

Amphiphilic Diblock Copolymers Containing Poly(*N*-hexylisocyanate): Monolayer Behavior at the Air–Water Interface

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ABSTRACT: The behavior of amphiphilic diblock copolymers containing 80–89% of poly(*N*-hexylisocyanate) (PHIC) with different hydrophobic segments spread at the air–water interface has been studied. Surface pressure–area isotherms (π -*A*) at the air–water interface were determined. It was found that these diblock copolymers form stable monolayers and the isotherms present a pseudoplateau region at low surface pressure, irrespective of the nature of the partner block: poly(styrene) (PS) or poly(isoprene). Surface pressure variation at the semidilute region of the monolayer was expressed in terms of the scaling laws as power function of the surface concentration. The critical exponents of the excluded volume v obtained for copolymers with PHIC

and PS blocks are 0.58 for the copolymer with 85% of PHIC and 15% of PS, and 0.63 for the copolymer with 89% of PHIC and 11% of PS. The hydrophobicity degree of the diblock copolymers was estimated from the determination of the surface energy values by wettability measurements. The morphology of the monolayers was determined by means of Brewster angle microscopy. Molecular dynamic simulation was performed to explain the experimental behavior of diblock copolymers at the air–water interface. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1395–1404, 2011

Key words: diblock copolymers; monolayers; self-organization

INTRODUCTION

Insoluble monomolecular layers at interfaces have been the subject of many experimental and theoretical studies.^{1–4} These works have been mainly performed on small amphiphilic molecules such as surfactants and lipids at gas–liquid or liquid–liquid interfaces and more recently the conformation of quasi two-dimensional layers of long polymer chains at interfaces have also been investigated.^{5–8} Polymers at surfaces and interfaces are of great industrial and academic interest, e.g., polymeric films find industrial applications in liquid–liquid extraction, stabilization of colloids, and Langmuir–Blodgett films,^{9,10} while spread monolayers can be investigated as models for two-dimensional systems or assembled films as model membranes.¹¹

During the last few decades, there have been significant efforts to study diblock copolymers at surfaces and interfaces. This fact is in great part due to fundamental interest in the interdependence of surfaces or interfaces and nanostructures, but it is also motivated by the technological importance of self-assembling nanostructures.^{12–19}

Kawaguchi et al.⁷ have reported surface pressure–area isotherms and fluorescence microscopy data of poly(*N*-hexylisocyanate) (PHIC) films spread at the air–water interface and concluded that PHIC forms a stable film. The experimental area suggested that PHIC lies on the water surface. Moreover, from the fluorescence microscopy images, the PHIC monolayer is observed in a liquid-like state.

As it is known,²⁰ the surface concentration of the copolymer monolayer spread at the air–water interface can be regulated easily by compression or expansion of the monolayer. It is thus possible to make an analogy between the intervals of superficial and bulk concentration frequently used in polymeric science. By this analogy, the extrapolated area to zero surface pressure, A_0 , and the collapse pressure, π_c , respond to phenomena that take place in the concentrated region.^{21,22} In the semidilute concentration region, surface pressure obeys a power law of the

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surface concentration and is independent of the molecular weight.²³ According to the scaling concepts,²⁴ the surface pressure in the semidilute region varies with the surface concentration in terms of the following expression^{25,26}:

$$\pi = \Gamma^{2\nu/2\nu-1} \quad (1)$$

where Γ is the surface concentration, and ν is the critical exponent of the excluded volume. The behavior of the monolayers formed by the copolymers studied in this work is discussed in terms of the scale concepts in the semidilute region. The determination of the surface energy (SE) of the copolymers is also of interest in different fields such as adhesion and adsorption.^{27,28} Adsorption of diblock copolymers at interfaces plays an important role in several biological and technological processes. The SE values were estimated from wettability measurements.

