Aggregation of Poly(styrene)−Poly(ethylene oxide) Diblock Copolymer Monolayers at the Air−Water Interface

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Introduction

Amphiphilic block copolymers form an important class of materials which have attracted considerable attention because of their outstanding solution properties and a wide range of applications.[1,2] These materials are very interesting from the point of view of fundamental research, as they exhibit self-assembling properties in the presence of a selective solvent or surface.[3−7] Surface micelles at the air−water interface, of different morphologies depending on the balance between block sizes, have been directly identified by TEM and AFM for block polyelectrolytes[8,9] and for nonionic diblock copolymers.[10]

The present work was mainly motivated by a previous work on monolayers of poly(styrene)−poly(ethylene oxide), PS_m−PEO_n diblock copolymers, with varying lengths of the PEO block, spread at the air−water interface.[11] As for grafted polymers,[12−14] a pancake, a quasi-brush state, and a brush state were observed. It was found that compression−expansion cycles of the π−A isotherms superpose in the quasi-brush but not in the brush and pancake regions.[11] The hysteresis observed at low surface pressures (pancake region) increases with PEO chain length and decreases with temperature. This was attributed to the irreversible entanglement and hydration of the PEO chains when immersed in the water subphase. The hysteresis at high surface pressures—in the brush region—exhibited an unusual minimum in the expansion curve. This peculiar shape of the π−A isotherms suggests that the system undergoes a metastable regime during the expansion and finally returns to the equilibrium when the compression and the expansion curves superimpose in the quasi-brush region. The increase of π with the

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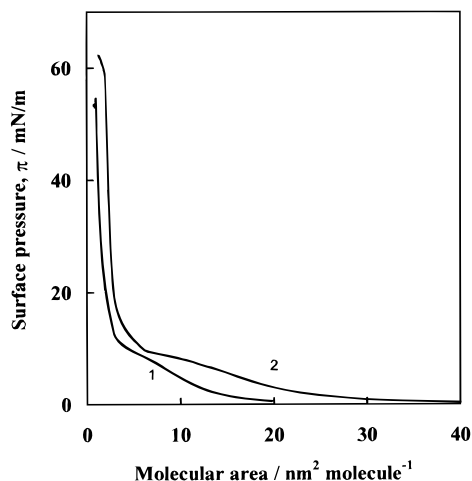
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Table 1.　Characteristics of the Polymers Used

copolymer	M_w (PS)	M_w (PEO)	m(PS)	n(PEO)	M_w/M_n
PS_{38}−PEO_{90} (ZGH1)	4000	3950	38	90	1.21
PS_{38}−PEO_{148} (ZGH2)	4000	6500	38	148	1.15
PS_{17}−PEO_{48}	1800	2100	17	48	1.06

area indicates a overexpanded monolayer due to the high cohesion and local order reached in the brush conformation which is not disrupted in the time scale of the expansion run. This effect tends to disappear with an increase of PEO length and temperature. Both effects difficult the organization of PEO chains and diminish the cohesion. To further clarify this subject, the initial work was extended to study the effect of the concentration of the spreading solution, initial surface concentration of the monolayer, and a number of other experimental variables, namely maximum surface pressure reached on the compression run, rate of the compression−expansion cycles, and number of successive cycles. The present work studies further the influence of the PEO length and shows that the minimum on the π−A isotherms of PS_{38}−PEO_{90} disappears in the presence of various amounts of stearic acid (SA). Dynamic light scattering measurements show aggregation of the block copolymers PS_{38}−PEO_{90} and PS_{38}−PEO_{148} in chloroform solutions, for the same range of concentrations used in the film balance measurements.

