Macromolecules **2006,** *39,* 9375−9384

Adsorbed and Spread Layers of Poly(ethylene oxide)−Poly(propylene oxide)−Poly(ethylene oxide) Block Copolymers at the Air−Water Interface Studied by Sum-Frequency Vibrational Spectroscopy and Tensiometry

Éva Kiss,*[,†] Tamás Keszthelyi,*[,‡] Gábor Kormány,[†] and Orsolya Hakkel[‡]

Department of Colloid Chemistry, L. Eötvös University, Budapest 112 P.O. Box 32, H-1518 Hungary, and Chemical Research Centre, P.O. Box 17., H-1525 Budapest, Hungary

Received May 23, 2006; Revised Manuscript Received September 13, 2006

ABSTRACT: The surface properties of three water-soluble and amphiphilic PEO−PPO−PEO triblock copolymers of different composition (Pluronic 6100, 6400, and 6800) are investigated by tensiometry and sum-frequency vibrational spectroscopy. We compared the concentration dependence of the structure of surface layers prepared by three different methods: (i) adsorption from aqueous solution, (ii) dropwise spreading from an organic solution onto a surface of constant area, and (iii) compression of the spread film in a Langmuir trough. The surface density and conformation of the polymers were deduced from the vibrational band intensities of the methyl groups of the central hydrophobic PPO block and from the surface tension isotherms. A transition range related to a conformational change was observed by tensiometry for the adsorbed and the compressed Langmuir films of Pluronics with short PEO blocks, whereas the Pluronic with longest PEO blocks displays a gradual change of surface pressure without the sign of a phase transition. This difference reveals the effect of the relative lengths of the hydrophilic and hydrophobic blocks on the structural changes in the surface layers of block copolymers. A clear indication of the influence of the hydrophilic blocks on the structure of the whole molecule at the interface was also observed in the sum-frequency experiments. Above a given concentration the Pluronic with longest PEO chains exhibited lower sum-frequency intensities and methyl symmetric/asymmetric amplitude ratios than the other Pluronic compounds for all of the layers formed by the various methods. The differences in the surface properties of the dropwise spread layers and of the compressed Langmuir layers exposed the importance of the kinetic aspects of polymer monolayer formation. In the case of the spread films the possible large degree of nonequilibrium chain entanglements might hinder the accomplishment of preferred orientation and conformation of the polymer chains.

Introduction

Langmuir and Langmuir−Blodgett films as molecularly ordered nanostructures formed from insoluble amphiphatic molecules have recently attracted substantial attention due to their widespread application in various fields such as biomaterials, sensors, electronics, optics, etc.[1−4] Besides the traditional surface-active molecules as fatty acids and their derivatives, polymers and nanoparticles appeared as functional components of composite Langmuir films which combine the special properties with the advantages of thin ordered films. The molecular properties of polymers like amphiphatic character are of crucial importance when they are built in the nanostructures. There is a requirement also in the case of polymers to accomplish the oriented arrangements of the molecules at the interface.

The investigation of polymer Langmuir layers goes back to the 1950s[5] when the classification of these polymer monolayers was given according to their ability to form stable film at the water surface. The shape of the surface pressure−area isotherm implicates two main types: the condensed and the expanded polymer layers,[5,6] the behavior of which was interpreted on the basis of the molecular structure. Nevertheless, only indirect information was available on the structure of the Langmuir monolayer until it became possible to determine exact parameters such as the thickness[7−10] and structural details within the layer[11,12] with the aid of ellipsometry and neutron reflectometry, respectively.

The water-soluble and at the same time film-forming polymers offer the special opportunity to compare the properties of the adsorbed and Langmuir films of those polymers. Only a few reports have appeared on this aspect of polymer monolayers up until now. *N*-Isopropylarcylamide films were studied by ellipsometry,[13] while similar behavior of adsorbed and spread films was described using Brewster angle microscopy (BAM)[14] and surface rheological techniques[15] for block copolymers. Surface-sensitive nonlinear optical techniques, like infrared−visible sum-frequency vibrational spectroscopy, allow us to reveal the structural characteristics and assess the conformational changes in the surface layer. Therefore, in the present work tensiometric measurements are combined with sum-frequency spectroscopy to investigate the adsorbed and spread molecular layers of block copolymers at the air/water interface.

The poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide), PEO−PPO−PEO, triblock copolymers (Pluronic) are water-soluble and amphiphilic in nature. Their surface activity and tendency to self-assembly in solution stem from the fact that the PPO block is relatively hydrophobic, whereas the PEO blocks are more hydrophilic. The orientation of the hydrated and mobile PEO blocks of a Pluronics adsorbed at solid surfaces is exploited in the stabilization of various colloidal systems as well as in biomedical applications when they are used to modify the surface properties of hydrophobic biomaterials.[16−19]

---

* Author to whom correspondence should be addressed.

[†] L. Eötvös University.

[‡] Chemical Research Centre.

10.1021/ma061161b CCC: $33.50

The existence of stable spread film of water-soluble polymers is explained by their amphiphilic and polymeric character.[20] Such behavior was obtained even for PEO homopolymers[21−24] arising from the amphiphilic nature of the monomer unit itself. For PEO−PPO−PEO copolymers the central hydrophobic block, acting as an anchoring element, further increases the stability of the Langmuir film,[14] which can be considered as insoluble because hours or days are necessary to complete the diffusive transport since the adsorption kinetics of these systems at sufficiently low bulk concentrations is extremely slow.[10]

Certain aspects of the interfacial behavior of poly(ethylene oxide) and poly(propylene oxide)[25] as well as of several of their block copolymers, Pluronics,[26] have been investigated by sum-frequency vibrational spectroscopy by Chen et al. It was found that the saturated solution/air interfaces of Pluronics obtained by adsorption from aqueous solution are covered by a dense layer of PPO blocks. In this layer the methyl side groups of the PPO blocks were found to form an ordered structure with the methyl groups orienting preferentially along the interface normal. On the other hand, at very low concentrations an abrupt change in methyl group orientation was observed, which, according to the authors, may explain the concentration-dependent behavior of the surface tension data.[26] The structure of the Pluronic copolymers at solution/air interfaces was found to be independent of the length of either the PPO or the PEO blocks.

The water solubility and the polymeric character of Pluronics allow us to study the properties of the adsorbed layer from aqueous solution and the films formed when the Pluronic is spread from an organic solution at the air−water interface. The surface concentration of the Pluronic was changed in two ways in the case of spread films: by compression in a Langmuir trough and by dropwise spreading onto a surface of constant area. We note here that the samples prepared by spreading from organic solution might not be at equilibrium under our experimental conditions, whereas the adsorbed films can be considered to be in equilibrium about 15 min after their preparation, except for the lowest bulk concentrations studied. However, even the nonequilibrium conditions used in our experiments are highly relevant, as in practical applications or in the experimental investigations of block copolymers the equilibrium conditions are not always achieved. Surface pressure and sum-frequency spectroscopic measurements were performed for the adsorbed and the two types of spread films applying three Pluronics of different composition. The architecture of the block copolymers with the same central PPO block and PEO chains with various length makes it possible to investigate the effect of the hydrophilic blocks on the conformation and orientation of the whole molecule in the surface layer. Our aim was to compare the properties of the block copolymer films formed in different processes and to elucidate the effect of surface concentration and molecular composition on the structure of the Pluronic layers.

