filtered, and it is assumed that a significant portion of the surfactant was lost. Even at such a low concentration, the 1:8 PEO-hex adsorbed rapidly to the graphite surface as compared to other surfactant polymer systems.[11] The surfactant solution was flowed into the system during a scan (Figure 5A). By the time the scan is completed, the polymer is observed to cover nearly the entire surface. In the subsequent scan (Figure 5B), large domains that had grown into each other were observed. The distinction between the domains disappears in several minutes, leaving a uniformly modified graphite surface (Figure 5C).

The observations of adsorption in a single monolayer and organization in three directions suggest that the PEO-hex 1:8 adsorbs via the same mechanism as observed for dextran surfactant polymer.[11] Epitaxial adsorption of the hexanal side chains to the graphite drives the adsorption and confines the PVAm backbone to the surface. The PEO side chains remain solvated and extend away from the surface. The large size of the domains and the rapidity of adsorption suggest that there is a higher level of cooperativity than observed for the dextran surfactant polymer. Equating the adsorption to two-dimensional crystallization, this means that propagation is much faster than nucleation. There is evidence to suggest that this is a result of the variation in hydrophobic chain grafting density rather than the variation in the hydrophilic group.[24]

From height measurement on the incomplete monolayer, the thickness of the full monolayer is estimated to be 1.2 nm. Assuming that all hexanal side chains adsorb epitaxially to the graphite (each hexanal occupying 0.45 nm^2) and there are 16 hexanal side chains per PEO, the minimum area covered by each PEO is 7.6 nm^2. Comparing this to surface pressure data suggests that the PEO side chains are in a partially extended conformation characterized by the first transition. This is consistent with the measured thickness. This indicates that the conformation of the PEO is not in an extended brush conformation. To create such a dense PEO layer in a brush conformation, the area per PEO side chain must be less than about 2.2 nm^2, corresponding to a side chain ratio of 1:5 or lower.

The 1:4 PEO-hex was not observed to order upon adsorption. Individual polymer chains adsorbed with no interaction with previously adsorbed chains. The adsorption continued until the surface was completely covered (Figure 6). After an extended period in the polymer solution (>16 h), small banded regions were observed on the surface. The bands have a characteristic width of 11 nm and range in length from 50 to 250 nm. The measured lengths correlate to the lengths of individual extended polymer chains (an extended 32 kDa backbone is 186 nm long). The orientation of the bands in three directions indicates epitaxial association with the surface.

The structure of the PEO-hex 1:4 initially adsorbed is disordered. According to the model, there are insufficient hexanal side chains to drive the extension of the backbone. For the 1:8 PEO-hex, the highly cooperative adsorption of the hexanals inhibits the adsorption of PEO directly to the surface. The 1:4 PEO-hex does not have such a strong interaction, allowing PEO to successfully compete for adsorption to the graphite surface.

Since the lengths of bands that occur after long adsorption times are consistent with the length of individual polymer molecules, it is proposed that each band is an individual polymer chain. So the question

