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Interfacial Behavior of Poly(styrene)–Poly(ethylene oxide) Diblock Copolymer Monolayers at the Air–Water Interface. Hydrophilic Block Chain Length and Temperature Influence

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Spread monolayers of poly(styrene)–poly(ethylene oxide) diblock copolymers ($\text{PS}_m\text{--PEO}_n$, $m = 38$, $n = 90$, 148, 250, and 445) have been studied at the air–water interface by measuring the surface pressure–area (π – A) isotherms at several temperatures. The π – A isotherms exhibit several regions which can be ascribed to different conformations of the polymer chains: 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 near 10 mN/m there is a transition between a high-density pancake and the quasi-brush regime. The compression and the subsequent expansion curves superpose at the transition and quasi-brush regions but not at the brush and pancake stages. This points to a high cohesion in the brush structure after compression and to some irreversible entanglement and hydration of the PEO chains when immersed in the subphase. These two local hystereses depend differently on the PEO chain length and temperature. The hysteresis observed at high surface pressures (brush conformation) decreases with the PEO length and temperature, whereas the low surface pressure hysteresis (pancake) increases with PEO chain length, decreases with temperature in the range 283–298 K, and increases in the range 298–315 K. A negative mean transition entropy change was obtained from the temperature dependence of the quasi-SSAL–quasi-brush transition. The results indicate that the extensive properties of the present diblock copolymers at the interface, such as the pancake limiting area and the mean transition entropy, when expressed by PEOmer, are independent of the PEO length.

I. Introduction

The adsorption of polymers at interfaces is relevant in many industrial applications, ranging from adhesion and lubrication to the stabilization and controlled flocculation of colloids.^{1,2} Adsorption of polymer chains at solid–liquid interfaces has been studied for soluble polymers in the liquid phase in two limiting cases: polymers that uniformly adsorb at the surface, forming a self-similar adsorbed layer (SSAL),³ and polymers with a single specific segment (usually an end group) that strongly adsorbs on the surface, while the other segments are solubilized in the liquid phase, forming a brush.⁴ The structures are quite different in the two cases; namely, the thickness of the SSAL structure is of the order of the radius of gyration of the free chain in a good solvent (R_g), while the thickness of the brush is much higher, owing to the stretching of the chains at higher surface chain densities. Both structures have been extensively studied and recently reviewed.^{4–6}

Block copolymers are particularly suited for adsorption at solid–liquid interfaces, since one block can anchor the polymer to the solid (the insoluble block), while the other (the buoy) is solubilized in the liquid phase. When the buoy has affinity for the solid, the adsorption behavior is intermediate between the two extreme cases and three regimes of absorption were first predicted by Alexander⁷ using scaling arguments: a two-dimensional dilute regime when the polymer chains are adsorbed on the substrate forming trains, loops, and tails (pancake), a three-dimensional regime when the soluble blocks are solubilized but do not overlap with each other (mushroom), and a three-dimensional regime of stretched chains (brush). A first-order transition (pancake to brush) was predicted to occur at low surface coverages when the chains start to overlap at areas per chain, A , around R_g^2 . Recently, Liguore⁸ reanalyzed the predictions of Alexander, describing the adsorbed polymer layer by the Guiselin model,⁹ where the self-similar adsorbed layer (SSAL) is viewed as a very polydisperse brush. A first-order phase transition was also predicted, but occurring at higher surface coverages than that predicted by Alexander, from a quasi-SSAL regime to a quasi-brush regime. Contrarily, no first-order phase transition was predicted by the self-consistent field theory, since a gradual change in the

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average configuration from the pancake to the brush state was observed.¹⁰

Systematic studies of copolymer adsorption have been performed mostly on solid–liquid interfaces,^{11,12} and relatively few studies have been devoted to fluid (liquid–liquid and air–liquid) interfaces.¹ Nevertheless, adsorption studies on fluid interfaces are very convenient, since the amount of polymer spread on the interface can be precisely controlled and the chain density (number of molecules per unit area) can be continuously varied with the Langmuir trough technique.

On the other hand, the structural evolution of an adsorbed polymer layer at a solid–liquid interface should be similar to that obtained by spreading a diblock on an air–liquid interface, since the insoluble block anchors the polymer at the interface while the other one can be solubilized in the liquid subphase. Therefore, these adsorption results are very important, since they mimic the adsorption of polymers at the solid–liquid interface.