Experimental Details

Materials. Poly(ethylene oxide)/poly(propylene oxide)/poly(ethylene oxide), PEO−PPO−PEO, triblock copolymers, Pluronic 6100, 6400, and 6800 (kindly provided by BASF Hungaria Ltd.), were used as received. The composition of the Pluronics is referred to (BASF Technische Information) by the size of central hydrophobic poly(propylene oxide), PPO, block which is composed of 30 PO units, while the hydrophilic poly(ethylene oxide) content of the whole molecule is given as 10, 40, and 80 wt %. The copolymers were characterized by gel permeation chromatography (GPC) using tetrahydrofuran as solvent. The molecular weight distribution determined by GPC analysis showed that the samples were of high purity and low polydispersity: $M_w/M_n = 1.02-1.03$. The molecular weights and the compositions of the copolymers are given in Table 1, together with the critical micellar concentration values. The hydrophobicity of the molecules decreases with the increasing type number (PEO content).

Table 1. Composition of the Pluronics Used in the Present Study

Pluronic type	M_w	no. of monomer units in the blocks PEO/PPO/PEO	critical micellar concentration c_M (mol/dm^3)[a]
6100	1980	3/30/3	$<3 \times 10^{-5}$
6400	2870	13/30/13	3.8×10^{-3}
6800	6710	56/30/56	2.3×10^{-2}

[a] Reference 43.

Concentration ranges where Pluronics were applied in the present study are below the corresponding critical micellar concentrations.

Dichloromethane (>99.9%, LiChrosolv, Merck) satisfying the surface-active purity requirement[20] was used as spreading solvent for the film preparations. Doubly distilled water applied as solvent to prepare the solutions for the adsorption measurements and as subphase for spread films was checked by its conductivity (<5 μS) and surface tension (>71.5 mN/m at 23 °C) values.

Sample Preparation and Tensiometry. Pluronic surface layers at the air−water interface were obtained by adsorption from the aqueous solution and by spreading of dichloromethane solution of the given Pluronic on the water surface. The surface concentration of Pluronics was varied by the different bulk concentrations in the first case while by stepwise increasing the spread amount or by compression of the Langmuir layer in the case of spread films.

Surface Pressure Measurements, Adsorbed Films. Surface tension was measured with an electrobalance using chromatography paper (no. 3001 604, England Whatman Int. Ltd.) as a Wilhelmy plate. The precisely cut filter papers were soaked in doubly distilled water and dried before use to prevent any surface contamination during the surface tension measurement. The sensitivity of the electrobalance was 0.02 mN/m.

Aqueous solutions of Pluronic 6100, 6400, and 6800 were prepared in the concentration range of $5 \times 10^{-5}-1\%$ w/v, which corresponds to $2.5 \times 10^{-7}-5 \times 10^{-3}$, $1.7 \times 10^{-7}-3.5 \times 10^{-3}$, and $7.5 \times 10^{-8}-1.5 \times 10^{-3}$ mol/dm^3 for the three Pluronic compounds, respectively. The samples were contained in a Teflon petri dish (4.4 cm diameter). The evaporation loss was prevented by enclosing the cell in a Plexiglas box with a solvent saturated atmosphere. The surface tension of the aqueous Pluronic solutions was recorded for 180 min. The values obtained at 15 min were given to further consideration since the films were typically on average measured at that age in the sum-frequency experiments reported below.

Triplicate runs were made to check the reproducibility of surface tension measurements, resulting in ±0.2 mN/m scattering as a typical value.

Spread Films. 15 mL of water was poured into a Teflon petri dish with a diameter of 4.4 cm. 5 μL portions of dichloromethane solution of the Pluronics were spread consecutively on the water surface with a microsyringe. Following each addition 15 min was allowed for the evaporation of the solvent, and the surface tension was determined by the same method as in the case of adsorbed films. The process was repeated until a similar surface pressure was reached than that obtained by compression of the Langmuir layer in the other experiments.

Langmuir Balance Experiments. The Pluronic polymer films were spread at the air/water interface in a Langmuir balance (18 cm × 6 cm × 0.6 cm) equipped with two Wilhelmy plate surface tension sensors. The Teflon trough was covered with a box of Plexiglas in order to minimize air turbulence and possible contamination. Spread monolayers were formed by depositing small amounts of the dichloromethane solution of Pluronics (0.04 g/dm^3) with a microsyringe in the Langmuir trough containing the subphase and allowing the solvent to evaporate for 10 min. Blank experiments were carried out with the same amounts of pure solvent, and no deviation from surface tension of pure water was detected during the compression−expansion cycle.

The surface pressure−area isotherms were determined at a barrier velocity of 24 cm^2/min. The special design of our Langmuir balance with a second surface tension sensor inserted at the rear side of the barrier allows us monitoring simultaneously the surface tension of the pure subphase during the film compression. If the surface film had not been stable and its partial dissolution had occurred during compression, this effect would have been sensitively detected by the rear side surface tension sensor.

The temperature was maintained at 23 ± 0.3 °C in all experiments.

Sum-Frequency Spectroscopy. Sum-frequency spectra of the adsorbed and spread Pluronic films on water surface were collected by an EKSPLA[27] (Vilnius, Lithuania) spectrometer. The sample holders and the Langmuir trough were the same as used in the surface pressure experiments. The visible beam (532 nm) is generated by doubling the fundamental output of a Nd:YAG laser (1064 nm wavelength, 20 ps pulse with, 20 Hz repetition rate), while the tunable IR beam is obtained from an optical parametric generation/difference frequency generation system, pumped by the third harmonic and the fundamental of the Nd:YAG laser. The IR and visible beams are temporally and spatially overlapped on the sample surface with incident angles of 55° and 60°, respectively. The beam energies at the sample were kept at 200 μJ/pulse. Sum frequency light is collected in the reflected direction through a holographic notch filter and monochromator and detected by a PMT. Spectral resolution is determined by the <6 cm^{-1} line width of the IR pulse. Spectra presented were measured using the ssp (s-polarized sum-frequency, s-polarized visible, and p-polarized IR radiation), sps, and ppp polarization combinations. Spectra were collected in the 2800−3000 cm^{-1} spectral region using 3 cm^{-1} increments and 100 laser pulses at each step. Three to five such spectra were collected and averaged at each bulk concentration or surface coverage.

According to the basic theory of sum-frequency generation,[28] the sum-frequency intensity in the reflected direction is proportional to the square modulus of the nonlinear susceptibility, $\chi^{(2)}$. For an azimuthally isotropic liquid interface only the χ_{yyz} component of the second-order susceptibility tensor contributes to the effective nonlinear susceptibility under the ssp polarization combination and only the χ_{yzy} component under the sps polarization combination. Under the ppp combination the effective susceptibility contains contributions form the χ_{xxz}, χ_{xzx}, χ_{zxx}, and χ_{zzz} tensor components. The susceptibility has a resonant and a nonresonant contribution:

$$\chi^{(2)} = \chi^{(2)}_{\mathrm{NR}} + \chi^{(2)}_{\mathrm{R}} = \chi^{(2)}_{\mathrm{NR}} + \sum_m \frac{\chi^{(2)}_m}{\omega_2 - \omega_m + i\Gamma_m} \tag{1}$$

where ω_2 is the frequency of the infrared beam, $\chi^{(2)}_m$ the resonant amplitude, ω_m the frequency, and Γ_m the corresponding damping constant of the *m*th characteristic vibrational normal mode of the interface, and $\chi^{(2)}_{\mathrm{NR}}$ is the nonresonant amplitude. From eq 1 it is seen that the sum-frequency intensity is resonantly enhanced when the infrared frequency matches the frequency of a molecular vibration. Thus, by scanning the frequency of the infrared laser beam, the vibrational spectrum of the interfacial molecules can be recorded. Accordingly, the spectra can be fit to the general formula

$$S(\omega_2) = |A_{\mathrm{NR}} e^{i\varphi_{\mathrm{NR}}} + \sum_m \frac{A_m e^{i\varphi_m}}{\omega_m - \omega_2 + i\Gamma_m}|^2 \tag{2}$$

