Interfacial Behavior of Poly(isoprene-b-methyl methacrylate) Diblock Copolymers and their Blends with Polystyrene at the Air–Water Interface

Sónia I. C. Lopes,† Amélia M. P. S. Gonçalves da Silva,*‡ Pedro Brogueira,‡ Susana Piçarra,§,‖ and J. M. G. Martinho‖

Centro de Química Estrutural e Centro de Química Física Molecular, Complexo I, and ICEMS, Instituto Superior Técnico, Universidade Técnica de Lisboa, 1049-001 Lisboa, Portugal, and Escola Superior de Tecnologia de Setúbal, Instituto Politécnico de Setúbal, Estefanilha 2910–761 Setúbal, Portugal

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The interfacial behavior of poly(isoprene-b-methyl methacrylate) diblock copolymers (PI-b-PMMA), with similar PMMA blocks but differing in the percentage of PI segments, SP19 (5% PI) and SP38 (52% PI), was studied at the air–water interface. The surface pressure–area (π–A) isotherms, compression–expansion cycles, and relaxation curves were compared with those of the PMMA homopolymer. The short hydrophobic PI block of SP19 does not contribute to the mean molecular area at low surface pressures and yet has a negative contribution (condensing effect) when the surface pressure increases. On the contrary, the long PI block of SP38 contributes considerably to the surface area from low to high surface pressures. The A–t relaxation curves compare well with those of PMMA at low surface pressures (π = 2 mN m⁻¹), but not at intermediate and high pressures (π = 10, 30 mN m⁻¹), where a clear dependence on the length of the PI block was observed. The quantitative analysis of the relaxation curves at high pressures shows both a fast and slow component, attributed mostly to the local and middle-to-long-range reorganization of PMMA chains, respectively. PI-b-PMMA diblocks and PMMA were further blended with PS. The PS and PMMA are immiscible at the air–water interface. The addition of PS does not change the π–A isotherm of PMMA, but the copolymers blended with PS form films that are more condensed at low pressures. The Langmuir–Blodgett (LB) films transferred onto mica substrates were analyzed by atomic force microscopy (AFM). The LB films of single diblocks are uniform, while those of PI-b-PMMA and PMMA blended with PS show aggregates with variable patterns.

Introduction

The current interest in the properties of interfacial layers formed by block copolymers stems from their ability to spontaneously organize into ordered surface patterns.1–4 In particular, amphiphilic diblock copolymers that comprise both hydrophobic and hydrophilic blocks form monolayers at the air–water interface; the hydrophobic block anchors the chains at the interface, while the hydrophilic block adsorbs or dissolves into the water subphase.5–8 Diblock copolymers have attracted much attention because various nanoscale aggregates with predictable morphologies can be formed by controlling the molecular weight, molecular structure, relative length of each block, and concentration of the spreading solution.9–16

The surface properties of the amphiphilic block copolymers have been widely studied by the Langmuir trough technique, which allows the control of the nanostructures formed at the air–water interface.17 The two-dimensional properties of the aggregates and the conformational changes of the polymer chains induced by compression of the floating film can be derived from surface pressure–area (π–A) measurements and, in some cases, observed in situ by surface-sensitive techniques.18 Further characterization (AFM, TEM, and spectroscopic analysis) of the interfacial structure of these films can be obtained after transferring the floating layer to solid substrates by the Langmuir–Blodgett (LB) technique.18–20 One of the most widely studied amphiphilic copolymers is certainly poly(styrene-b-ethylene oxide) (PS-b-
PEO), which shows at the air—water interface a very rich variety of nanostructures (dotts, spaghetti, rings, chainlike aggregates, etc.), resulting from the spontaneous copolymer aggregation.11–15

Under compression, the hydrophobic PS blocks aggregate at the interface, while the hydrophilic PEO block dissolves into the water subphase.5,6 Different morphologies have been observed, depending on the relative chain length of the hydrophilic and hydrophobic blocks,14,15 the surface pressure,13 and the concentration of the spreading solution.14,15,21 Very interesting results were also obtained with PS-b-PMMA diblock copolymers, in which the surface-active poly(methyl methacrylate) (PMMA) replaces the water-soluble PEO block.22–26 As both PS and PMMA blocks are water-insoluble, the copolymer molecules remain at the air—water interface and self-assemble at high surface coverage, forming surface micelles.23 At low surface pressures, the surface-active PMMA forms an expanded monolayer at the interface and the hydrophobic PS block forms condensed globules. Upon compression, the PMMA chains are forced to densely pack with the ester groups oriented toward the water subphase, while the glassy PS block (Tg ≈ 100 °C)27 anchors the polymer floating film to the interface and assures the stability of surface aggregates. Several applications, as diverse as protective coatings and dielectric films for solid-state electronics, require, besides stability, a good flexibility in order to improve processability. This can be achieved by using copolymers containing blocks of low glass transition temperature in order to improve the viscoelastic properties of the film.28,29