In this work we use poly(styrene)–poly(ethylene oxide), PS_m–PEO_n diblock copolymers with varying length of the PEO block, spread at the air–water interface. The PS block is insoluble in water and anchors the polymer at the interface, while the PEO block is hydrophilic with some affinity for the interface. The same copolymers were studied by Bijsterbosch *et al.*¹⁰ at 296 K in a limited range of surface pressures (0–15 mN/m). They observed a transition near 10 mN/m and some hysteresis on the π – A compression–expansion cycle isotherm at low surface coverage. We have extended the π – A isotherms to higher surface pressures, and the effect of temperature was analyzed in detail. Hysteresis was observed both at low and high surface coverages. At low coverage, hysteresis increases with the length of the PEO block and is mainly attributed to the difficulty of the long chains to return to the initial conformation at the interface, after being forced to dissolve in the water subphase. This probably results from the entanglement of the chains in water at moderate surface pressures that refrains them from attaining the initial conformation at the interface, during and after expansion. The hysteresis observed at high surface pressures decreases with the PEO molecular weight and temperature. For the shorter PEO block the expansion curve goes through a minimum. We believe that during expansion the brush structure goes through a metastable (overexpanded) state, favored by the high cohesion reached at high surface pressures. As far as we are aware it is the first time this effect has been reported in the literature.

A diffuse first-order phase transition, occurring at higher surface coverage than that predicted by Alexander,⁷ was interpreted in the context of the Ligoure model.⁸ A systematic study of the influence of temperature on the π – A isotherms was performed, and the results were interpreted in terms of the effect of temperature on the solubility and mobility of the PEO chains.

II. Experimental Section

Materials. The diblock copolymers of type PS₃₈–PEO_n, named ZGH1 ($n = 90$), ZGH2 ($n = 148$), ZGH3 ($n = 250$), and ZGH4 ($n = 445$), were synthesized in the group of Dr. G. Riess, Mulhouse, France, and kindly supplied by M. A. Winnik, University of

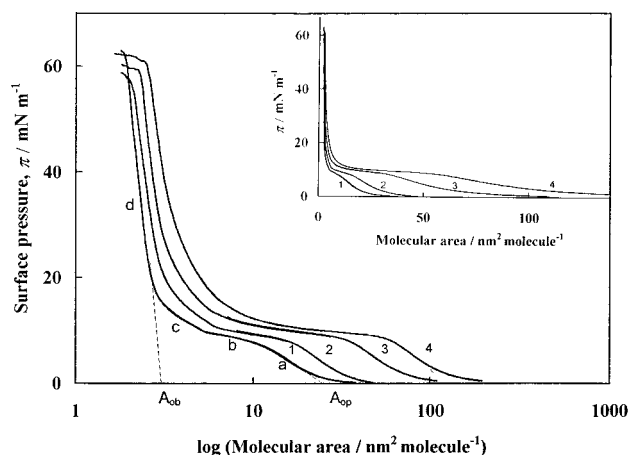


Figure 1. Surface pressure vs area per molecule at 298 K for copolymers: ZGH1(1); ZGH2 (2); ZGH3 (3); ZGH4 (4).

Table 1. Characteristics of the Polymers Used

polymer	M_w (PS)	M_w (PEO)	n (PEO)	M_w/M_n
ZGH1	4000	3950	90	1.21
ZGH2	4000	6500	148	1.15
ZGH3	4000	11000	250	1.20
ZGH4	4000	19600	445	1.17

Toronto, Canada. Chloroform, better than 99.4%, was obtained from Rieder-de Häen and used without further purification. The characteristics of these polymers are presented in Table 1. The water used in the subphase was purified with the Millipore Milli-Q system, to obtain resistivities 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 surface tension measurements were performed with the Wilhelmy plate technique. Care was taken to clean the film balance before measurements.¹³ The surface of the water was swept several times until a satisfactory isotherm of the clean surface was obtained. A blank experiment was done by spreading pure chloroform on the water surface.

Solutions of copolymers in chloroform were prepared with concentrations in the range 0.1–1.0 g/dm³. Precisely measured volumes of these solutions were spread on the water surface by using a SGE gas-tight microliter syringe. After complete evaporation of the solvent (15 min) the floating layer on the subphase was symmetrically compressed by two mobile barriers at a constant speed of 25 mm²/s. Compression–expansion cycles were performed at speeds ranging from 2.5 to 25 mm²/s. The temperature of the subphase was maintained within ± 0.1 °C by a water bath circulator. Most surface pressure–area isotherms were measured several times. The typical reproducibility at a given area was ± 0.2 mN/m.

III. Results and Discussion

The results will be presented and discussed in three parts: (1) the monolayer behavior of the four diblock copolymers at 298 K; (2) the hysteresis at high and low surface pressures; and (3) the temperature dependence of ZGH1 and ZGH4 π – A isotherms in the 283–318 K range.

III.1. Monolayer Behavior at 289 K. The surface pressure–area (π – A) isotherms of the four diblock copolymers at 298 K are presented in Figure 1. Since our film balance only allows an area compression factor of about 10, the isotherms are composed of two parts which match each other within experimental error. Several regions, which can be assigned to the polymer conformations or conformational transitions, predicted by the

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scaling theories of grafted polymers (pancake, quasi-brush, and brush),¹⁴ can be distinguished in the compression isotherms:

(a) At low surface pressures a typical liquid-expanded monolayer is observed. At low coverage the diblock copolymers remain at the air–water interface anchored by the PS block condensed in an insoluble globule, while the PEO segments, due to their affinity for water, adopt a flattened conformation with the majority of the segments in contact with the water subphase—a pancake-like structure. This structure is described by Alexander,⁷ as a two-dimensional regime that evolves to a self-similar adsorbed layer (SSAL)⁸ with an increase of pressure. The isotherms are shifted from ZGH1 to ZGH4 to progressively larger areas due to the increase of the length of the PEO block.