In the case of the ssp and sps polarization combinations there is only contribution from a single susceptibility tensor component, and it can be shown[29] that the φ_m phases corresponding to the individual molecular vibrations are equal. In the case of the ppp polarization combination there is contribution from four tensor components, and the φ_m phases of the individual vibrations can be different from each other.[29]

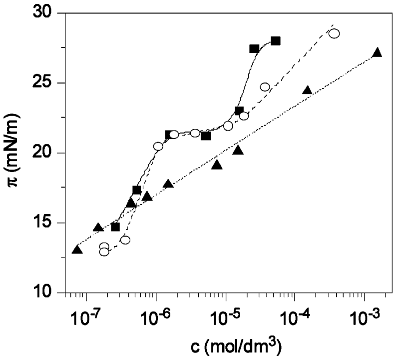

Figure 1. Surface pressure (at 15 min) of adsorbed Pluronic 6100 (■), 6400 (○), and 6800 (▲) layers as a function of bulk concentration. Symbols are measured data points; lines are only guides to the eye.

The intensities of the individual vibrational bands are given by[30]

$$I_m = \int_{-\infty}^{+\infty} |\frac{A_m}{\omega_m - \omega_2 + i\Gamma_m}|^2 \, d\omega_2 = \frac{{A_m}^2}{\Gamma_m} \tag{3}$$

and this is the quantity used in the later sections when analyzing the concentration and surface tension dependences.

In the literature certain ratios of the susceptibility tensor components, or alternatively of the corresponding peak amplitudes, are often used to extract information on the orientation distribution of methyl groups from the sum-frequency spectra.[31,32] The $|\chi_{yyz,\mathrm{s}}/\chi_{yyz,\mathrm{as}}|$ ratio, corresponding to the $R \equiv |A_{\mathrm{ssp,s}}/A_{\mathrm{ssp,as}}|$ methyl symmetric stretch to methyl antisymmetric stretch amplitude ratio of the ssp spectra, has been successfully applied to the orientational analysis of methyl groups.[33,34]

Results and Discussion

Adsorbed Layers. The surface pressure, π, which is the decrease of surface tension of water, γ_0, due to the presence of adsorbed or spread Pluronic layer ($\pi = \gamma_0 - \gamma$) is displayed in each type of experiments for the sake of comparison.

Surface pressures of aqueous Pluronic type 6100, 6400, and 6800 solutions were determined in the concentration range of 7.5×10^{-8}−5×10^{-3} mol/dm^3 as a function of time. To relate the adsorption behavior to the results of the sum-frequency experiments, the surface pressures obtained at 15 min were selected which best reflect the condition of the adsorbed film measured by sum-frequency spectroscopy. These values correspond to the equilibrium ones above the concentration of 10^{-6} mol/dm.^{3} At lower concentrations the surface pressures obtained at 15 min cannot be considered as equilibrium values; the deviation from the values measured after 120 min, however, does not exceed 3, 2, and 0.7 mN/m in the case of Pluronic 6100, 6400, and 6800, respectively.

Surface pressures as a function of molar concentration are plotted for the aqueous solutions of the three Pluronics in Figure 1 (the error does not exceed the size of the symbols). A considerable surface activity can be observed even in the lowest concentration range. Pluronic 6800 displays a gradual increase of the surface pressure with increasing bulk concentration, while the surface pressure vs bulk concentration curves of both Pluronic 6400 and 6100 exhibit a region of almost constant surface pressure.

The sum-frequency spectra of an adsorbed monolayer of Pluronic 6100 measured with the ssp, ppp, and sps polarization combinations are shown in Figure 2. These spectra were recorded at a bulk concentration of 2.5×10^{-5} mol/dm.^{3} Figure 3 displays the sum-frequency ssp spectra of adsorbed monolayers of Pluronic 6100 at three different bulk concentrations.

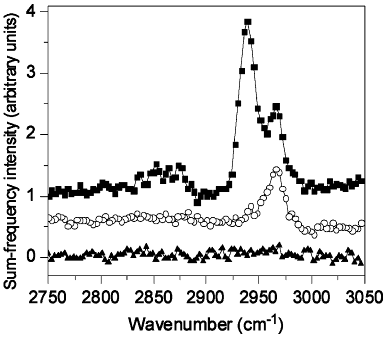

Figure 2. Sum-frequency ssp (■), ppp (○), and sps (▲) spectra of adsorbed monolayers of Pluronic 6100 at a bulk concentration of 2.5 × 10^{-5} mol/dm.^{3} The spectra have been vertically displaced for clarity. Symbols are measured data points; solid lines are only guides to the eye.

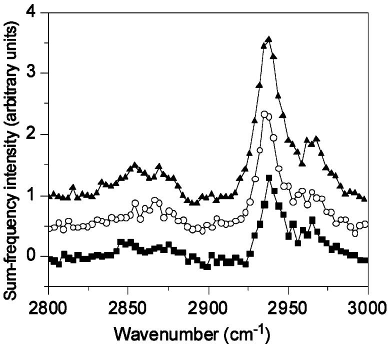

Figure 3. Sum-frequency ssp spectra of adsorbed monolayers of Pluronic 6100 at bulk concentrations of 2.5 × 10^{-7} (■), 2.5 × 10^{-6} (○), and 5 × 10^{-5} (▲) mol/dm.^{3} The spectra have been vertically displaced for clarity. Symbols are measured data points; solid lines are only guides to the eye.

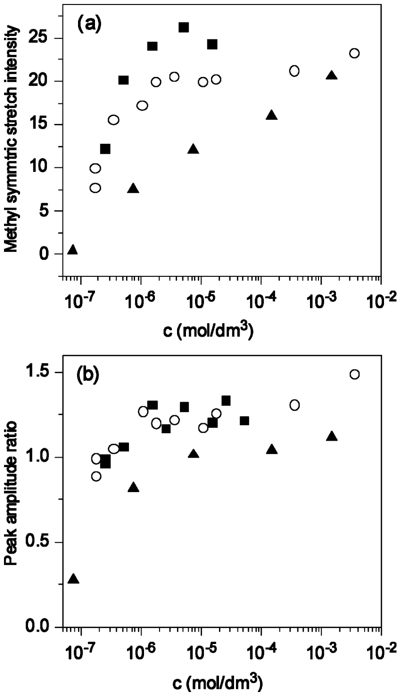

Figure 4. The ssp intensity of the methyl symmetric stretch (a) and the ratio, *R*, of the methyl symmetric to antisymmetric stretch ssp amplitudes (b) as a function of bulk molar concentration for adsorbed Pluronic 6100 (■), 6400 (○), and 6800 (▲) layers.