The aim of this work is to investigate the changes in surface activity and the molecular organization of the monolayers of a diblock copolymer containing PHIC, with two different hydrophobic blocks, and to demonstrate that the hydrophobic segments may not change the experimental area. This behavior could mean that PHIC lies on the water surface.

To our knowledge, this is the first reported investigation of PHIC-based block copolymers behavior at the air–water interface. To describe the surface organization of these block copolymers at the air–water interface, molecular dynamic simulation (MDS) was performed.

MATERIALS AND METHODS

Copolymer preparation

Diblock copolymers were synthesized by sequential anionic polymerization (samples PHS1 and PHI)²⁹ and titanium-mediated coordination polymerization (samples PHS2 and PHS3).³⁰ The hydrophobic block consists of a poly(styrene) (PS) chain having 21, 22, and 1074 repeating units for samples PHS1, PHS2, and PHS3, respectively (Table I). The hydrophilic PHIC block is composed of 38–248 monomer

units. Another copolymer is composed of PHIC and poly(isoprene) (PI) blocks. For the specific sample, the degree of polymerization of the PI block is 241. The copolymer compositions were determined from the ¹H NMR spectra, recorded in chloroform-*d* at 303 K with a Varian Unity Plus 300/54 NMR spectrometer.

Monolayers

The monolayers were obtained by spreading chloroform, cyclohexane, or toluene solutions of PHS1, PHS2, PHS3, and PHI on the water surface. The concentration of the spreading solutions was 1 mg/mL. The temperature of the water subphase (Milli-Q) was kept constant at 298 K. Between 20 and 30 min after spreading, the monolayers were compressed continuously.

Surface pressure-area isotherms

The surface pressure-area isotherms (π - A) were obtained using a Langmuir film trough (NIMA-1232D1D2) at 298 K with water subphase, pH = 5.6. The Langmuir monolayers were obtained by depositing small drops with a microsyringe, about 10 μ L of the copolymer solution on the air–water interface. Before compression, the film was allowed to equilibrate for about 30 min to ensure full evaporation of the spreading solvent and also, to allow the molecules to reach the equilibrium. The compression velocity was 10 cm² min⁻¹. The experiments were performed in triplicate.

The Langmuir isotherms were treated by the classic way, i.e., the projected area to zero pressure A_0 , was obtained from the linear variation of surface pressure π with surface concentration in the condensed region; the collapse pressure π_c was also estimated in this concentration region and the static elasticity ϵ_0 was analyzed at different surface concentrations of diblock copolymers.

Contact angles: SE

The SEs of the copolymers were determined by wettability measurements with water and

TABLE I
Composition and Molecular Characterization of PHS1, PHS2, PHS3, and PHI Copolymers

Diblock copolymer	Composition (% PHIC)	$\bar{M}_w \times 10^{-3}$	I	Y^a	X	Y
PHS1	85	14.6	1.18	21	49	21
PHS2	89	20.3	1.22	22	71	22
PHS3	8	121.4	1.19	1074	38	1074
PHI	80	82.4	1.25	0	258	241

X , polymerization degree of PHIC; Y , polymerization degree of PS or PI; Y^a , chain length of PS segment; $I = (M_w/M_n) =$ polydispersity index.

diiodomethane. Polymer films were cast onto glass slides for optical microscopy. The cast films were dried for 30 min at 333 K under vacuum. The wettability of the polymer films was determined by static contact angle (CA) measurements. Static CAs were determined using a contact angle system OCA by Dataphysics with a conventional goniometer and high-performance video camera, controlled by OCA20 software. A syringe connected to a Teflon capillary of about 2-mm inner diameter was used to supply liquid into the sessile drops from above. A sessile drop of about 0.4–0.5 cm radius was used. The CAs were measured carefully from the left and right side of the drop and subsequently averaged. These procedures were repeated for six drops of each liquid on three new surfaces. All readings were then averaged to give an average CA. All experiments were performed at room temperature.