This work studies for the first time the influence of the physical state (glassy or rubbery) of the hydrophilic block (A) on the interfacial behavior of A-b-PMMA diblock copolymers. The interfacial behavior of two PI-b-PMMA copolymers with a similar PMMA block but differing in the % PI segments, SP19 (5% PI) and SP38 (52% PI), is different from that found for PS-b-PMMA copolymers.22 The PS and PI homopolymers are hydrophobic but behave differently at the air—water interface: at room temperature, PS is vitreous and forms stable films of solid aggregates, while PI is viscoelastic (Tg ≈ −68 °C)27 and exhibits a very compressible monolayer. The π-A isotherms of the PI-b-PMMA block copolymers depend on the length of the PI block. At low surface pressures, the short PI block in SP19 does not contribute to the surface area and yet has a negative contribution (condensing effect) when the surface pressure increases. On the contrary, the long PI block in SP38 contributes to the surface area from low to high surface pressures. The AFM images of the SP19 and SP38 LB films on mica substrates do not evidence stable aggregates. However, aggregation can be observed when these copolymers are blended with PS. The size and distribution of PS aggregates on mica substrates vary with the length of the PI block. This procedure can be used to tailor the structures and dimensions of surface aggregates.15,30–34

Table 1. Characteristics of PI-b-PMMA Diblock Copolymers

<table>
<thead>
<tr>
<th>Block Copolymer</th>
<th>Mw (PI)</th>
<th>Mw (PMMA)</th>
<th>Mw/Mn</th>
<th>% of PI segments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP19</td>
<td>2800</td>
<td>73 000</td>
<td>1.2</td>
<td>5</td>
</tr>
<tr>
<td>SP38</td>
<td>54 000</td>
<td>72 000</td>
<td>1.2</td>
<td>52</td>
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Experimental Section

Materials. Isoprene (99%, Aldrich) and methyl methacrylate (99%, from Aldrich) were both dried with CaH2 over several days, distilled at reduced pressure, and kept under inert atmosphere before use; sec-butylthiolium (1.17 M in cyclohexane, from Aldrich), n-butyllithium (2.5 M in hexanes, from Aldrich), and triethylaluminum (1.9 M in hexanes, from Aldrich) were kept under inert atmosphere; THF (99%+, from Aldrich) and cyclohexane (>99%, Fluka) were dried with Na and CaH2, respectively, and were freshly distilled before use. Methanol (A.C.S., from Aldrich and chloroform (p.a. grade, ≥99.8%) from Fluka were used without further purification. 1-(9-phenanthryl)-1-phenylethylene was synthesized according to the procedures described by Bachmann36 and Bergmann et al.37 The homopolymers PMMA (Mw = 120 000) and PI (Mw = 40 000) were purchased from Aldrich and used as received. The polyurethane (Mw = 96 000, Mw/Mn = 1.07) was synthesized by anionic polymerization.

Polymer Synthesis and Characterization. The PI-b-PMMA diblock copolymers were synthesized by anionic polymerization in THF at −78 °C using 1 equiv of sec-butylthiolium and 28 equiv (SP19) or 325 equiv (SP38) of isoprene for the polymerization of the first block.37,38 Isoprene was purified with n-butyllithium immediately before use. An excess of 1-(9-phenanthryl)-1-phenylethylene dissolved in THF was added to the reaction mixture when the first block polymerization was complete. A small aliquot for the first block was removed for characterization. It was then added 312 equiv (SP19) or 280 equiv (SP38) of MMA monomer (freshly distilled from triethylaluminum) in order to start the polymerization of the second block. The reaction was quenched by addition of an excess of degassed methanol, followed by precipitation in the same solvent. Slight traces of PI homopolymers in the samples were removed by Soxhlet extractions with cyclohexane for several days. Table 1 shows theGPC characterization of the copolymers using PS standards. The block copolymers contain a phenanthrene at the block joint points to be used in further fluorescence measurements.

Film Balance Measurements. The surface pressure—area (π—A) isotherms were obtained in a KSV 5000 Langmuir—Blodgett System (KSV Instruments Ltd., Helsinki), installed in a laminar flow hood. The water used in the subphase was purified with the Millipore Milli-Q system, to obtain the resistivity as high as 18.2 MΩ,cm, at pH 5.7. The surface pressure measurements were performed with the Wilhemy plate technique.