Experimental Section

Materials. The characteristics of the poly(styrene)−poly(ethylene oxide) diblock copolymers are presented in Table 1. The PS_{38}−PEO_{90}, PS_{38}−PEO_{90} (named ZGH1, ZGH2 in the previous paper) were synthesized in the group of Dr. G. Riess, Mulhouse, France, and kindly supplied by M. A. Winnik, University of Toronto, Canada. PS_{17}−PEO_{48} was purchased from Polymer Source, Inc. Dorval, Quebec. Stearic acid (>99%) from BDH and Chloroform (>99.4%) obtained from Rieder-de Häen were used without further purification. Water was purified with the Millipore Milli-Q system, to obtain a resistivity as high as 18 MΩ.cm, at pH 5.7.

Film Balance Measurements. The π−A isotherms were obtained by using a KSV 5000 Langmuir−Blodgett system, KSV Instruments Ltd., Helsinki, installed in a laminar flow hood. The procedure is described elsewhere.[11]

Solutions of copolymers in chloroform were prepared with concentrations in the range 0.25−2.5 g/dm³. Compression−expansion cycles were performed at speeds ranging from 5 to 125 mm²/s. The temperature of the subphase was maintained at 25.0 ± 0.1 °C by a water bath circulator. Most surface pressure−area isotherms were measured several times. The uncertainties were estimated at ± 0.2 mN/m for π and ≤ 0.05 nm² molecule⁻¹ for molecular areas.

Dynamic Light Scattering. Light scattering measurements were carried out in a standard multiangle laser light scattering equipment from Brookhaven Instruments Inc., model 2030 AT. The light source was a 35 mW He−Ne laser, which produces vertical polarized light at $\lambda = 632.8$ nm (Spectra Physics model 127). The scattering cells (10 cm³ cylindrical ampules) were immersed in a Decalin bath with temperature control by water circulation (25.0 ± 0.5 °C). The signal analyzer consists of a 128 channel autocorrelator (Brookhaven, model 2030 AT) were the last 6 channels are used for baseline calculations. The intensity autocorrelation plots were analyzed by the nonnegative least-squares method (NNLS) to obtain the distribution of relaxation times.

Results and Discussion

Length of the PEO Block. It was shown that the local minimum of the hysteresis at high surface pressures

Figure 1. Surface pressure vs area per molecule at 298 K for copolymers: $PS_{17}-PEO_{48}$ (1); $PS_{38}-PEO_{90}$ (2). The concentration of the spreading solutions used were 0.50 g/dm^3 (1); and 0.26 g/dm^3 (2). Compression rate: 10 mm min^{-1}.
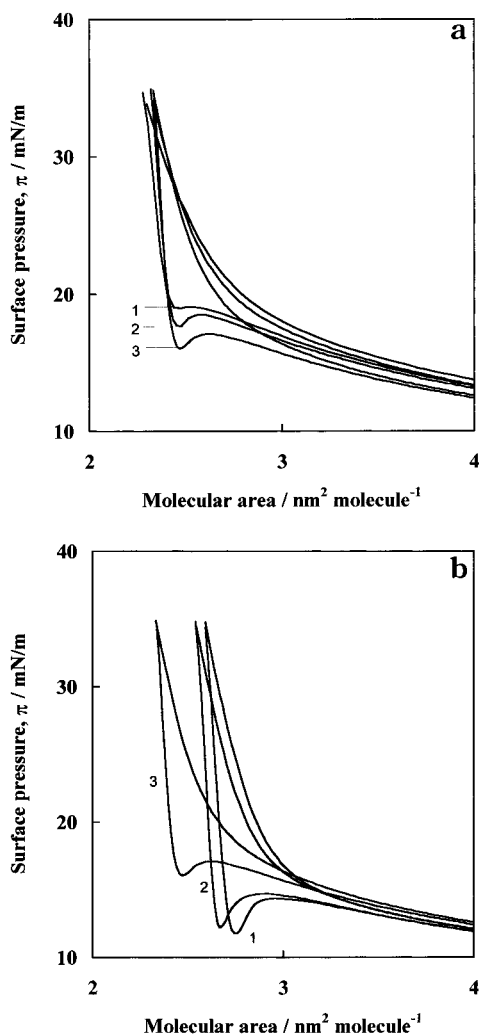