Table 2. Fitted Peak Positions and Line Widths (ω_m, Γ_m) for the Pluronics

mode	ω_m [cm^{-1}]	Γ_m [cm^{-1}]
backbone CH stretch	2860	12.5
backbone CH stretch	2880	12.5
PPO block CH$_3$(s)	2942	7
PPO block CH$_3$(as)	2971	7

The lowest of these concentrations lies below the region of almost constant surface pressure, and the next one is within this region, whereas the highest concentration is above the constant surface pressure region. The sum-frequency spectra obtained from the adsorbed layers of the other two Pluronic copolymers—6400 and 6800—are very similar. Our ssp spectra also very closely resemble the sum-frequency spectra of Pluronics published by Chen et al.[26] In each case the ssp spectrum is dominated by a pair of peaks at 2942 and 2971 cm^{-1}. The intense peak at 2942 cm^{-1} is assigned to the symmetric stretch mode of the side chain methyl groups of the PPO block, while the lower intensity peak at 2971 cm^{-1} is attributed to the antisymmetric stretch of the same groups.[26] In the spectra presented by Chen et al. a broad peak of lesser intensity is also observed at 2865 cm^{-1}, which the authors assigned to the C−H stretch from the PPO backbone. In our spectra we also observe a broad spectral feature around 2870 cm^{-1}. Unlike Chen et al., we have only been able to model this feature using two peaks, centered at approximately 2860 and 2880 cm^{-1}. The most likely assignment for these peaks is that they arise from the CH and CH$_2$ moieties of the PPO backbone, with possible contribution of the CH$_2$ groups of the PEO block. We have fitted the spectra to eq 2 using the four peaks discussed above. The peak positions and line widths were obtained by iteratively fitting the ssp and ppp spectra of adsorbed monolayers of the three Pluronics measured at relatively high bulk concentrations (Pluronic 6100: 2.5 × 10^{-5} mol/dm^3; Pluronic 6400: 3.5 × 10^{-4} mol/dm^3; Pluronic 6800: 1.5 × 10^{-3} mol/dm^3). The parameters obtained from these fits are listed in Table 2. When investigating the effect of the bulk concentration on the sum-frequency spectra of the adsorbed layers (or in a similar fashion the effect of surface density in the case of the spread layers), these parameters were kept fixed at the values given in Table 2, and only the peak amplitudes were allowed to vary.

The intensity, according to eq 3, of the methyl symmetric stretch peak at 2942 cm^{-1} in the ssp spectrum is plotted in Figure 4a as a function of bulk molar concentration for the three Pluronic solutions. (The error on the peak intensities is estimated to be <10%.) The changes observed in the intensity of this peak can be interpreted in terms of the change of the adsorbed amount accompanied by the orientation changes of the side chain methyl groups of the PPO block. The strength of the methyl symmetric stretch mode in the ssp spectrum increases as the average tilt of the methyl groups decreases and also as the number density of the methyl groups in the adsorbed layer increases.[35] The intensity of this peak can therefore be viewed as being proportional to the amount of oriented methyl groups in the PPO block. As mentioned above, the $R \equiv |A_{\mathrm{ssp,s}}/A_{\mathrm{ssp,as}}|$ ratio of the methyl symmetric stretch and the antisymmetric stretch amplitudes from the ssp spectra can be used to obtain information about the orientation of the methyl groups.[33,34] A higher peak ratio implies that the methyl groups are either tilted by a smaller angle with respect to the surface normal or that the methyl groups possess a narrower orientational distribution. As seen from Figure 4a, the behavior of Pluronic 6800 is different from the two other Pluronic compounds. With increasing bulk concentration, the sum-frequency intensity is first increasing and then above ~10^{-6} mol/dm^3 seems to approach a limiting value for Pluronics 6100 and 6400 that bear shorter PEO chains. We should note here that if the unit of % w/w is used for the

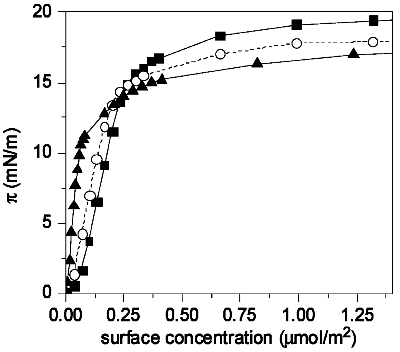

Figure 5. Surface pressure of Pluronic 6100 (■), 6400 (○), and 6800 (▲) layers obtained by dropwise spreading on a water surface.

concentration in the sum-frequency intensity plots, our data for Pluronic 6400 very closely resemble those obtained by Chen et al. (see Figure 3 of ref 26). On the other hand, the values for Pluronic 6800 are steadily increasing with the bulk concentration although the intensities are significantly lower at any given bulk concentration, indicating the presence of a smaller amount of oriented PPO blocks in the adsorbed layer. A similar behavior can be observed in the peak ratio, *R*, plotted in Figure 4b.

The change in the slope of the surface pressure vs molar concentration graphs observed for Pluronic 6400 and 6100 (Figure 1) might be the indication of a pseudo-phase transition connected to a conformational change of the block copolymer molecules in the surface layer. The surface pressure range where this transition appears is between 20 and 22 mN/m. Such behavior as a function of surface concentration is predicted for block copolymer adsorption from a theoretical model[36,37] developed for multiblock copolymers based on the scaling theories[38,39] and observed for PEO−PPO−PEO triblock copolymers, where the phase transition indicated by the surface pressure was found to be in accordance with the strong increase in the ellipsometric thickness of the layer due to conformational change and with morphological properties (BAM) as well.[14]

The onset of almost constant sum-frequency intensity at 10^{-6} mol/dm^3 for Pluronics 6100 and 6400 coincides with the beginning of the region of constant surface tension observed for these polymers (Figure 1), in accord with the notion of a possible pseudo-phase transition in connection with a change in polymer conformation. For Pluronic 6800 both the surface pressure and the sum-frequency intensity show a monotonous increase with the bulk polymer concentration without a discernible change of slope, implying that in this concentration range no conformational change is present for Pluronic 6800 in which the relative sizes of the hydrophilic and hydrophobic blocks are very different as compared to the two other Pluronics. The lower peak amplitude ratio for Pluronic 6800 indicates that the orientation of the methyl groups in the PPO blocks parallel to the surface normal is less pronounced for Pluronic 6800 with long PEO blocks.

Spread Layers. Surface pressures achieved by dropwise spreading of Pluronic solutions onto the water surface are displayed as a function of surface concentration of the three Pluronics in Figure 5. Lower surface pressures can be reached by spreading various amounts of Pluronic on the water surface than by adsorption from aqueous solutions in the concentration range studied here. From Figure 5 it appears that a saturation value is reached above ~1 μmol/m^2. The values of the saturation surface pressures correspond to the hydrophobicity order of the three Pluronics (6100 > 6400 > 6800) deduced from their relative PPO content. The surface pressure at the low surface concentrations, however, presents the opposite order, as Pluronic 6800 increases the surface pressure most effectively up to 0.2 μmol/m^2.

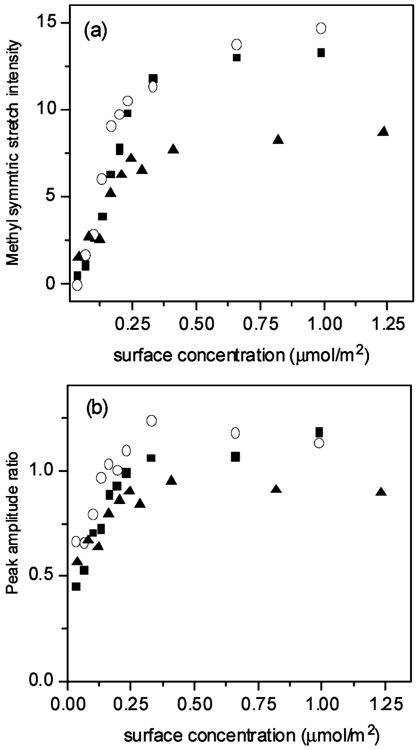

Figure 6. The ssp intensity of the methyl symmetric stretch (a) and the ratio, *R*, of the methyl symmetric to antisymmetric stretch ssp amplitudes (b) as a function of surface density for the spread layers of Pluronic 6100 (■), 6400 (○), and 6800 (▲).