(b) At a surface pressure near 10 mN/m, a break or pseudoplateau can be observed in the isotherms. This pseudoplateau coincides with the one observed for the PEO homopolymer,¹⁵ and it is associated with the dissolution of the PEO chains into the water subphase.¹⁶ There is a conformational transition during which the PEO segments, anchored at the surface by the insoluble PS block, leave the surface and go into the water subphase, forming caps. The slightly continuous variation of π with A observed in the present work at the phase transition, probably due to the polydispersity of the PEO blocks, does not permit us to consider it a true first-order transition, as this would require that π remain independent of A . However, the transformation that occurs between a liquid-expanded state and a liquid-condensed state for a variety of lipid films has been considered a diffuse first-order transition because π varies continuously with A .^{17,18} If it is assumed that the pseudoplateau is a diffuse first-order transition, it can be identified with the one predicted by Ligoure⁸ from a quasi-SSAL to a quasi-brush regime. The Ligoure quasi-SSAL regime is assigned to a dense pancake structure with a considerable PEO chain overlapping. The extension of this pseudoplateau increases with the length of the PEO block because the area occupied by the pancake at the onset of the transition is strongly dependent on the PEO size. A slight increase of the transition surface pressure with the PEO block length is visible in Figure 1. The same effect was observed by Baekmark *et al.*¹⁹ with two lipopolymers of different PEO molecular weight. Sauer and Yu¹⁵ found a plateau at 8.5 mN/m for a 18K PEO and at 10.2 mN/m for 145K and 252K PEO. These results compare quite well with $\pi_t = 8.6$ mN/m for the 19.6K ZGH4.

(c) Between the plateau and the condensed state, a short region of almost constant slope is clearly visible for ZGH1 and ZGH2. The constant slope denotes some type of organization favored by the shorter PEO chains and is assigned to an intermediate stage (quasi-brush). For the ZGH3 and ZGH4 isotherms the surface pressure evolves from the plateau to the condensed region with a continuously slightly increasing slope.

(d) At high surface coverages the isotherms show a steep rise due to the high resistance to compression of the diblock polymers in the brush structure. The brush is viewed as chains of PEO tightly packed inside the water subphase, anchored at the surface by the PS block, in a three-

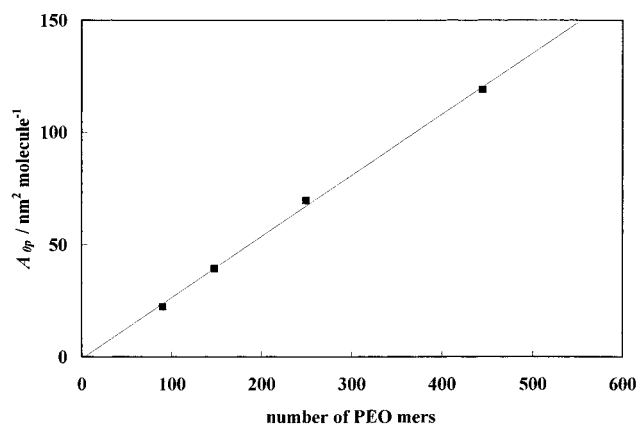


Figure 2. Limiting pancake area A_{op} vs the number of PEOmers at 298 K.

Table 2. Overview of Transition Surface Pressure (π /mN/m), Molecular Areas (A/nm^2), and Square Conformational Radius (R^2/nm^2)

polymer	π_t	A_t	A_m	A_{cal}	R_g^2	$R_{g\sqrt{A_m}}$	$R_{g\sqrt{A_{ob}}}$
ZGH1	7.5	11.5	5.9	18.0	45	2.8	3.9
ZGH2	7.5	18.4	6.3	29.6	81	3.6	4.9
ZGH3	8.3	34.5	9.6	50.0	152	4.0	6.3
ZGH4	8.6	51.7	17.4	89.0	396	4.8	9.6

dimensional regime of stretched chains. Although the studied copolymers have equal-sized PS blocks, the isotherms do not superpose at this stage, showing that the area per molecule for the brush configuration is slightly dependent on the size of the PEO block. The quasi-brush–brush transition is not clearly visible in the experimental isotherms, not even for ZGH1. Instead of a kink point or a break in the isotherm, there is a continuous change of slope.

A close analysis of the isotherms shows that the monolayers, throughout the different stages, are highly dense when compared to both the PEO homopolymer at the air–water interface and the self adsorbed polymers at the liquid–solid interface.

As shown in Figure 2 the pancake limiting area A_{op} (obtained by the customary extrapolation of the pancake region in the compression isotherm to $\pi = 0$, see Figure 1) varies linearly with the number of PEOmers. The area per PEOmer obtained from the slope (0.27 nm^2) is lower than the value found in the literature for the homopolymer (0.40 – 0.48 nm^2).¹⁵ This suggests a more compact structure for the block copolymer in the pancake structure. Furthermore, the area occupied by the PS globule seems negligible (the interception at the origin is almost zero).