Figure 2. Compression−expansion cycles of surface pressure vs area isotherms for several molar ratios of SA/PS$_{38}$−PEO$_{90}$: 0:1 (1); 2.5:1 (2). Compression−expansion rate: 10 mm min^{-1}.

becomes more pronounced with the length decrease of the PEO block, in a series of block copolymers from PS$_{38}$−PEO$_{445}$ (ZGH4) to PS$_{38}$−PEO$_{90}$ (ZGH1).[11] To investigate how the hysteresis develops with the further decrease of the PEO block length, Figure 1 shows the isotherms of the PS$_{17}$−PEO$_{48}$ and PS$_{38}$−PEO$_{90}$ block copolymers. Since our film balance does not allow an area compression factor higher than about 10, both isotherms are composed of two parts (obtained from independent experiments) which match each other perfectly. Surprisingly, the compression and the subsequent expansion curves of PS$_{17}$−PEO$_{48}$ superpose perfectly in all regions. There is no hysteresis at both low and high surface pressures, contrary to the expectation based on previous results. The overall shape of the $\pi-A$ isotherm for the shorter diblock copolymer (curve 1) is similar to the one of PS$_{38}$−PEO$_{90}$ (curve 2), exhibiting the same regions, which can be ascribed to different conformations of the polymer chains:[11,12] a pancake structure at low surface pressures and high areas when the isolated chains are adsorbed by both the PS globule and the PEO segments at the interface; an intermediate structure, quasi-brush, when the PEO segments are solubilized in the subphase; and finally a brush developed at low surface areas when the PEO chains are obliged to stretch away from the interface to avoid overlapping. At surface pressures in the range 9−10 mN/m there is a transition between a high-density pancake and a quasi-brush regime (solubilization of the PEO blocks).[15] The quasi-brush structure of PS$_{17}$−PEO$_{48}$ in the range 12−20 mN/m is more condensed (higher slope) than the corresponding structure of PS$_{38}$−PEO$_{90}$ in the range 10−15 mN/m. Curve 1 shifts to lower areas, when compared with curve 2, due to the fact that the PS and PEO blocks are approximately half the length of those in PS$_{38}$−PEO$_{90}$. The pancake limiting area per repeat unit, obtained by the customary extrapolation of the pancake region in the compression isotherm to $\pi = 0$, is 0.31 nm^2. This value is slightly higher than the value found in the previous paper (0.27 nm^2), which is lower than the corresponding value, found in the literature, for the PEO homopolymer (0.40−0.48 nm^2).[15] These results show that the density of the pancake (where the PS globule contribution is negligible) is higher for the PS$_m$−PEO$_n$ block copolymers than for the PEO homopolymer. The hysteresis observed in the brush region for PS$_{38}$−PEO$_{90}$ (see
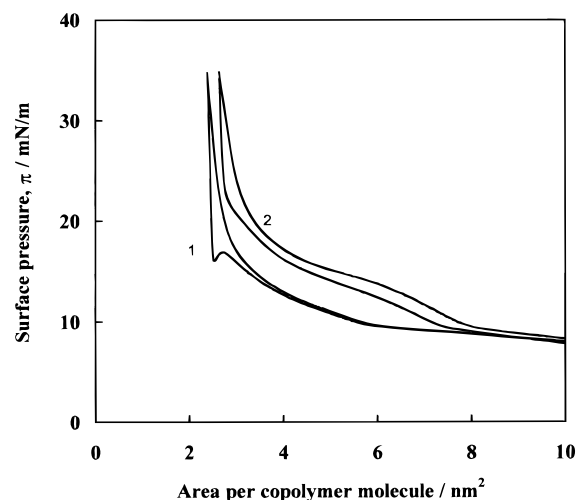
Figure 3), but not for PS$_{17}$−PEO$_{48}$, indicates that there is a critical length of the PEO$_n$ block (48 < n < 90) required to promote the hysteresis. Furthermore, the PS$_{17}$−PEO$_{48}$ expansion isotherm does not depend on the initial surface concentration or on the concentration of the spreading solution, contrary to the results presented in the previous paper and explored below for PS$_{38}$−PEO$_{90}$.