Polymer solutions in chloroform were prepared in the range 0.5–0.03 g L−1. Known volumes of the solution were spread on the water surface by using a SGE gastight microliter syringe. Two mobile barriers at a constant speed of 5 mm min−1 compressed symmetrically the floating layer after complete evaporation of the solvent (15–60 min). The temperature of the subphase was maintained at 20.0 °C ± 0.2 °C by a water bath circulator. The π—A isotherms were in general measured at least three times.
The effect of experimental factors, such as the compression speed, the waiting time before compression, and the concentration of the spreading solution, was also investigated. The \( \pi-A \) curve slightly deviated when the compression speed changed from 15 to 5 mm.min\(^{-1} \), and then the lower speed was adopted for the following measurements. The waiting interval before compression, ranging from 15 to 60 min, does not deviate among the \( \pi-A \) curves of the three polymers. The effect of concentration is more significant and will be referred to later. Unless stated, all the results herein presented were obtained by using spreading solutions of 0.03 g.L\(^{-1} \).

**Relaxation Measurements.** The relaxation curves were obtained by two procedures: after the monolayer compression until the target surface pressure \( \pi_0 \), the relaxation of \( \pi \) at constant \( A_0 \) (\( \pi-A \) curves) and the relaxation of \( A \) at constant \( \pi_0 \) (\( A-\pi \) curves). For the \( \pi-A \) measurements, the surface pressure was recorded as a function of time at constant area \( A_0 \) (stopped barriers). For the \( A-\pi \) measurements, the surface pressure was maintained at the initial value \( \pi_0 \) by the continuous adjustment of the barriers position, and the time evolution of the area was recorded.

**Langmuir–Blodgett Deposition.** The floating films at the air–water interface were transferred to freshly cleaved mica substrates by the vertical dipping method. The substrates were clamped parallel to the barriers and immersed in the subphase before spreading the monolayer material. After complete evaporation of the solvent, the floating layer was compressed up to the target surface pressure. Upon a relaxation period, the deposition was performed at constant surface pressure (2 and 20 mN.m\(^{-1} \)), with a dipping speed of 5 mm.min\(^{-1} \), and then the lower speed was adopted for the following measurements.

**Atomic Force Microscopy (AFM).** A D3100 with a Nanoscope IIIa controller from Digital Instruments (DI) was used to obtain the AFM images. The measurements were performed in tapping mode under ambient conditions. A commercial tapping mode etched silicon probe (TESP) from DI and a 90 \( \times \) 90 \( \mu \)m\(^2 \) scanner were used. The free tip was set to 1.3 V. Images consisted of raster-scanned, electronic renderings of the sample surfaces.

**Results and Discussion**

This work reports a detailed study of the interfacial phase behavior of PMMA and PI homopolymers and two PI-b-PMMA copolymers (SP19 and SP38), as single components and when blended with PS at the air–water interface. Both copolymers have a similar PMMA block but differ in the length of the PI block. The SP38 copolymer has almost equal number of PI and PMMA segments (52% PI), while SP19 has a very short PI block (5% PI).

**\( \pi-A \) Isotherms of Single Components.** Figure 1 shows the \( \pi-A \) isotherms of PMMA and PI homopolymers and SP19 and SP38 diblock copolymers. The plots were constructed with the \( x \)-axis referring to the area per segment of PMMA in the SP19 and SP38 diblocks and the area per segment of the homopolymers. The PI is strongly hydrophobic and does not form a stable film at the air–water interface. Upon compression of the monolayer, a thick multilayer forms with an extremely low area per segment (<2 Å\(^2 \)). Contrarily, PMMA forms stable and reproducible monolayers at the air–water interface. Several regions can be distinguished in the compression isotherm of PMMA, assigned to different polymer conformations or conformational transitions at the interface.

(a) **Expanded Regime.** At low surface pressures (\( \pi <10 \) mN.m\(^{-1} \)), a typical liquid expanded monolayer is observed. The limiting surface area per segment of 15.5 Å\(^2 \) was determined by extrapolating the 2–10 mN.m\(^{-1} \) almost linear region to zero surface pressure. This value agrees with those reported by Kawaguchi and Sauer\(^{39} \)(15.8 Å\(^2 \)), Kumaki and Hashimoto\(^{20} \)(16 Å\(^2 \)), and Seo et al.\(^{21} \) (15–16 Å\(^2 \)). The surface area per segment is smaller than predicted from the molecular structure of the monomer (e.g., the cross section of a saturated hydrocarbon chain is 18 Å\(^2 \)). This shows that a significant number of segments are not in contact with the water subphase, i.e., the PMMA chains adopt a two-dimensional “pancake” resulting from a loop-and-train configuration of individual overlapped chains.

(b) **Transition Regime.** For surface pressures in the range 10–15 mN.m\(^{-1} \), the slope of the \( \pi-A \) isotherm significantly decreases. This pseudo plateau can be ascribed to a conformational transition of polymer chains into a more compact and organized state to maximize the lateral interactions between chains.