The sum-frequency ssp intensities of the symmetric stretch mode of the side chain methyl groups of the PPO block are plotted as the function of surface molar concentration in Figure 6a. Initially, the intensity of the methyl symmetric stretch increases rapidly with the Pluronic surface concentration. At about 0.2 μmol/m^2 surface concentration a significant decrease in the slope is observed, in the same range where the reversal in the order of the surface pressures takes place. Considering that the central block is identical in the three Pluronics, the same surface concentrations represent the same surface number density of PPO blocks for the three polymers. As a result, at a given surface concentration similar sum-frequency intensity would be expected for Pluronic 6100, 6400, and 6800. Conversely, the most hydrophilic Pluronic 6800 gives rise to significantly lower sum-frequency intensity above ~0.2 μmol/m^2 than the two others, although the concentration of the PPO blocks in surface layer is the same in all the cases.

The surface molar concentration dependence of the methyl symmetric to antisymmetric stretch ssp amplitude ratio, *R*, is plotted in Figure 6b for the three Pluronics. The initial increase of the amplitude ratio points to the increasing orientation of the methyl groups in the PPO block with increasing surface concentration below ~0.2 μmol/m^2. Above this surface concentration the amplitude ratio remains constant, and this final value of the amplitude ratio is somewhat smaller for Pluronic 6800 with the longest PEO segments than for Pluronics 6100 and 6400.

The observation that a reversal in the order of the surface pressures of the three Pluronics takes place in a narrow surface concentration range is in accordance with the interpretation of interfacial properties of spread PEO-containing block copolymer layers based on the scaling theory.[40,41] In the low concentration range the block copolymers lie flat parallel to the surface plane (the so-called pancake configuration) with a significant contribution of the PEO chains to increase the surface pressure. In this range, raising the surface concentration by dropwise spreading of the three Pluronics leads to an increase of both the number density of and the orientation of side-chain methyl groups in the PPO blocks as seen from the sum-frequency intensity and amplitude ratio data of Figure 6a,b. The 0.2−0.25 μmol/m^2 concentration range, where the order of the surface pressures of the three Pluronics becomes reversed and follows the hydrophobicity order and where the decrease in the slope of the sum-frequency intensity curves occurs, corresponds to a transition from flat saturated monolayer to a brushlike configuration. Above this coverage, the polymer chains are compressed and PEO blocks are expected to adopt a high-density layer forced to stretch into the water subphase,[38,39] although a partial solubilization of PPO blocks by the expelled PEO segments cannot be excluded either. In this range further increasing the surface concentration leads to no increase of orientation of the side-chain methyl groups, and the number density of oriented methyl groups increases only very slightly. Our findings also indicate that there is a difference between the structure of the Pluronic layer depending on the length of PEO chains in a given range of surface concentration. The lower final values of the amplitude ratio for Pluronic 6800 implies that the long PEO chains might hinder the orientation of methyl groups of the central PPO block, possibly through partial solubilization, as mentioned above.

Compressed Langmuir Layers. Surface pressure−area isotherms were obtained compressing and expanding the Langmuir monolayer of Pluronic 6100, 6400, and 6800 (Figure 7) formed on the surface of a water subphase. The Langmuir films presented a notable stability. The repetition of the compression−expansion cycle resulted in similar isotherms without a detectable shift that would indicate the loss of the material from the surface. The zero surface pressure recorded by the second Wilhelmy plate sensor mounted at the rear side of the barrier supports that there is no considerable dissolution of Pluronic in the course of the measurement in the surface pressure range used here. This finding is in accordance with other authors' opinions[8,10,14,15] emphasizing the stability of spread PEO and PEO-block copolymer films unless high surface concentration (>1 μg/cm^2) or intense compression is applied.

A significant hysteresis between the compression and expansion parts of the isotherms can be observed for the Pluronic 6100 and 6400 layers, while the degree of hysteresis is much lower for the 6800 copolymer. Since we applied a fairly high barrier speed (24 cm^2/min), it is reasonable to assume that the hysteresis is due to structural rearrangements that are slower than the time scale of the surface area change. It was demonstrated in another type of compression−expansion process when the barrier was moved in consecutive steps stopping for 300 s intervals that the surface pressures are dynamic ones measured, especially upon expansion of the layer. The increase of these values during the relaxation time proved to be proportional to the extent of hysteresis.

The surface concentration dependences of both the sum-frequency methyl symmetric stretch intensity and the symmetric-to-antisymmetric stretch amplitude ratio of the compressed Langmuir layers are shown in Figure 8. These curves present a similar trend to that observed for the films prepared by dropwise spreading, namely rapid increase at low surface molar concentrations, followed by a very slowly increasing, almost constant region. The different organization of the PPO block of Pluronic 6800 compared to the PPO blocks of polymers with short PEO chains (Pluronics 6400 and 6100) is evident. In the concentration range of above 0.2 μmol/m^2 both the symmetric stretch intensity and the amplitude ratio are considerably lower for the polymer Pluronic 6800 with the long PEO blocks.

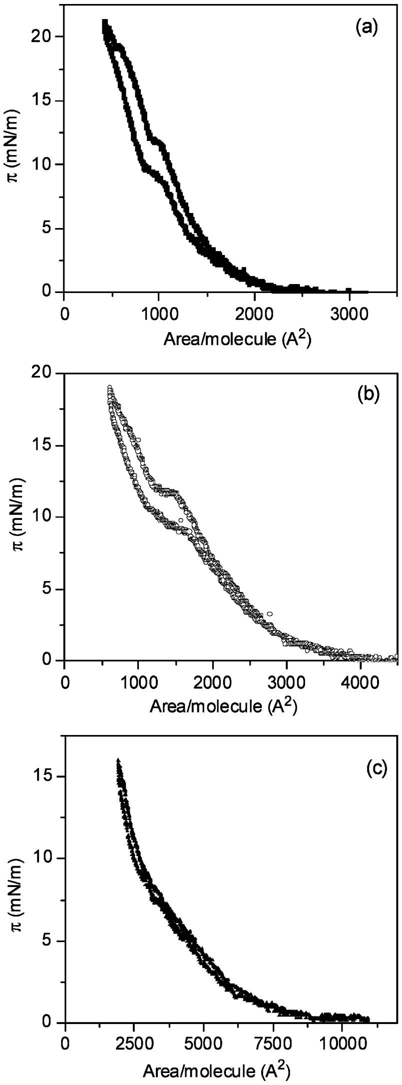

Figure 7. Surface pressure−area isotherms of Pluronic 6100 (a), 6400 (b), and 6800 (c).