The molecular area at the onset of the transition, A_t (Table 2), was determined at the crossing of the extrapolations from the straight lines fitted to the plateau and to the pancake region. With the assumption of a dense polymer monolayer at the onset of the quasi-SSAL–quasi-brush transition and an area of 0.20 nm^2 per PEO monomer,¹⁹ the molecular areas A_{cal} are obtained. The poor agreement of these values with A_t ($A_t < A_{cal}$) is a further evidence of the high density of PEO monolayer at the transition surface pressure. These values denote a strong overlapping regime (quasi SSAL) instead of a two-dimensional dilute regime (isolated pancakes). A first-order transition is predicted by the Alexander model to occur at molecular areas about R_g^2 ($R_g \approx \text{Flory radius}^{14} \approx aN^{3/5}$, where N is the monomer number and $a = 0.45 \text{ nm}$ ¹⁹ is the diameter of the PEOmer). From the comparison of data in Table 2 ($A_t \ll R_g^2$) we can conclude that the pseudoplateau observed in the present results is consistent with the “quasi-SSAL–quasi-brush” transition

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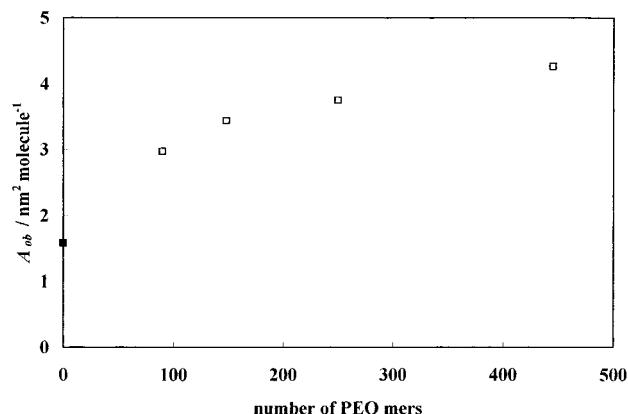


Figure 3. Limiting brush area A_{ob} vs the number of PEOmers at 298 K.

predicted by Ligoure.⁸ Furthermore this model predicts that in the quasi-brush regime the chains are stretched to about two times the R_g value. The values of $R_g/\sqrt{A_m}$ (Table 2) show that the polymers studied are more stretched than predicted by the model and also that stretching increases with the PEO block molecular weight.

The limiting brush area A_{ob} (see Figure 1) is slightly dependent on the PEO segment size (Figure 3) and is always higher than the value of the pure PS₃₈ homopolymer (1.58 nm²). This value, was obtained by the relation proposed by Kumaki *et al.*,²⁰ $A_o (\text{\AA}^2) = 0.04M$, from poly(styrene) monolayers of different molecular weight, M . These results indicate that at this stage the area at the interface is determined by the immersed chains of PEO in a brush conformation.

Ou-Yang and Gao²¹ have noticed that, in brushes formed by block copolymers adsorbed from aqueous solutions on PS microspheres, the water soluble block is stretched to about four or five times its R_g in solution. The values of the ratio $R_g/\sqrt{A_{ob}}$ (Table 2) compare with those findings of Ou-Yang and Gao for ZGH1 and ZGH2 and are higher for ZGH3 and ZGH4, showing that the polymer stretching in a quasi brush conformation also increases with the PEO length.

III.2. Hysteresis. The first compression isotherms of each copolymer do not superpose to the following expansion both at high surface pressures (brush conformation, Figure 4a) and at low surface pressures (pancake conformation, Figure 4b). Both hysteresis regimes, as well as their temperature and chain length dependence, have proven to be extremely informative.

The hysteresis observed at high surface pressures (Figure 4a) exhibits an unusual minimum. In the expansion isotherm of ZGH1, after compressing up to 35 mN/m, the surface pressure decreases abruptly, reaches a minimum at $\pi = 10.5$ mN/m, increases again, and finally follows the compression isotherm. As the length of PEO increases, the minimum becomes less pronounced and the surface pressure at the local minimum increases. No minimum is observed for ZGH3, and almost no hysteresis is found for ZGH4. The particular shape of the π - A curve suggests that the system undergoes a metastable regime during expansion and finally returns to equilibrium. In other words, the existence of the minimum seems to indicate that the monolayer becomes overexpanded, a situation equivalent to that exhibited by three-dimensional fluids in solid-liquid and liquid-gas transitions.²² As far as we