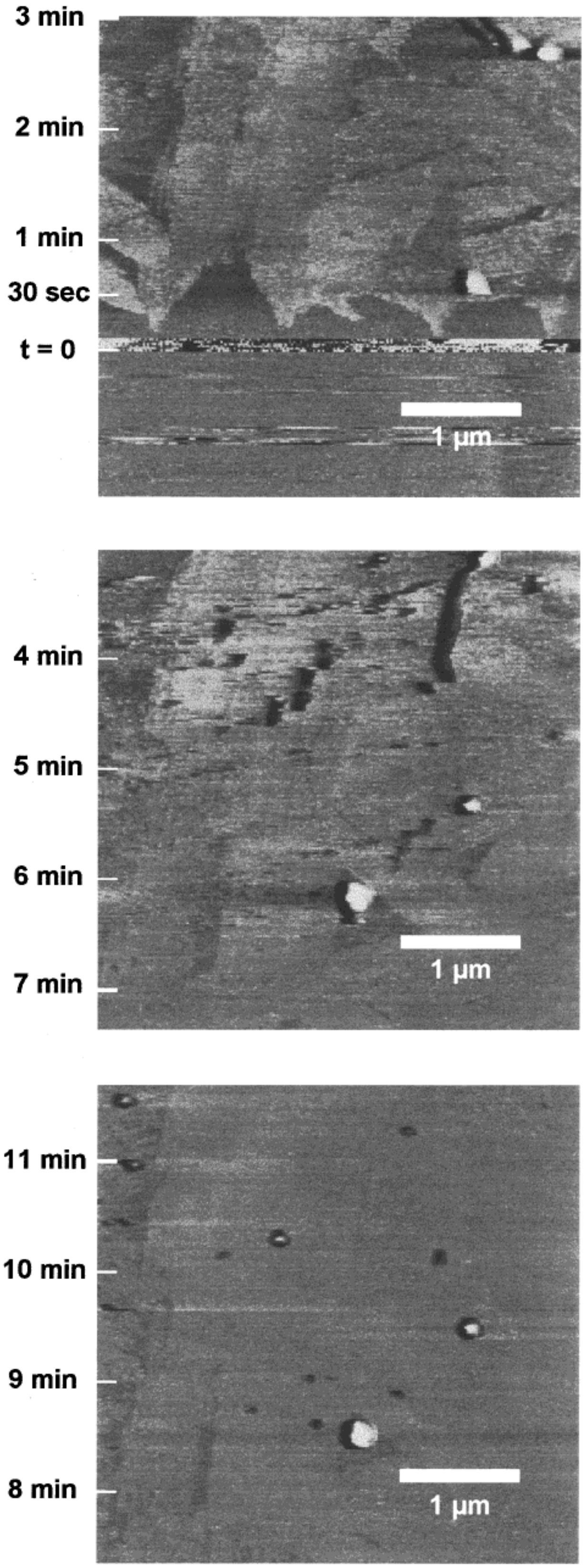

Figure 5. AFM images of the adsorption of 1:8 PEO-hex surfactant polymer. The rapid adsorption of 1:8 PEO-hex was observed during these three consecutive AFM scans. The scan rate was 2 lines/s, which corresponds to the time denoted along the image. The surfactant entered the fluid cell at $t = 0$. A complete monolayer is observed to form in less than 1 min. Domains of oriented adsorbate (in three directions) are initially observed and eventually fade until a complete and compact monolayer is observed in less than 10 min.

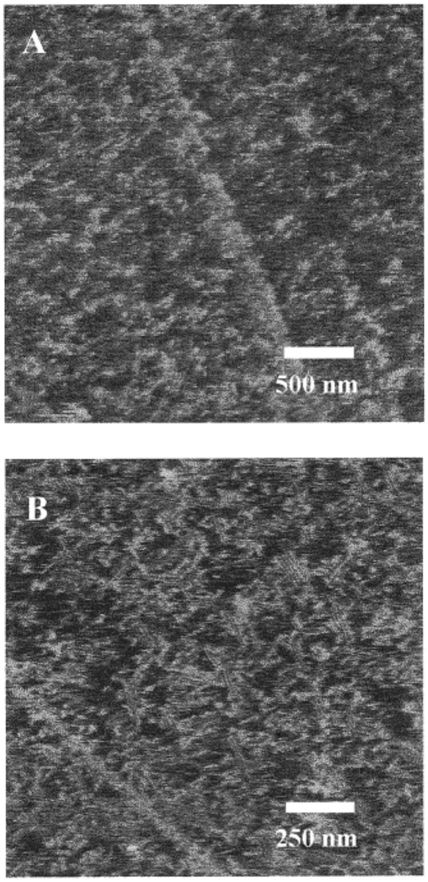

Figure 6. AFM images of PEO-hex 1:4 surfactant polymer. Initially, the PEO-hex 1:4 adsorbs with no order onto the HOPG (A). After 16 h (B), small regions of ordered bands are observed. The lengths of the bands are between 50 and 250 nm, corresponding to the length of individual polymer chains. The characteristic band spacing is 11 nm.

arises as to the origin of the 11 nm lateral spacing. This is much greater than the length of the hexanal side chains (0.75 nm). A fully extended 2 kDa PEO chain is around the correct magnitude (17 nm), suggesting the spacing is a result of the PEO side chains. It is proposed that the PEO will spread to form a monolayer (pancake conformation) at the graphite surface. Presuming that there is a preference for the side chains not to cross over the backbone, there are two possibilities to create the 11 nm spacing, the average extent of the side chains being 5.5 or 11 nm. The surface pressure data show that there are an average of six PEO side chains per polymer. For PEO extending only 5.5 nm, to keep the chains apart the grafting density of PEO would need to be an order of magnitude larger than this. The PEO must then extend from the backbone closer to 11 nm. To form the ordered bands, the PEO side chains would need to force the backbone to extend, which requires intramolecular interactions. It is suggested that only molecules with larger than average PEO length would satisfy this criterion, which is why only a limited number of chains are observed in this conformation. This interpretation suggests that the PEO forms a relatively a spread layer at the interface.