The shapes of the surface pressure−area isotherms (Figure 7) reflect an expanded type monolayer with a transition and a condensed like state at high surface concentrations. A short but characteristic pseudoplateau region appears in the case of the Pluronics with short PEO chains, comprising 3−3 and 13−13 PEO units for Pluronic 6100 and 6400, respectively. The various regions of the isotherm can be assigned to different conformations or conformational transitions of the polymer chains interpreted by the scaling theory.[38,39] According to that, at low coverage the triblock copolymer remains at the air−water interface anchored by the central PPO block, while the PEO blocks adopt a flattened conformation. As the monolayer is compressed, we see a pseudoplateau which is a signature of a conformational change, probably the partial dissolution of PEO chains which start to extend into the water subphase because the polymer chains overlap. Upon further compression there is a steep increase in surface pressure where the overlap of PPO segments and also the PEO chains extending into the subphase dominate the structure. Comparing Pluronic 6100 and 6400

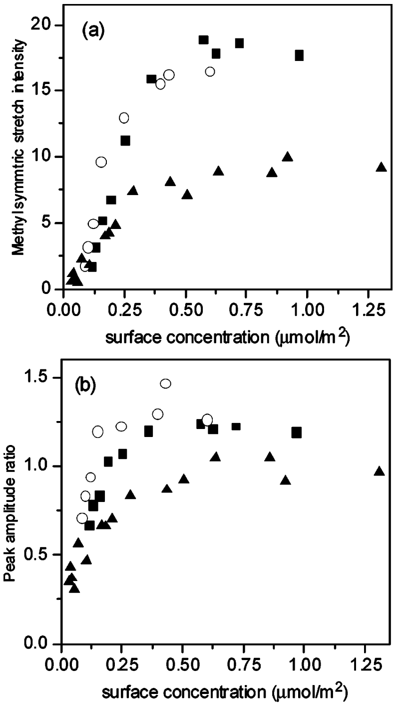

Figure 8. The ssp intensity of the methyl symmetric stretch (a) and the ratio, *R*, of the methyl symmetric to antisymmetric stretch ssp amplitudes (b) as a function of surface density for the compressed Langmuir layers of Pluronic 6100 (■), 6400 (○), and 6800 (▲).

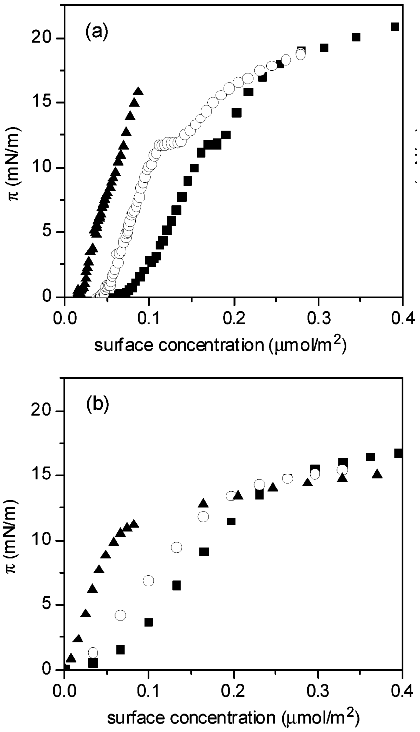

Figure 9. Surface pressure as a function of surface concentration of Pluronic 6100 (■), 6400 (○), and 6800 (▲) spread at the water surface as a Langmuir film (a) and by stepwise addition (b).

layers, we see that the transition is more first-order type as the PEO chain length increases, similarly that observed previously for PS−PEO block copolymers.[40,42]

The isotherm of Pluronic 6800 exhibits two main features different from the other Pluronics: the small hysteresis and the absence of clear phase transition connected to flat to brush conformational change. According to the molecular composition (56/30/56), the central PPO block represents a small contribution to the surface behavior of this polymer. The layer is highly compressible with steadily increasing dilatational modulus. Probably there is no distinctive conformational change upon compression associated with a narrow concentration range. The weak hysteresis is in conformity with the assumption of a gradual and reversible conformational change. It can be concluded that the relative length of various blocks in the polymer molecule is of paramount importance in the development of brush conformation.

Presenting the surface pressures of the Langmuir layers as a function of surface concentrations allows the comparison with the corresponding results of spread films obtained by stepwise addition (Figure 9) and also with the sum-frequency results. Both the surface pressure values and the shapes of the curves show that the properties of the layers are highly dependent on the way of manipulation of the surface concentration. The surface pressure of the compressed Langmuir layer is significantly higher than in the case of spread films where the surface coverage was changed by dropwise increasing the amount of spread material. The considerable difference in the structure of polymer layers is also shown by the presence or absence of the plateau region which is the sign of a phase transition. In the case of stepwise addition of spread Pluronic only the reverse of the order of the three polymers indicated the possible change in the structure of surface layer as a function of surface concentration. This phase transition, characterized by plateaus with constant surface pressure at 0.11−0.13 μmol/m^2 for Pluronic 6400 and at 0.16−0.18 μmol/m^2 for Pluronic 6100, is not obvious in the plots of the sum-frequency intensity and amplitude ratio. This would imply that the phase transition is mainly connected to a conformational change of the PEO chains which has a relatively small influence on the conformation of the central PPO block.

The above experiences turn our attention to the importance of kinetic aspects of monolayer formation in the case of polymers. Preparing a Langmuir film from polymers, special care must be taken to achieve not only the complete spreading of the polymer solution on the water surface but also the complete expansion and disentanglement of the polymer molecules. The high concentration of the spreading solution and the fast evaporation of the solvent might contribute to the freezing of the structure of polymer layer, resulting in a highly nonequilibrium conformation and various nanoscale surface morphologies.[42] A probable explanation of the difference observed in Figure 9 can be that larger degrees of chain entanglement occurred upon the consecutive addition of the material, thereby restricting the thermodynamically favorable spreading of the PEO blocks. Consequently, there is no such clear sign of conformational changes (pseudo-phase transition) as it is presented by the expanded Langmuir layers.

Comparison of Layer Structure. The influence of the method of surface film formation on the structure of the Pluronic layer at the air/water interface can be examined by comparing the sum-frequency results obtained for the adsorbed and spread films. The ratio, *R*, of the methyl symmetric-to-antisymmetric stretch amplitudes in the ssp spectra can be used to characterize the structural change of the molecules with the bulk or surface concentrations. In the case of the adsorbed layers this parameter exhibits a weak increase and then reaches a saturation value as the function of bulk concentration. The surface concentration dependence of the amplitude ratio shows a similar trend for both the dropwise spread films and the compressed Langmuir layers. The ratio increases within a narrow concentration range and remains almost constant for surface concentrations greater than 0.3 μmol/m^2. It should be noted that the amplitude ratios characterizing the orientation of methyl groups of the PPO blocks of the Pluronics are relatively low values, indicating that the methyl groups are tilted significantly away from the surface normal and that they also possess a rather broad orientational distribution. Considerably higher ratios have been obtained for methyl groups situated at the end of longer alkyl side chains of comb polymers.[33]

The three Pluronic compounds of different compositions used in our study bear the same PPO central block. In our analysis of the sum-frequency spectra we concentrated on the two peaks assigned to the normal vibrations of the methyl groups. As the methyl groups are only present in the PPO blocks, similar sum-frequency intensities and orientational parameters would be expected for the three Pluronics. However, the behavior of Pluronic 6800 differs significantly from the two other Pluronics as it exhibits lower symmetric to antisymmetric stretch amplitude ratios. This relation was found to be valid independently of the film preparation method. The methyl groups of the central PPO block seem to be less oriented in Pluronic 6800 than in Pluronics 6400 and 6100, which have shorter PEO chains. That is a clear indication of the influence of hydrophilic blocks on the structure of the whole molecule at the interface. This effect appears to be governed by the ratio of lengths of the PPO and PEO blocks.