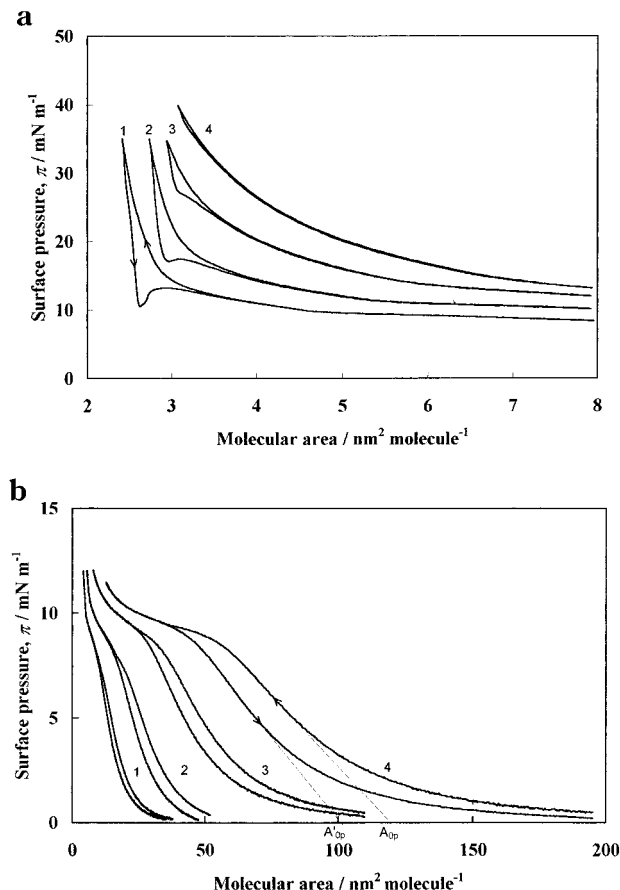


Figure 4. Surface pressure–area compression–expansion cycles at 298 K, at high surface pressures (a) and at low surface pressures (b) for copolymers: ZGH1 (1); ZGH2 (2); ZGH3 (3); ZGH4 (4).

are aware, it is the first time this behavior is reported for a monolayer.

It is known that PEO has a unique behavior among polyethers.^{23,24} The polymer chains in aqueous solution, although highly hydrated, retain part of their helical structure.^{25,26} This organization is probably related to the fact that water is becoming a less good solvent for PEO chains at higher polymer concentration than it is at very dilute concentration.^{27,28} We believe that the unusual behavior now reported can be related to high cohesion and short range local order between the PEO helical chains in the brush conformation. The chain length influence on hysteresis indicates that organization is favored by the shorter PEO blocks (Figure 4a).

The influence of the rate of compression–expansion cycle was also considered, since kinetic aspects, such as a slow intrinsic dilation of the monolayer, might be involved. In a first attempt, the rate of expansion was changed by a factor of 10 causing a shift of the isotherm to lower areas, without affecting the overall shape.

Hysteresis observed at low surface pressures can be quantified by $(A_{op} - A'_{op})$ where A'_{op} is the pancake limiting area in the expansion isotherm (see Figure 4b). The hysteresis increases with the length of the PEO segment

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Table 3. Hysteresis quantified by $(A_{op} - A'_{op})/\text{nm}^2$

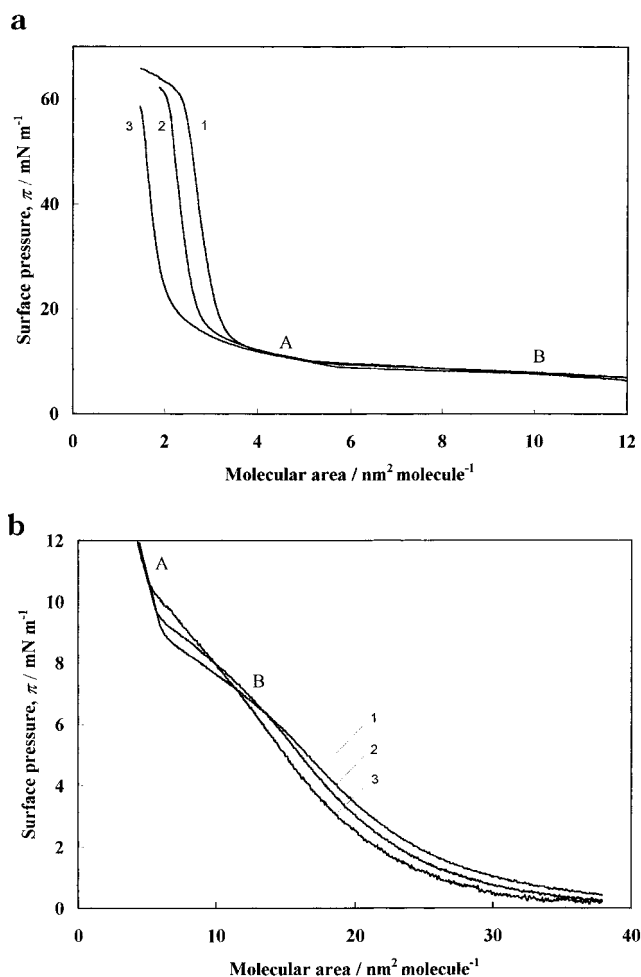
$\pi_{\text{max}}/\text{mN m}^{-1}$	$(A_{op} - A'_{op})/\text{nm}^2$		cycle ($\pi_{\text{max}} = 12 \text{ mN m}^{-1}$)	$(A_{op} - A'_{op})/\text{nm}^2$	
	ZGH4	ZGH1		ZGH1	ZGH4
7	0.0	2.7	1	20.0	
10	10.3	0.6	2	7.6	
12	20.0	4.3	3		