Light Scattering Measurements. The autocorrelation traces of the PS$_m$−PEO$_n$ copolymer (PS$_{38}$−PEO$_{90}$, PS$_{38}$−PEO$_{148}$) solutions in chloroform show aggregation of the block copolymers in concentrations similar to the ones used in film balance measurements (0.25−2.5 g/dm^3). After filtration of the solutions (0.45 μm pore filter) the aggregates disappear and the autocorrelation trace show a very fast mode corresponding to isolated chains (∼2 nm radius). Nevertheless, the aggregates reappear in the filtered solutions some days after. The number of aggregates increase with polymer concentration without a significant change of its dimensions. Contrary to the observations with copolymers PS$_{38}$−PEO$_{90}$ and PS$_{38}$−PEO$_{148}$, solutions of the PS$_{17}$−PEO$_{48}$ copolymer in the same concentration range do not show aggregates.

The autocorrelation traces of the aggregated solutions are complex (they show at least a bimodal distribution), and the aggregates cannot be associated with single micelles or aggregates of micelles. Nevertheless, the autocorrelation traces show that the dimensions of the aggregates increase with the length of the PEO block and with the addition of stearic acid.

Addition of Stearic Acid. The effect of SA on PS$_{38}$−PEO$_{90}$ $\pi-A$ isotherms is shown in Figure 2. When SA is added to PS$_{38}$−PEO$_{90}$, the following effects were observed, being enhanced with increasing SA/polymer molar ratio: the shift of the isotherm (brush and quasi-brush regions) to high areas per copolymer molecule; the progressive vanishing of the minimum in the brush region of the expansion isotherm; the appearance of hysteresis in the quasi-brush region, which is absent in the pure PS$_{38}$−PEO$_{90}$. Evidence of interaction (miscibility) between the SA and the copolymer is given by the changes observed in the shape of the $\pi-A$ compression−expansion isotherm and by the negative deviation of the mean molecular area (0.75 ± 0.02 nm^2 molecule^{-1}) for the 2.5:1 SA/polymer molar ratio at $\pi = 35$ mN/m, relative to the average of the molecular areas of the pure components area (0.83 ± 0.02 nm^2 molecule^{-1}) at the same surface pressure. The interaction of SA molecules with the PS block seems quite
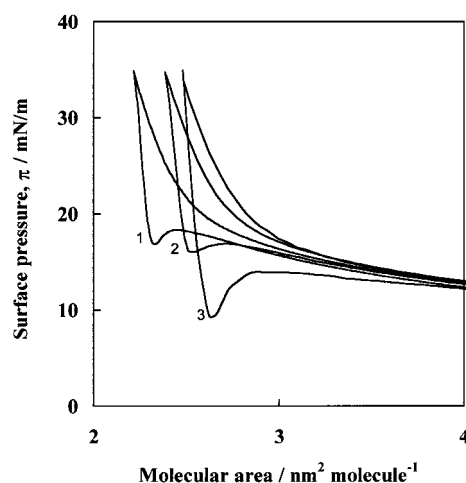
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Figure 3. Compression−expansion cycles of surface pressure vs area isotherms (a) for several initial surface concentrations of PS_{38}−PEO_{90}, obtained from the same spreading solution (0.26 g/dm^3), at the air−water interface (3.8×10^{-2} molecule/nm^2 (1); 6.4×10^{-2} molecule/nm^2 (2); 8.7×10^{-2} molecule/nm^2 (3)) and (b) for the same initial surface concentration (8.7×10^{-2} molecule/nm^2) obtained from different concentrations of PS_{38}−PEO_{90} in the spreading solution (0.26 g/dm^3 (1); 1.31 g/dm^3 (2); 2.6 g/dm^3 (3)). Curve 3 is common to both part a and part b. Compression−expansion rate: 10 mm min^{-1}.