A similar deviation of the surface behavior of Pluronic 6800 from the two other block copolymers is observed in the tensiometric measurements. The phase transition related to the flat-to-brush conformational change of the triblock copolymer molecules in the surface layer was detected for Pluronics 6100 and 6400, while Pluronic 6800 shows a gradual change of surface pressure with concentration without the sign of a phase transition. The effect of the hydrophobic central block on the surface pressure and surface dilatational properties of the layer is suppressed when the relative length of the hydrophilic blocks is high.

In order to facilitate comparison between the results obtained for the different preparation methods, the sum-frequency amplitude ratio is plotted in Figure 10 as a function of the surface pressure for the adsorbed and compressed films of the three Pluronics. In all three cases the amplitude ratio increases with increasing surface pressure; however, the shapes of the curves are different, reflecting the differences in the surface behavior of the Pluronics. In the case of Pluronics 6100 and 6400 the phase transition from flat to brush conformation at ~12 mN/m is indicated by a decrease in the slope of the amplitude ratio vs surface pressure plot, while the opposite trend is observed for Pluronic 6800. For Pluronic 6400 the plateau region of the surface pressure vs surface concentration diagram (Figure 9a) extends for a larger range of surface concentrations than for Pluronic 6100. Correspondingly, Pluronic 6400 exhibits a more pronounced change in the slope of the amplitude ratio vs surface pressure plot at the phase transition where the PEO blocks start to extend into the subphase. In the case of Pluronic 6100 the phase transition is accompanied by a smaller change in the orientation of the methyl groups of the PPO blocks. For Pluronic 6800 the surface pressure vs surface concentration diagram (Figure 9c) does not show a phase transition, and at each surface pressure the value of the peak amplitude ratio is considerably lower than for the other two Pluronics. This indicates that due to the different block ratio of Pluronic 6800 the contribution of the PEO blocks to the surface pressure is greater, and as a consequence relatively large surface pressure is attained without a significant orientation of the methyl groups of the PPO block.

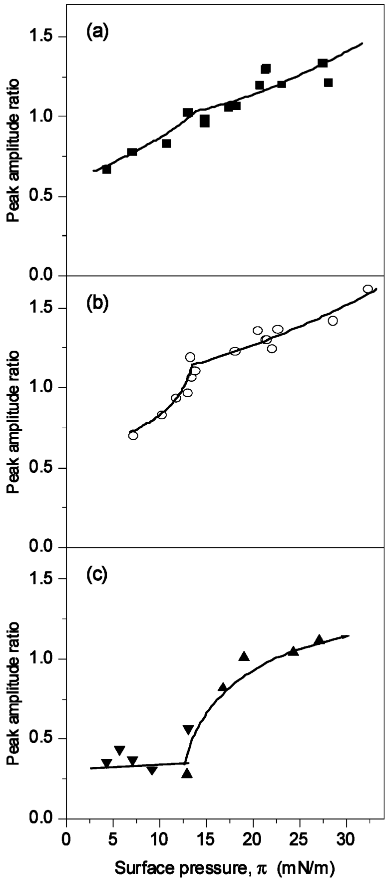

Figure 10. Ratio, *R*, of the methyl symmetric-to-antisymmetric stretch ssp amplitudes as a function of surface pressure for compressed Langmuir films and adsorbed layers of (a) Pluronic 6100 (■), (b). Pluronic 6400 (○), and (c) Pluronic 6800 (▲).

The sum-frequency results also indicate that the earlier models based on the scaling theory cannot be used for polymers with all block length ratios. Whereas for Pluronics 6100 and 6400 the results of both the surface tension and the sum-frequency measurements could be well interpreted on the basis of the above models, the surface behavior of Pluronic 6800, where the PEO blocks are almost twice as long as the central PPO block, is quite different. The methyl groups of the PPO block were found to be less oriented, and additionally their orientation increases almost linearly with surface concentration, indicating there is no sudden change of conformation in within a narrow concentration range. Thus, both the surface tension and the sum-frequency results indicate that in terms of the interfacial structure Pluronic 6800 cannot be described with the models developed for block copolymer layers.

Finally, we note that while our results for Pluronics 6100 and 6400 at low surface pressures largely agree with the conformational changes proposed in ref 15, we do not observe significant changes in the amplitude ratio vs surface pressure plot above at high surface pressures, although a plateau with constant surface pressure of 20 and 22 mN/m is present in the surface pressure vs bulk concentration curves. According to the model of ref 15, in this surface pressure range the PPO blocks start to form loops and tails in the aqueous PEO layer. A possible explanation of the sum-frequency results might be that desorption of PPO segments from the interface is accompanied by an increased ordering of the methyl groups in the remaining PPO blocks, resulting in a slowly increasing amplitude ratio.

Conclusions

Surface layers of triblock copolymers Pluronic 6100, 6400, and 6800 were prepared by adsorption and by two spreading methods at the air/water interface in order to get information on the effects of polymer composition and film formation method on the structure of the surface layers. The behavior of the three copolymers was characterized by surface pressure measurements and sum frequency spectroscopy and compared as a function of bulk and surface concentrations. The surface density and conformation of the polymers were deduced from the vibrational band intensities of the methyl groups of the central hydrophobic PPO block. The intensity of the methyl symmetric stretch peak at 2942 cm^{-1} in the ssp spectrum is related to the amount of oriented methyl groups, while the methyl symmetric stretch to methyl antisymmetric stretch amplitude ratio of the ssp spectra can be applied to the orientation analysis of methyl groups in the PPO block.

As a general trend we found that both the methyl symmetric stretch intensity and the methyl symmetric to asymmetric amplitude ratio, R, increase with the bulk or surface concentration. It is also a common feature of the layers formed by the various methods that above a given concentration Pluronic 6800 with long PEO chains exhibits lower sum-frequency intensities and R values than the two other Pluronic compounds. This indicates that the orientation of methyl groups in the central PPO block is influenced by the presence of sufficiently long PEO chains. A plausible explanation for the observed reduced orientation could be the partial solubilization of the central PPO block by the PEO chains.

A clear indication of a surface phase transition was observed by tensiometry for the adsorbed and the compressed Langmuir films of Pluronic 6100 and 6400. This phase transition is described as a flat to brush conformational change of the block copolymers by reference to the position of PEO chains. In the flat (or pancake) conformation both the hydrophobic PPO blocks and the hydrophilic PEO blocks block lie parallel to the surface plane, whereas in the brush conformation the PEO blocks penetrate the subphase. Pluronic 6800 did not show this phase transition, probably due to the very different relative block sizes as compared to the two other Pluronics. The fact that the presence of this phase transition is not apparent in the sum-frequency spectra of the compressed Langmuir films supports the notion that it is mainly connected to the conformational change of the PEO chains (penetration into the subphase) which has no appreciable influence on the conformation of the central PPO block.

The different surface behavior of Pluronic 6800 from the two other Pluronics represents the dependence of the structure of the surface layer on the relative block sizes. The deviation is manifested in the following phenomena: (i) the surface pressure of the adsorbed or spread layers is gradually increasing with bulk or surface concentrations without a pseudoplateau range that would indicate the conformational phase transition; (ii) above a given surface concentration the side methyl groups of Pluronic 6800 are less oriented compared to the Pluronics with shorter PEO chains; (iii) the Langmuir films of Pluronic 6800 show a gradual change of surface pressure with surface concentration resulting in a compressibility without extreme values; (iv) the hysteresis upon compression and expansion of the Langmuir film of Pluronic 6800 is smaller than of the two other Pluronics. This points to the absence of dynamic effects involving a distinct conformational change of Pluronic 6800 in the time scale of our measurement.