and decreases with the number of succeeding cycles (Table 3). Also meaningful is the fact that hysteresis increases with the maximum surface pressure of the cycle and there is a minimum compressing pressure, π_t (located at the beginning of the conformational transition) below which no hysteresis is observed (Table 3). The expansion curves do not return to the starting pressures even at very large areas. This low-pressure hysteresis can be attributed to several factors: (i) entanglement of PEO chains during the quasi-SSAL–quasi-brush transition; (ii) a different arrangement of the expanded PEO chains in terms of hydration and conformation, compared to the one adopted after spreading and before the first compression; (iii) material loss from the monolayer by solubilization in the subphase.

The entanglement of polymers depends on the degree of chain interpenetration and strongly slows down the polymer dynamics. The extent of entanglement depends on molecular weight, and there is a minimum value below which no entanglement is observed, the so-called critical entanglement molecular weight (M_c). The experimental M_c value for PEO has been reported²⁹ to be about 4400. It is interesting to note that the molecular weight of the PEO block in ZGH1 (3950) is just below M_c , while those of the other copolymers are already considerably above this value.

The copolymers of the present study have been studied at low surface pressures by Bijsterbosh *et al.*¹⁰ The main features detected by these authors have been confirmed in the present work. However, they interpret hysteresis, observed only in the first cycle, as resulting from sample contamination with PEO homopolymer. This would be pushed irreversibly into the subphase at the first compression, since it is not anchored to the interface by the PS block. We found that the hysteresis persists (considerably for the longer polymers) after the first cycle, decreasing on succeeding cycles. This supports that hysteresis is mainly due to the first two factors besides some contamination or loss of material that may also be present.

A similar interpretation has been done by Baekmark *et al.*,¹⁹ for lipopolymers consisting of poly(ethylene oxide), $n = 45$ and $n = 110$, coupled to distearoylphosphatidylethanolamine (DSPE). They attributed hysteresis to some entanglement of the PEO chains and ruled out the possibility of material loss from the monolayer. They have observed a very weak hysteresis for the lipopolymer with the shorter PEO segment ($n = 45$) and considerable hysteresis in the first and second compression–expansion cycles for the longer one ($n = 110$), much higher than that found for ZGH1 in this work. It seems, therefore, that chain interpenetration is present in the longer lipopolymer (PEO₁₁₀) to a much higher extent than in ZGH1 (PEO₉₀) in spite of the approximate size of the PEO segments. This is probably due to the contribution of the DSPE polar group to the hydrophilicity of the lipopolymer, associated with the smaller size of the hydrophobic part composed of two stearyl chains. Thus, strong interactions between lipopolymer hydrophilic groups may become important at low areas, promoting a higher approximation

**Figure 5.** Surface pressure vs area per molecule of ZGH1 at high surface pressures (a) and at low surface pressures (b): 283 K (1); 298 K (2), 316 K (3).

and consequently higher interpenetration between the PEO chains immersed in the subphase.

III.3. Temperature Effect. Isotherms of ZGH1 and ZGH4 at several temperatures in the range 283–318 K are presented in Figures 5 and 6, respectively. (Two different scales are used, for the high and low surface pressure regions.) The set of isotherms for each copolymer crosses twice, at point B, just before the quasi-SSAL–quasi-brush transition at about 8 mN/m, and at point A, after the transition at about 11 mN/m for ZGH1 and at 15 mN/m for ZGH4. Therefore, the temperature dependence of the phase transition (pseudoplateau) is opposite to that observed both in the pancake and in the brush regions of the monolayer. The plateau surface pressure increases with increasing temperature. This means that the adsorption of PEO segments at the interface is favored at high temperature. Alternatively, this reflects the temperature dependence of the PEO solubilization process. The surface–subphase partitioning is favored at lower temperatures (curve 1), since the dissolution occurs at lower surface pressures, indicating that the dissolution of PEO in water should be an exothermic process. Calorimetric studies on the dissolution process and structure of PEO aqueous solutions prove that this is indeed the case.²⁵ The explanation may rely on hydrogen bonding between the oxygen in the PEO chain and the water molecules. As the importance of hydrogen bonding decreases with the temperature, it seems reasonable that the solubility of PEO in water also decreases with temperature.