Figure 4. Compression−expansion cycles of surface pressure vs area isotherms for several compression−expansion rates of PS_{38}−PEO_{90} monolayers: 2 mm/min (1); 10 mm/min (2); 50 mm/min (3).

unlikely as the PS does not spread at the air−water interface, remaining as an insoluble globule. The effects enumerated above are compatible with the preferential interaction of SA molecules with PEO chains. Dynamic light scattering measurements show that the addition of stearic acid to the copolymer solutions leads to the formation of very large aggregates. These aggregates result probably from the incorporation of SA molecules between the PEO chains. These effects are compatible with the shift of the isotherm to higher areas per polymer molecule and the vanishing of the minimum as the SA/polymer molar ratio increases.

The only significant effect of the SA added to PS_{17}−PEO_{48} is the shift of the isotherms to higher molecular areas.

PS_{38}−PEO_{90} Hysteresis. *Surface Concentration.* In a series of experiments in which the volume of spreading solution dispersed on the water surface was increased, it was found that the local minimum in the expansion isotherm is accentuated. Figure 3a shows the influence

of the polymer amount added to constant interface area on the hysteresis at high pressures. As the copolymer amount added increases, the isotherms start at surface concentrations progressively higher and the surface pressure of the minimum in the brush region decreases. This evidences that the compression−expansion cycle starting at very low surface concentration should be reversible in the brush and quasi-brush regions. (This could not be proved as the Langmuir trough used does not allow an area compression factor higher than about 10.)

Figure 3b shows that, when the same amount of polymer is spread at the interface, using spreading solutions of different concentrations, the surface pressure at the local minimum decreases and the isotherms are shifted to higher molecular areas, as the concentration of the spreading solution increases.

This behavior suggests the existence of some kind of aggregation of the copolymer chains, retained from the spreading solution (Figure 3b) and/or from the high-density pancake (Figure 3a), which is (at least partially) maintained in the water subphase after the PEO solubilization. There is, in both cases, a slight increase of the molecular areas of the brush when the hysteresis increases (see Figure 3). Aggregation may hinder the movements of the PEO chains immersed in the subphase and render difficult the ordering and close-packing in the brush.

Succeeding Compression−Expansion Cycles. The overall shape of the isotherm with a minimum is maintained over the successive cycles, although progressively shifted to lower areas. The surface pressure at the minimum increases significantly from the first to the second cycle, becoming almost constant after the third cycle. This shows that after the former two cycles the remaining effect is the better packing of the brushes, shifting the isotherm to lower areas.

Rate of Compression−Expansion Cycles. The linear movement of the barriers adopted for the whole study was 10 mm min^{-1}, except for curves 1 and 3 in Figure 4. When a higher sweep rate is used (50 mm min^{-1}, curve 3), the minimum becomes significantly deeper, while a five times slower rate (2 mm min^{-1}, curve 1) does not affect the minimum, only the isotherm deviates to lower areas.

The results of the successive cycles and of different sweep rates can be explained as a function of the same

time variable. The minimum is less pronounced at long time intervals after spreading, and at slower sweep rates. This means that the interaction between PEO chains decreases with time, probably due to the slow solubilization of single PEO blocks in water. Moreover, it appears that this effect allows a better packing in the brushes, and the isotherms deviate progressively to lower areas.

Maximum Surface Pressure. It was observed that the hysteresis becomes more pronounced with the maximum surface pressure reached in the compression run. This demonstrates that, the packing and the local order of the PEO are enhanced by the increase of the target surface pressure.