Brewster angle microscopy

The Brewster angle microscopy (BAM)³¹ was employed to visualize the morphology of the copolymer monolayers at the air–water interface. All the experiments were performed using a Nanofilm ellipsometer model EP³ with an Nd-YAG laser, wave length of 532 nm as radiation source. A *p*-polarized laser beam was reflected off the air–water interface at an incident angle of 52–54°. The reflected beam passes through a focal lens into the analyzer at a known angle of incident polarization and finally to charge-couple device (CCD) camera. This instrument was placed above the Langmuir trough.

Molecular dynamic simulation

To explain the balance of specific interactions of isocyanate groups and hexyl groups of PHIC at interface, MDS was carried out under periodic boundary conditions.^{32,33} MDS was performed using the Discover_3 (Accelrys) program with the ESFF force field. The three-dimensional models were built using Insight II program. The initial conformation of seven oligomers (with 5 RU) was relaxed using an annealing protocol. Then the minimized oligomer was repeated four times on a plane XY of the surface of a water layer. To simulate air–water interface, a box was built considering the following conditions: the plane *x* and *y* was built considering two different experimental conditions, along the *z* axis a water layer was built with a thickness of 20 Å, keeping the water between $-10.0 < z < 10.0$, the rest of the cell was simulated in vacuum, similar to the environment conditions. The PBC cell was built simulating two different surface areas, 15 and 27 Å²/repeating unit. All these systems were relaxed by 500 ps.

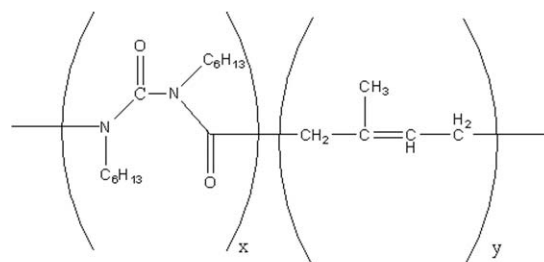
Upon relaxation, molecular dynamics was carried out for 1 ns at 298 K for each system.

RESULTS AND DISCUSSION

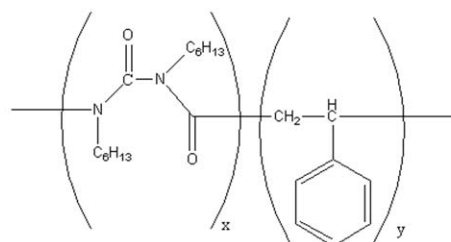
Surface pressure-area isotherms

Table I lists the composition and molecular characterization of the diblock copolymers previously reported.^{29,30} The chemical structures of the studied copolymers are represented in Scheme 1. The surface properties of these diblock copolymers containing PHIC were studied by surface pressure measurements under compression. The surface pressure-area isotherms (π -*A*) for the copolymers and the corresponding homopolymers on pure water (pH, 5.6) at 298 K are shown in Figures 1 and 2, for block copolymers, the mean area per repeating unit was calculated using the average molecular weights of the repeating units.

When the PS block becomes larger (PHS3), the monolayer seems to be no longer stable and the π -*A* curve tends clearly toward an isotherm of pure PS. Despite the fact that some authors have reported π versus *A* data for PS onto water, it seems widely accepted that PS does not form true Langmuir monolayers.¹ In this case, there is only a slight increase in the surface pressure upon compression, suggesting the presence of aggregates at the interface.



Poly(N-hexylisocyanate)-b-Poly(isoprene) (PHI)



Poly(N-hexylisocyanate)-b-Poly(styrene) (PHS)

Scheme 1 Molecular structures of poly(*N*-hexylisocyanate)-*b*-poly(isoprene) (PHI) and poly(*N*-hexylisocyanate)-*b*-poly(styrene) (PHS).