With the assumption of the pseudoplateau as a diffuse first-order phase transition^{17,18} its temperature depen-

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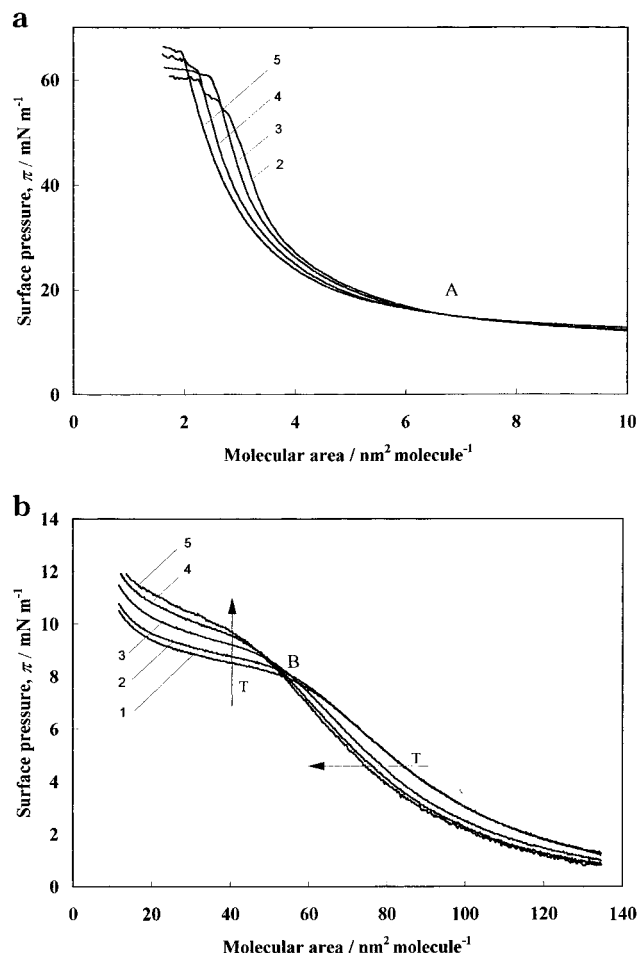


Figure 6. Surface pressure vs area per molecule of ZGH4 at high surface pressures (a) and at low surface pressures (b): 283 K (1); 288 K (2); 298 K (3); 318 K (4); 316 K (5).

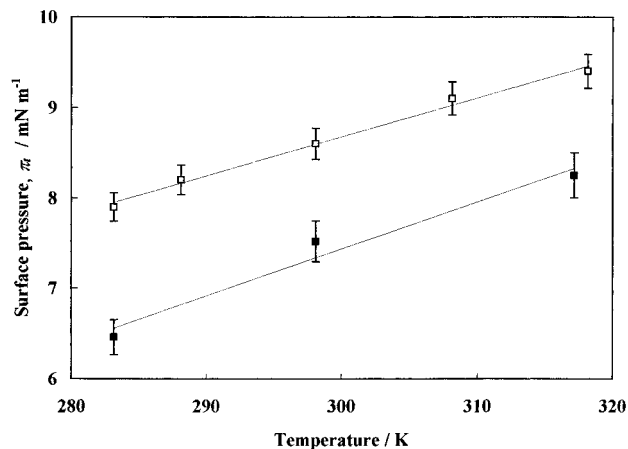


Figure 7. Transition surface pressure as a function of temperature for ZGH1 (■) and ZGH4 (□).

dence was analyzed. A plot of the surface pressure of the quasi-SSAL-quasi-brush transition as a function of temperature is shown in Figure 7 for ZGH1 and ZGH4. From the two-dimensional Clapeyron equation,³⁰ $d\pi_t/dT = \Delta S_t/\Delta A_t$, and estimating a mean transition area change for each polymer, ΔA_t , the mean transition entropy change, ΔS_t , was obtained. The values in Boltzman constant units (k_B), $-22k_B$ for ZGH1 ($n = 90$) and $-110k_B$ for ZGH4 ($n = 445$), show a linear dependence on the number of PEOmers (n) and are in excellent agreement with the

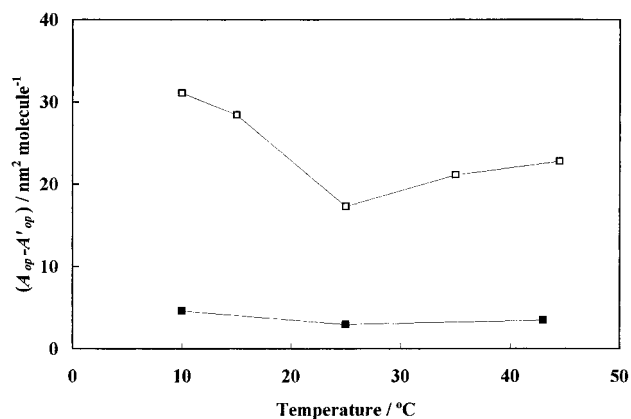


Figure 8. Hysteresis in terms of $(A_{op} - A'_{op})$ as a function of temperature: ZGH1 (■); ZGH4 (□).

value obtained for DSPE-EO₄₅ ($n = 45$), $-10k_B$.¹⁹ These results seem to indicate that the transition entropy change is not affected by the nature of the hydrophobic block and that the value ΔS per monomer does not depend on the PEO block molecular weight. Since the Clapeyron coefficient is positive and the area decreases on compression ($\Delta A_t < 0$), the transition entropy change is negative, implying the formation of a more organized structure. This decrease in the entropy of the system is favored by the hydrophobicity of PEO chains. The interaction between the methylene group of the PEO chain and the water molecules is very weak when compared with the strong directional hydrogen bonds between water molecules. This unfavorable balance for water promotes the organization of both PEO and water molecules in the vicinity of PEO chains in order to maximize the interactions.