(c) **Condensed Regime.** Above the pseudo plateau, the \( \pi-A \) isotherm rises with a nearly constant slope owing to the compaction of chains, until the collapse at ~50 mN.m\(^{-1} \). The low value of the area per segment at the collapse surface pressure (7 Å\(^2 \)) indicates the formation of a thick film of entangled chains.

(d) **Three-Dimensional (3D) Regime.** Above the collapse, the surface pressure continuously rises, although with a smaller slope, probably due to a progressive squeezing out of PMMA chains from the “monolayer” to form a thicker structure (3D). This is supported by the irreversible compression–expansion cycles.

performed until high surface pressures (Figure 3B) as will be shown below.

The compression isotherm of the diblock copolymer SP19 follows the \( \pi-A \) curve of PMMA at low surface pressures and deviates to smaller areas for \( \pi > 5 \text{ mN.m}^{-1} \). This indicates that the PI segments do not contribute to the surface area at low pressures, and that upon compression promote a significant condensing effect in the floating film. The isotherm of SP38 strongly deviates to larger areas than those of PMMA, showing that the contribution of the PI segments to the surface area cannot be discarded. The area per segment of PMMA is two times higher for SP38 than for PMMA homopolymer at very low surface pressures, decreasing to about 1.5 times in the condensed regime.

According to Hosoi et al., the mechanism of two-dimensional self-assembling of diblock copolymers with immiscible blocks at the air—water interface differs from the classic bulk microphase segregation, because the effects of surface tension gradients, entanglement vitrification, and diffusion need to be considered. In the spreading solution, the copolymer exists in the form of a random coil, because chloroform is a good solvent for both polymer blocks. When a droplet of this spreading solution is deposited at the air—water interface, the polymer chains immediately adopt a bimellar configuration (3D) in which the surface active PMMA adsorbs at the interface and the hydrophobic PI block, that is strongly incompatible with PMMA and water, tends to be segregated toward the air as a swollen polymer brush. Subsequently, as the solvent evaporates, the PMMA “pancake” spreads over larger areas, and the PI block evolves to a configuration that depends on the PI molecular weight. Figure 1 includes a scheme of the several morphologies adopted by the copolymers along the \( \pi-A \) isotherm. At low surface pressures, the isolated PI blocks of SP19 (2.8 kDa) on the top of PMMA pancake do not contribute to the mean molecular area. Upon compression, the lateral interactions between the PI chains in the upper layer become possible, inducing the PI aggregation in small micelle cores. The formation of these aggregates promotes rearrangements of the PMMA chains at the interface, which result in a condensing effect of the floating film (Figure 1). For the SP38 copolymer, the molecular weight of the PI block (54 kDa) is higher than the critical molecular weight for entanglements of PI (Mc \( \approx 10000 \)). Therefore, the long and entangled PI chains self-assemble as fluid lenses or large micelle cores that slide down to the interface during the solvent evaporation, forcing the rearrangement of the PMMA chains. This leads to a significant increase of the surface area, in agreement with the strong positive deviation of the \( \pi-A \) isotherm (Figure 1). The coarsening of the PI domains at the interface is kinetically prevented by the PMMA chains. By pressure increase, the PI lenses are progressively displaced to upper layers, and the surface concentration of PMMA segments increases. At high surface pressure, a significant fraction of PI leaves the water subphase, and the shape of the isotherm become mostly controlled by the rearrangement of the PMMA segments in contact with water. As expected, in the condensed regime, the isotherms of both copolymers and PMMA are nearly parallel.

In the past years, it has been observed that the concentration of the spreading solution influences both the shape of the \( \pi-A \) isotherm and the surface aggregation. In this work, we found that the expanded regimes of \( \pi-A \) isotherms of both diblocks are influenced by the polymer concentration in the spreading solution (Figure 2), while that of PMMA is invariant in all surface pressure regions. At low surface pressures, the isotherms deviate to smaller areas when the concentration increases from 0.03 to 0.5 mg/mL, while in the condensed regime at high surface pressures, no significant changes were observed. Contrarily, Cheyne and Moffitt found that the \( \pi-A \) isotherms of PS-\( b \)-PEO diblock copolymers show a concentration dependence only in the condensed regime. In this case, the PS-\( b \)-PEO diblock copolymers are predominantly hydrophobic (11.4 and 18.9, wt% PEO), and the \( \pi-A \) condensed regime is controlled by the dominant PS block. Then, the increase of polymer concentration in the spreading solution favors polymer aggregation in the solution, prior to solvent evaporation at the air—water interface.

In this work, the condensed regimes of the \( \pi-A \) isotherms of SP19 and SP38 are mostly controlled by the surface-active PMMA block, such that the expanded regime is more sensitive to the influence of the PI block. Thus, some aggregation retained from the spreading solution and favored by the presence of PI blocks is only detectable in the expanded regime.