Conclusion

The surface activity of PEO plays an important role in the surface active behavior of PEO-hex surfactant polymers, unlike side chains with no amphiphilic character such as dextran oligosaccharide surfactant polymers.[11,12] In the compression of spread monolayers, desorption of the PEO side chains from the interface results in two transitions. At high pressures, the hexanal side chains confine the surfactant polymers to the interface. We have demonstrated that the isotherms can be scaled quantitatively to determine the side chain composition in the surfactant polymers. If the hexanal content is sufficiently high (e.g., 1:8 PEO-hex), they will dominate the adsorption onto a graphite substrate. However, the PEO can play a role if the hexanal content is low. These results are important for interpreting the results of the recently reported bacterial resistance of adsorbed monolayers of PEO surfactant polymers and for other comblike polymers with surface active properties.

References and Notes

(1) Harris, J. M. In *Poly(ethylene glycol) Chemistry, Topics in Applied Chemistry*; Katritzky, A. R., Sabongi, G. J., Eds.; Plenum Press: New York, 1992; p 385.
(2) Griffith, L. G. *Acta Mater.* **2000**, *48*, 263−277.
(3) Irvine, D. J.; Mayes, A. M.; Satija, S. K.; Barker, J. G.; Sofia-Allgor, S. J.; Griffith, L. G. *J. Biomed. Mater. Res.* **1998**, *40*, 498−509.
(4) Chapman, R. G.; Ostuni, E.; Liang, M. N.; Meluleni, G.; Kim, E.; Yan, L.; Pier, G.; Warren, H. S.; Whitesides, G. M. *Langmuir* **2001**, *17*, 1225−1233.
(5) Schillen, K.; Claesson, P. M.; Malmsted, M.; Linse, P.; Booth, C. *J. Phys. Chem.* **1997**, *101*, 4238−4252.
(6) Xu, Z.; Holland, N. B.; Marchant, R. E. *Langmuir* **2001**, *17*, 377−383.
(7) Baekmark, T. R.; Elender, G.; Lasic, D. D.; Sackmann, E. *Langmuir* **1995**, *11*, 3975.
(8) Cox, J. K.; Yu, K.; Eisenberg, A.; Lennox, R. B. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4417−4421.
(9) Richards, R. W.; Rochford, B. R.; Webster, J. R. P. *Polymer* **1997**, *38*, 1169−1177.
(10) Vacheethasanee, K.; Marchant, R. E. *J. Biomed. Mater. Res.* **2000**, *50*, 302−312.
(11) Holland, N. B.; Qiu, Y.; Ruegsegger, M.; Marchant, R. E. *Nature* **1998**, *392*, 799−801.
(12) Qiu, Y.; Zhang, T. H.; Ruegsegger, M.; Marchant, R. E. *Macromolecules* **1998**, *31*, 165−171.
(13) Couper, A.; Eley, D. D. *J. Polym. Sci.* **1948**, *3*, 345−349.
(14) Kuzmenka, D. J.; Granick, S. *Polym. Commun.* **1988**, *29*, 64−66.
(15) Shuler, R. L.; Zisman, W. A. *J. Phys. Chem.* **1970**, *74*, 1523−534.
(16) Glass, J. E. *J. Phys. Chem.* **1968**, *72*, 4459−4467.
(17) Kuzmenka, D. J.; Granick, S. *Macromolecules* **1988**, *21*, 779−782.
(18) Sauer, B. B.; Yu, H. *Macromolecules* **1989**, *22*, 786−791.
(19) Kim, M. W.; Cao, B. H. *Europhys Lett.* **1993**, *24*, 229−234.
(20) Baekmark, T. R.; Elender, G.; Lasic, D. D.; Sackmann, E. *Langmuir* **1995**, *11*, 3975−3987.
(21) Wiesenthal, T.; Baekmark, T.; Merkel, R. *Langmuir* **1999**, *15*, 6837−6844.
(22) Naumann, C.; Brooks, C.; Fuller, G.; Knoll, W.; Frank, C. *Langmuir* **1999**, *15*, 7752−7761.
(23) Currie, E. P. K.; Leermakers, F. A. M.; Stuart, M. A. C.; Fleer, G. J. *Macromolecules* **1999**, *32*, 487−498.
(24) Holland, N. B. Polymers, Surfactants, and Proteins at Biomaterial Interfaces: Observation, Manipulation and Measurement of Surface Interactions Using Atomic Force Microscopy. In *Macromolecular Science*; Case Western Reserve University: Cleveland, OH, 1999.

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