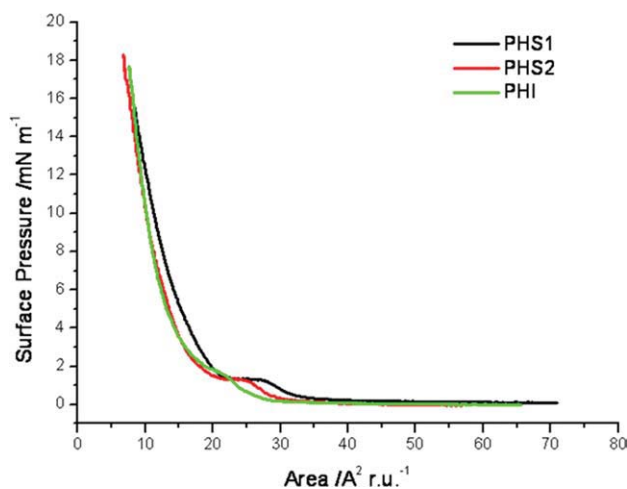


Figure 1 Langmuir isotherms (π - A) for PHS1, PHS2, and PHI using toluene as spreading solvent. Compression velocity $10 \text{ cm}^2 \text{ min}^{-1}$, temperature: 298 K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To evaluate the stability of the monolayers, hysteresis experiments consisting of four cycles of compression and expansion were done. All the studied monolayers showed a similar behavior (Fig. 3). The isotherms of PHS1 and PHI showed hysteresis during the first compression–expansion cycle. These results suggest that the monolayers adopt a different conformation after the first compression involving some energy storage during the first expansion. It seems that the time extent of the experiment is not enough to allow the full relaxation of the monolayer. However, during the subsequent cycles, the hysteresis is much less pronounced. The surface pressure achieved in all the compressions is constant, show-

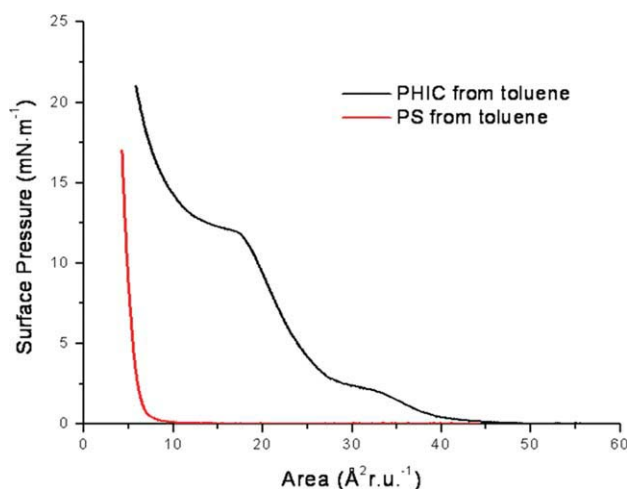


Figure 2 Langmuir isotherms (π - A) for homopolymers PS and PHIC. Compression velocity $10 \text{ cm}^2 \text{ min}^{-1}$, temperature: 298 K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

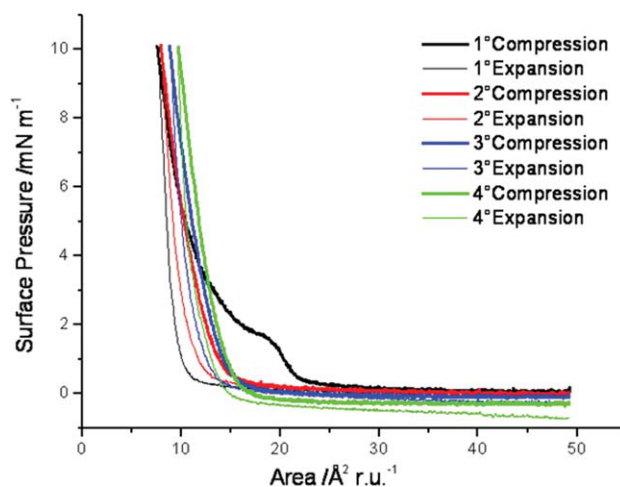


Figure 3 Compression–expansion cycles for PHI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ing that no material loss is taking place during the experiments.^{4–6}