Hysteresis. Figure 3A shows the first compression—expansion cycles for PMMA, obtained up to \( \pi_{\text{max}} = 10 \text{ mN.m}^{-1} \) (cycle 1), 20 \text{ mN.m}^{-1} (cycle 2), and 30 \text{ mN.m}^{-1} (cycle 3). Cycle 1, recorded before the transition regime, is reversible; i.e., the compression and expansion isotherms are almost coincident. However, when the compression goes beyond the transition surface pressure (cycles 2 and 3), hysteresis occurs; i.e., the successive compression and expansion runs do not coincide. The expansion curves drop sharply at the beginning of the expansion runs and become nearly parallel to the compression curve below the transition regime. This is attributed, in accordance with Seo et al., to the high viscosity of the monolayer of entangled chains, that generates intermediate metastable states, during the movement of the barriers in the Langmuir trough. The transition regime becomes more pronounced during the expansion than in the compression run, and the successive compression—expansion cycles (omitted) closely follow the first cycle, discarding the PMMA solubility into the subphase. Significant negative deviations appear for \( \pi_{\text{max}} \geq 50 \text{ mN.m}^{-1} \) (Figure 3B), suggesting the irreversible collapse of the monolayer.

The hysteresis of the SP19 copolymer (omitted) is similar to the one of PMMA, which suggests a negligible influence of the short PI block. For the SP38 copolymers, a peculiar hysteresis was observed. After compression above the transition regime, the expansion isotherm of SP38 crosses the compression curve at the transition regime, deviating to larger areas than those observed during the compression run (Figure 4). The deviations

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to larger areas increase during the successive compression–expansion cycles performed up to 10 mN.m\(^{-1}\) (see insert of Figure 4), suggesting that the surface area increases with time at low surface pressures.

**Relaxation.** In order to investigate the time dependence of the surface area of the spreading film, relaxation measurements were performed at several surface pressures. After the monolayer compression until the target surface pressure \(\pi_0\), the relaxation curves were obtained by two procedures:\(^{44-46}\) the relaxation of \(\pi\) at constant \(A_0\) (\(\pi-t\) curves) and the relaxation of \(A\) at constant \(\pi_0\) (\(A-t\) curves). As the information extracted from both relaxation curves is identical, only the \(A-t\) curves are shown. Figure 5 shows the time evolution of the normalized surface area (\(A/A_0\)), where \(A_0\) stands for the initial surface area, for both copolymers and PMMA at the constant surface pressure, \(\pi_0 = 2, 10,\) and 30 mN.m\(^{-1}\). Figure 5A shows that, for \(\pi_0 = 2\) mN.m\(^{-1}\), all the polymers show an expansion with time. The minimum, in the relaxation curves of the copolymers, is attributed to the initial condensing effect of the PI block in competition with the expansion of the PMMA. The overall expansion is essentially due to the stretch of the PMMA chains by varying the initial pancake conformation of the PMMA segments to maximize the hydrogen bonds between the ester groups and the water molecules.

Figure 5B shows the relaxation curves of all polymers at \(\pi_0 = 10\) mN.m\(^{-1}\). The SP38 relaxation shows that after a short period the area increases continuously to reach a plateau at longer times. In contrast, the area of SP19 decreases about 3% during the initial 50 min to remain practically constant afterward. In between, the surface area of PMMA remains almost constant, as the area slightly decreases during the initial 80 min less than 1% to increase very slowly afterward.

The higher expansion rate of SP38 is attributed to the relaxation of the kinetically trapped lenses of PI, randomly dispersed at the interface between the PMMA domains. At \(\pi_0 = 10\) mN.m\(^{-1}\), the viscous PI domains that were partially squeezed out from the interface to an upper layer, during the compression, slide down to the first layer during the relaxation, increasing the area occupied at the interface.

The relaxation curves of SP19 and PMMA are similar. Indeed, after an initial period both curves become parallel, reflecting the relaxation of the PMMA segments to favor the hydrogen bonds between the ester groups and the water molecules. The more pronounced decrease of area of SP19 compared to PMMA is due to the condensing effect of PI that helps the reorganization of the PMMA chains to a more compact configuration.

The relaxation curves at 30 mN.m\(^{-1}\) (Figure 5C) follow the same general trend observed for other materials at high surface pressures.\(^{44}\) The relative area shows a very fast decrease (7–10%, during 20 min), that is followed by a very slow relaxation to attain the equilibrium. A decrease of 12–15% after 60 min can also be explained by an increase of the film thickness or by the reorganization of chains to adopt more compact conformations. As the compression was not sufficiently slow to allow the equilibrium at each intermediate stage, the polymer film exists in a metastable configuration. This evolution, probably accomplished by the decrease of the number of contacts with the water subphase and an increase of the film thickness, suggests a complex process occurring at the interface: a fast local reorientation of the chain segments and the middle-to-long-range organization of the whole chains at the air–water interface. The relaxation curves of PMMA and SP19 are nearly parallel, with the SP19 deviating to lower areas, due to the initial condensing effect of the short PI block.