Thus, both the surface tension and the sum-frequency results indicate that in terms of the interfacial structure Pluronic 6800 cannot be described with the models developed for block copolymer layers.

The differences in the surface properties of the spread layers obtained by consecutive addition of the polymers onto a constant surface area and of the compressed Langmuir layer revealed some kinetic aspects of monolayer formation in the case of polymers. In the case of the spread films the possible large degree of nonequilibrium chain entanglements might hinder the accomplishment of preferred orientation and conformational change.

Acknowledgment. Dr. M. Szesztay is thanked for the realization of the GPC experiments and for helpful discussions. The authors are grateful to Mrs. Hórvölgyi for valuable assistance and to Dr. Zoltán Pászti for fruitful discussions about the sum-frequency results and their interpretation. This work was supported by the Hungarian Scientific Research Fund (OTKA No. T047368, T060197).

References and Notes

(1) Petty, M. C. *Langmuir-Blodgett Films;* Cambridge University Press: New York, 1996.
(2) Bhushan, B. *Springer Handbook of Nanotechnology*; Springer-Verlag: Berlin, 2004.
(3) Kajiyama, T.; Aizawa, M. *New Developments in Construction and Functions of Organic Thin Films*; Elsevier: Amsterdam, 1996.
(4) Huck, W. T. S. *Nanoscale Assembly Chemical Techniques*; Springer Science + Business Media: Berlin, 2005.
(5) Crisp, D. J. Surface Fims of Polymers In *Surface Phenomena in Chemical Biology*; Danielli, J. F., Pankhurst, K. G. A., Riddiford, A. C., Eds.; Pergamon Press: London, 1958; pp 23−54.
(6) Jones, R. A. L.; Richards, R. W. *Polymers at Surfaces and Interfaces;* Cambridge University Press: New York, 1999; pp 317−371.
(7) Sauer, B. B.; Yu, H.; Yazdanian, M.; Zografi, G.; Kim, M. W. *Macromolecules* **1989**, *22*, 2332−2337.
(8) Saito, W.; Mori, O.; Ikeo, Y.; Kawaguchi, M.; Imae, T.; Kato, T. *Macromolecules* **1995**, *28*, 7945−7946.
(9) Kawaguchi, M.; Tohyama, M.; Mutoh, Y.; Takahashi, A. *Langmuir* **1988**, *4*, 407−410.
(10) Noskov, B. A.; Akentiev, A. V.; Grigoriev, D. O.; Loglio, G.; Miller, R. *J. Colloid Interface Sci.* **2005**, *282* 38−45.
(11) Vieira, J. B.; Li, Z. X.; Thomas, R. K.; Penfold, J. *J. Phys. Chem. B* **2002**, *106*, 10641−10648.
(12) Mouri, E.; Matsumoto, K.; Matsuoka, H. *Langmuir* **2005**, *21*, 1840−1847.
(13) Kawaguchi, M.; Hirose, Y.; Kato, T. *Langmuir* **1996**, *12*, 3523−3526.
(14) Munoz, M. G.; Munroy, F.; Ortega, F.; Rubio, R. G.; Langevin, D. *Langmuir* **2000**, *16*, 1083−1101.
(15) Blomqvist, B. R.; Warnheim, T.; Claesson, P. M. *Langmuir* **2005**, *21*, 6373−6384.
(16) Harris, J. M., Zalipsky, S., Eds.; *Poly(ethylene glycol) Chemistry and Biological Application;* American Chemical Society: Washington, DC, 1997.
(17) Gölander, C.-G.; Kiss, É. *J. Colloid Interface Sci.* **1988**, *121*, 240−253.
(18) Glass, J. E. *Polyethylene oxide and protein resistance: principles, problems, and possibilities*; American Chemical Society: Washington, DC, 1994.
(19) Kiss, É.; Takács, M. G.; Bertóti, I.; Vargha-Butler, E. I. *Polym. Adv Technol.* **2003**, *14*, 839−846.
(20) McRitchie, F. *Chemistry at Interfaces*; Academic Press: San Diego, 1990; pp 146−153.
(21) Kawaguchi, M.; Komatsu, S.; Matsuzumi, M.; Takahashi, A. *J. Colloid Interface Sci.* **1984**, *102*, 356−360.
(22) Bailey, F. E., Jr.; Koleske, J. V. *Poly(Ethylene oxide)*; Academic Press: New York, 1976.
(23) Kuzmenka, D. J.; Granick, S. *Macromolecules* **1988**, *21*, 779−782.
(24) Richards, R. W.; Taylor, M. R. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 601−610.
(25) Chen, C. Y.; Even, M. A.; Wang, J.; Chen, Z. *Macromolecules* **2002**, *35*, 9130−9135.
(26) Chen, C. Y.; Even, M. A.; Chen, Z. *Macromolecules* **2003**, *36*, 4478−4484.
(27) http:/www.ekspla.com/products/SFG/sfg1.htm.

(28) Shen, Y. R. In *Frontiers in Laser Spectroscopy*; Proceedings of the International School of Physics ‘‘Enrico Fermi,” Course CXX; Hänsch, T.; Inguscio, M., Eds.; North Holland: Amsterdam, 1994; pp 139−165.
(29) Pászti, Z.; Wang, J.; Clarke, M. L.; Chen, Z. *J. Phys. Chem. B* **2004**, *108*, 7779−7787.
(30) Himmelhaus, M.; Eisert, F.; Buck, M.; Grunze, M. *J. Phys. Chem. B* **2000**, *104*, 576−584.
(31) Bell, G. R.; Bain, C. D.; Ward, R. N. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 515−523.
(32) Wang, J; Pászti, Z.; Even, M. A.; Chen, Z. *J. Am. Chem. Soc.* **2002**, *124*, 7016−7023.
(33) Harp, G. P.; Rangwalla, H.; Yeganeh, M. S.; Dhinojwala, A. *J. Am. Chem. Soc.* **2003**, *125*, 11283−11290.
(34) Rao, A.; Rangwalla, H.; Varshney, V.; Dhinojwala, A. *Langmuir* **2004**, *20*, 7183−7188.
(35) Varga, I.; Keszthelyi, T.; Mészáros, R.; Hakkel, O.; Gilányi, T. *J. Phys. Chem. B* **2005**, *109*, 872−878.
(36) Aguie-Beghin, V.; Leclerc, E.; Daud, M.; Dulliard, R. *J. Colloid Interface Sci.* **1999**, *214*, 143−155.
(37) Hambardzumyan, A.; Aguie-Beghin, V.; Daud, M.; Dulliard, R. *Langmuir* **2004**, *20*, 756−763.
(38) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983−987.
(39) De Gennes, P. G. *Macromolecules* **1980**, *13*, 1069−1075.
(40) Faure, M. C.; Bassereau, P.; Lee, L. T.; Menelle, A.; Lheveder, C. *Macromolecules* **1999**, *32*, 8538−8550.
(41) Myrvold, R.; Hansen, F. K.; Balinov, B.; Skurtveit, R. *J. Colloid Interface Sci.* **1999**, *215*, 409−419.
(42) Cheyne, R. B.; Moffitt, M. G. *Langmuir* **2005**, *21*, 5453−5460.
(43) Chu, B.; Zhou, Z. In *Nonionic Surfactants*, *Polyoxyalkylene Block Copolymers*; Nace, V. M., Ed.; Marcel Dekker: New York, 1996; pp 67−143.

MA061161B