Except for the transition plateau, the monolayers are deviated to lower areas as temperature increases. This behavior is in agreement with studies of PEO in aqueous solution.²⁵ The PEO homopolymer is said to adopt a more compact conformation as temperature increases, probably due to an increase in the free rotation of the chain links. In addition, a weakening of polymer-solvent interactions occurs at higher temperatures, decreasing the number of water molecules associated to the PEO chains by hydrogen bonding, leading to a smaller volume occupied by the PEO chains. This interpretation should apply to both the pancake and the brush conformations. The less solvated PEO chains by hydrogen bonding at higher temperatures allow a more condensed brush conformation and eventually a more stable conformation, as indicated by the increase of the collapse surface pressure. An identical temperature dependence was observed for the lipopolymer DSPE-EO₄₅ at low surface pressures and in the pseudo-plateau region where the lipopolymer behavior is dominated by the PEO block.¹⁹ In Figure 2a of the referred work a crossover is visible in the 8–9 mN/m range, not mentioned by the authors. For higher surface pressures the comparison is not valid, as those polymers exhibit another conformational transition, not observed in the present work, probably related to the phospholipid group.

Another remarkable finding in this study is the temperature effect on the low surface pressure hysteresis. As shown in Figure 8 for ZGH1 and ZGH4, hysteresis decreases between 283 and 298 K and increases in the 298–315 K range. This can be explained by the opposite temperature dependence of two factors, the solubility of PEO in water and the interpenetration of the PEO chains. A higher solubility in the subphase will cause a higher hysteresis. In the same way the greater the interpenetration, the greater the hysteresis. Since solubility

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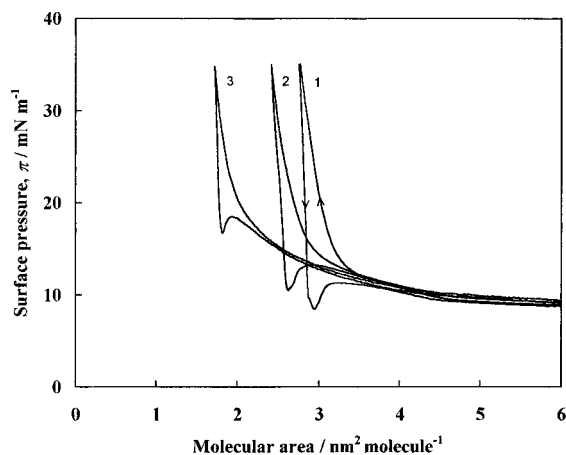


Figure 9. Surface pressure–area compression–expansion cycles for ZGH1: 283 K (1); 298 K (2); 313 K (3).

decreases with temperature, hysteresis will decrease in the range 283–298 K. On the other hand, the interpenetration of the progressively less solvated PEO chains increases with temperature, leading to an increase of hysteresis in the 298–315 K range.

The hysteresis observed at high surface pressures decreases with the temperature (Figure 9): π_{\min} increases with temperature, while the shift to low areas decreases. This results from the action of thermal motion against cohesion and organization of PEO.

IV. Conclusions

A series of four diblock copolymers, composed of poly(styrene) and poly(ethylene oxide), of varying hydrophilic block length was studied at the air–water interface by surface pressure measurements in the range 283–315 K.

The present work shows that diblock amphiphilic copolymers are suitable to test the scaling theories of

grafted polymers. The π – A isotherms show several regions ascribed to pancake, quasi-brush, and brush stages. The observation of a pseudoplateau is semiquantitatively consistent with the first-order phase transition from a quasi-SSAL to a quasi-brush predicted by Ligoure. The compression–expansion cycles show hysteresis in the brush and pancake regions. The former points to some organization of PEO chains immersed in the subphase as it increases with chain length decrease, while the latter was attributed to the entanglement of the PEO chains during compression, which avoids the recovery of the initial configuration after spreading. It has been shown that the entanglement of the soluble PEO chains, dangling in the water subphase, increases with the PEO length and varies with the temperature, going through a minimum near 298 K. This minimum was related to the decreasing importance of hydrogen bonding when temperature increases and to a chain interpenetration increase of less solvated PEO chains.

Both the pancake limiting area and the mean transition entropy depend linearly on the number of PEOmers for the block copolymers studied. The mean transition entropy obtained from the temperature dependence of the conformational transition is negative confirming that the dissolution of PEO in water is exothermic. The pancake limiting area and the mean transition entropy per PEOmer obtained from the π – A isotherms do not depend on the PEO length.

The unusual conformation of the compression–expansion cycle, going through a minimum for ZGH1 and ZGH2, is not completely understood and deserves further investigation.

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