The \(A-t\) relaxation curves at low surface pressures (\(\pi = 2, 10\) mN.m\(^{-1}\)) contain rich information, but their complexity does not allow a further quantitative analysis. Contrarily, the relaxation curves at 30 mN.m\(^{-1}\) are simpler and reproducible. The relaxation curves of Figure 5C can be well-fitted with a sum of two exponentials, with relaxation times, \(\tau_1, \tau_2\), and pre-exponential factors \(a_1, a_2\), plus a constant, \(A_\infty/A_0\), where \(A_\infty\) stands for the value of area reached at infinite time.


The variation of area, from the initial stage to the value reached at infinite time (1\(A_\infty/A_0\)), is relatively small but clearly dependent on the length of the PI block: the decrease in area is 17% for PMMA, 20% for SP19, and 29% for SP38.

The fractional contributions of the fast (\(F_1\)) and slow (\(F_2\)) relaxation processes

\[F_1 = \frac{a_1 \tau_1}{a_1 \tau_1 + a_2 \tau_2} \times 100\]

and

\[F_2 = \frac{a_2 \tau_2}{a_1 \tau_1 + a_2 \tau_2} \times 100\]

show that the long relaxation dominates the global process, even though a strong reduction in area occurs at early times.

The short relaxation time is, within the experimental error, identical for PMMA and the two copolymers (6.1 ± 0.3 min), suggesting that the fast relaxation process is controlled by the local reorganization of the PMMA chains. The long relaxation time is identical for PMMA (112 min) and SP19 diblock (115 min) but longer for the SP38 copolymer (185 min). This indicates that the long relaxation process is dominated by the rearrangement of the PMMA block, even though delayed by the PI block in SP38. At high surface pressures, the high viscosity of PI domains, partially atop the PMMA layers (scheme in Figure 1), constrains the relaxation of the PMMA segments. In contrast, the small PI cores in SP19 do not affect significantly the long relaxation time of PMMA chains.

**Polymer Blends.** Figure 6 shows the \(\pi-A\) isotherms of the PI/PMMA (A), PS/PMMA (B), and PI/PS (C) blends in a 1:1 molar ratio (thick lines) with the corresponding theoretical curve (crosses) calculated from the isotherm of single components, assuming ideal mixing. The \(\pi-A\) isotherm of the PI/PMMA blend shows a strong positive deviation to the theoretical curve (Figure 6A) and has a shape similar to that of the \(\pi-A\) isotherms of SP19 and SP38 (Figure 1). This clearly shows that the area occupied by the PI homopolymer at the interface in the presence of PMMA is larger than that occupied in the pure PI film. The dynamic mechanism (deposition–evaporation/spreading) described above for the formation of the SP38 monolayer also applies to the PI/PMMA blend. After the solvent evaporation, the entangled PI chains diffuse to the interface, becoming trapped in the middle of the PMMA pancakes spread at the water surface. Upon compression, the PMMA chains hinder the growth of the PI domains by coarsening. These results suggest that the PI/PMMA (1:1) blend (33% PI segments) at the interface has a similar behavior to the symmetric SP38 copolymer.

The \(\pi-A\) isotherm of the PS/PMMA blend (Figure 6B) shows a negative deviation relative to the theoretical curve, which is compatible with the occurrence of phase segregation, as a consequence of the PS and PMMA immiscibility. The PS condenses in rigid globules above the PMMA matrix following the deposition–evaporation/spreading mechanism. The vitreous globules of PS remain in the upper layer after solvent evaporation and do not contribute to the area at the interface. This hypothesis was further confirmed by the superposition of the PS/PMMA isotherm with the calculated curve, assuming that only the PMMA contributes to the area (omitted).

The \(\pi-A\) isotherm of the PS/PI blend (Figure 6C) is similar to the theoretical curve at low surface pressures, deviating to smaller areas at high pressures. At low surface pressures, both PS and PI homopolymers contribute to the surface area. Upon compression, the flexible PI domains collapse, dragging some PS aggregates toward the formation of a multilayer structure.

Table 2 shows that the isotherms of PS/SP19 and PS/SP38 blends (solid lines) deviate to smaller areas relative to the theoretical curves (crosses) at low surface pressures, becoming

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(A_\infty/A_0)</th>
<th>(a_1)</th>
<th>(\tau_1/\text{min})</th>
<th>(a_2)</th>
<th>(\tau_2/\text{min})</th>
<th>(F_1(%))</th>
<th>(F_2(%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>0.83</td>
<td>0.06</td>
<td>6.3</td>
<td>0.09</td>
<td>112</td>
<td>3.6</td>
<td>96.4</td>
</tr>
<tr>
<td>SP19</td>
<td>0.80</td>
<td>0.08</td>
<td>6.4</td>
<td>0.10</td>
<td>115</td>
<td>4.2</td>
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<tr>
<td>SP38</td>
<td>0.71</td>
<td>0.08</td>
<td>5.8</td>
<td>0.20</td>
<td>185</td>
<td>1.2</td>
<td>98.8</td>
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almost coincident at high pressures. The negative deviation is due to the PS condensation at the upper layer, without any contribution to the surface area. Such an arrangement will produce a thicker film, with the blends becoming more uncompressible than predicted by the theoretical curves at low surface pressures.

AFM Images. The LB monolayers of blends were prepared by transferring the floating films onto freshly cleaved mica substrates, at constant surface pressure. The AFM images of the SP19 and SP38 LB films do not show aggregates (except when formed from high polymer concentrations in the spreading solution), in opposition to the observed results with PS-\(b\)-PMMA diblock copolymers.\(^{23}\) The rubbery properties of the PI block do not allow the observation of structures, because the film is worn out during the scanning and the AFM images appear uniform.\(^{47}\)

Figure 6. The \(\pi-A\) isotherms of the PI/PMMA (A), PS/PMMA (B), and PI/PS (C) blends in a 1:1 molar ratio (thick lines) with the corresponding theoretical curves (crosses) calculated assuming ideal mixing of the single components.

Since PS vitrifies after spreading at the air-water interface,\(^{48}\) all the LB polymer blends with PS show aggregates.

Figure 8 shows the AFM images of the PS film, transferred onto a mica substrate at 2 mN.m\(^{-1}\). Image (a) displays globular aggregates of PS of diameter \(d\) (parallel to the interface) and height \(h\) (perpendicular to the interface) in the ranges \(d = 100-250\) nm and \(h = 5-16\) nm. These dimensions were averaged from 30 cross sections taken through the middle of aggregates. The small aggregates (\(h < 10\) nm) organize following preferential directions like chains—the “chainlike” structure,\(^{49}\) while the large ones (\(h > 10\) nm) appear mostly isolated. The zoom shown in Figure 8b shows a dominant chainlike structure of small aggregates with sparse large aggregates. Figure 8c shows a typical cross section through several chains of small aggregates. The height dispersion, mainly due to the size distribution, also has a contribution from the cross section misalignment relative to the center of the aggregates.

Figure 9a–d shows the AFM images of PS/PMMA LB films. The PS/PMMA blend displays a bimodal distribution of PS aggregates dispersed in a matrix of PMMA: the small aggregates (\(h\approx 3-4\) nm and \(d\approx 70\) nm) in a chainlike structure are the most abundant, while the large aggregates (\(h\approx 21\) nm and \(d\approx 310\) nm) are rare. The zoom of a small region of (a) is shown in (c), and typical cross sections are included in (b) and (d), respectively. The cross section (b) was taken through big and small aggregates simultaneously. Cross section (d) was taken along small aggregates to allow a better vertical scale and a detailed analysis of the profile. The general morphology of globular PS aggregates is retained in the PS/PMMA blend although with a different size distribution. The “small aggregates” are smaller, while the “large aggregates” are bigger relative to the pure PS aggregates on mica. The coexistence of small and large aggregates evidence phase separation. The “small aggregates” of PS are apparently smaller in the PS/PMMA blend than on the solid substrate, probably because the presence of PMMA pancakes reduces the coalescence of PS.

Figure 10 shows the AFM images of PS/SP38 LB films transferred onto mica substrates at 2 mN.m\(^{-1}\) (a) and 20 mN.m\(^{-1}\) (c) with the typical cross sections shown in Figure 10b and d, respectively. The PS/SP38 blend (Figure 10a) shows significant differences from the image of the PS/PMMA blend (Figure 9a). The chainlike structure is almost absent in PS/SP38, and aggregates of variable sizes (\(h\approx 3-6\) nm; \(d\approx 80-100\) nm) and (\(h\approx 10-15\) nm; \(d\approx 150-215\) nm) appear loosely dispersed
in the film matrix. Image (c) for the LB monolayer, transferred at 20 mN/m, shows a similar morphology to that observed at low surface pressures, but with larger aggregates \((h_s = 6-9 \text{ nm}; d_s = 130-140 \text{ nm})\) and \((h_l = 10-19 \text{ nm}; d_l = 150-300 \text{ nm})\). The increase of surface pressure favors the formation of large aggregates (c) with broad size dispersion, as shown by the cross section profile (d). The comparison of Figure 9a with Figure 10a shows that the PI block in the copolymers influences the distribution of PS aggregates.

Figure 11 shows the AFM images of PS/SP19 LB films transferred onto mica substrates at 2 mN.m\(^{-1}\) (a) and 20 mN.m\(^{-1}\) (c), with the corresponding cross sections in Figure 11b and d. The most relevant feature is the high density of small aggregates that appear either isolated or in a chainlike structure. The cross section profile (b) illustrates the nearly constant height of the frequent small aggregates \((h_s \approx 4-5 \text{ nm}; d_s \approx 70-90 \text{ nm})\), while the large aggregates \((h_l = 12-18 \text{ nm}; d_l = 140-280 \text{ nm})\) are scarce.

It is worth noting that the transfer ratio of the LB deposition performed at 20 mN.m\(^{-1}\) was very low \((0.2-0.3)\) for the films presented in Figures 10c and 11c. This can be attributed to the elastomeric properties of the rubbery blends; i.e., the compressed monolayers at the air–water interface expand onto the mica substrate during the transfer process.

These results show that the PI chains covalently bonded to the PMMA chains influence the size and distribution of PS aggregates in the upper layer. As in the absence of PI, the size of the glassy polystyrene aggregates does not change with pressure,\(^{24,48}\) we conclude that PI favors the formation of larger PS aggregates, probably by a softening effect. Under the assumption that the hydrophobic PS preferentially aggregates nearby the PI domains, the differences are consistent with the relative size and distribution of PI domains in the two blends. The density of aggregates is higher for the PS/SP19 blend than for PS/SP38, in good agreement with the relative areas per chain of Figure 7. The chainlike structure of the PS aggregates disappears and the average size increases by increasing the length of the PI block.

In spite of the rubbery properties of the PI block that do not allow the AFM observation of aggregates in SP19 and SP38, the indirect information from the blends with PS is valuable and supports the interpretation proposed for the behavior of SP19 and SP38 at the air–water interface. It is now appropriate to compare the self-assembly of SP19 and SP38 at the interface, with the microstructures generated by PI-b-PMMA copolymers in the bulk phase. The strong incompatibility between the blocks induces the formation of rich microstructures in the bulk, with morphologies that depend on the relative length of the two blocks. Copolymers with blocks of identical length form in bulk lamellar structures, while strongly asymmetric copolymers form spherical microstructures. At the air–water interface, kinetically stable microstructures are generated during the evaporation of solvent due to the appearance of other driving forces. The symmetric SP38 copolymer should rearrange, forming surface micelles (large cores, trapped structures) instead of the lamellar structures adopted in bulk, while the asymmetric SP19 copolymer forms surface micelles (small cores) that are analogous to the spheres found in the bulk phase.\(^{50}\)

**Conclusion**

The \(\pi-A\) measurements revealed that the interfacial behavior of PI-b-PMMA block copolymers depends on the length of the PI block. The long hydrophobic PI block in SP38 contributes to

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the mean molecular area, while the short PI block of SP19 induces a condensing effect in the floating film. The peculiar behavior of PI-\textit{b}-PMMA copolymers was interpreted on the basis of the dynamic deposition–spreading–evaporation mechanism for the formation of the floating films of copolymers with immiscible blocks at the air–water interface. The small PI blocks of SP19

Figure 9. AFM images of PS/PMMA LB films (a). The zoom of a small region of (a) is shown in (c), and typical cross sections are included in (b) and (d), respectively.

Figure 10. AFM images of PS/SP38 LB films transferred onto mica substrates at 2 mN.m$^{-1}$ (a) and 20 mN.m$^{-1}$ (c). Typical cross sections are also included in (b) and (d), respectively.
remain on the top of the PMMA pancake, not contributing to the mean molecular area. Additionally, upon compression, there is a condensing effect due to the PI aggregation in micelle cores. In contrast, the long PI blocks of the nearly symmetric diblock copolymer SP38 segregate into viscous domains kinetically trapped by the PMMA pancakes at the interface, thus contributing to the mean molecular area. Upon compression, these rubbery PI domains are progressively squeezed out from the interface to the upper layer. The behavior of SP38 is consistent with the behavior of the PI/PMMA (1:1) blend at the air-water interface.

The compression-expansion cycles combined with the relaxation curves indicated that the behavior of the diblock copolymers is controlled by the prominent surface-active PMMA block. At low surface pressures, the PMMA chains, in a loop-and-train conformation, relax to larger molecular areas by increasing the number of contacts with the water subphase. The relaxation at high pressures is composed of both a fast and a slow component. The fast process is associated to the local rearrangement of PMMA chains, while the slow process results from the middle-to-long-range reorganization of PMMA chains.

Although the PI domains in LB films of PI-b-PMMA diblocks could not be observed, because the AFM images of the LB films of SP19 and SP38 appear homogeneous, they can influence the size and distribution of aggregates in blends with PS. The size of aggregates varying with surface pressure indicates that the glassy globules of PS become softer in the presence of PI. This effect of PI on PS aggregation gives a new insight into the surface aggregation and can be used to influence the patterning and dimensions of surface aggregates.

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