The limiting area (A_0), based on π - A isotherms (Fig. 1) are listed in Table II. The A_0 values for the PHSs decrease upon increasing PS composition in the copolymers. This could be explained because the copolymer could adopt one specific organization at the air–water interface. For larger surface area, the diblock copolymers containing 85% (PHS1), 89% (PHS2), and 80% (PHI) of PHIC, the corresponding surface pressure was very low and the isotherms show a pseudoplateau region, irrespective of the nature of the other segment, either PS or PI (Fig. 1). This may also indicate that the surface pressure gain by hydrogen bonding between the isocyanate groups

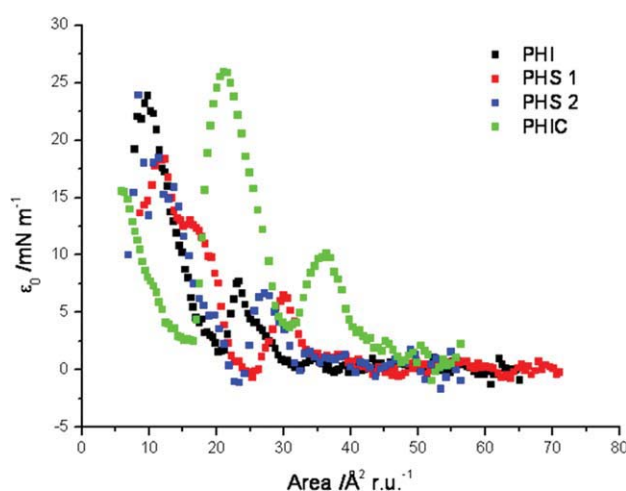


Figure 4 Static elasticity, ϵ_0 versus area ($\text{\AA}^2/\text{repeating unit}$) plots for PHS1, PHS2, PHI, and PHIC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Area Per Repeating Unit Projected at Zero Surface Pressure, A_0 and Collapse Pressure, π_C Values of PHIC and Block Copolymers

Diblock copolymer	% PHIC	A_0 (\AA^2 r.u. $^{-1}$)	π_C (mNm^{-1}) ^a
PHIC	100	27.7	–
PHS1	89	17.3	$\sim >11$
PHS2	85	14.6	$\sim >11$
PHI	80	13.3	$\sim >11$

^a According to hysteresis experiments (Fig. 3).

and water is partially compensated by the surface pressure loss because of the cohesive interaction among the hexyl groups. This is the explanation for the behavior of PHIC spread at the air–water interface, reported by Kawaguchi et al.⁷ some years ago. However, in the case of the copolymers studied here, it was not observed the second pseudoplateau region of the PHIC homopolymer. This behavior could be explained if it is considered that the monolayer collapses before reaching this region.

The presence of the pseudoplateau in the isotherms may imply a change in the surface organization of the copolymer systems within this region due to a possible phase transition, or the collapse of the monolayer. As the compression continues, the surface pressure sharply increases, resulting in appa-

rently a heterogeneous film. (see BAM images in Figs. 5 and 6).

The determination of the collapse pressure is not a very clear topic in polymeric science. Unlike small molecules, monolayers of polymers do not always collapse in an abrupt way, making difficult to identify the exact surface pressure at which this occurs. This feature makes obligatory to observe more than a single aspect to identify the collapse.

Several hysteresis experiments were carried out varying the target pressure, to identify the maximum pressure that could be kept constant by keeping the area fixed. This may indicate the pressure beyond which the monolayer become unstable or collapsed. The behavior of all the studied copolymers was very similar, showing a collapse pressure of about 11 mN/m (Table II). BAM experiments were also done to help clarify this subject.³¹

Figure 2 shows for comparison the experimental isotherms for PHIC and PS homopolymers; both were spread from toluene. With these results, it is possible to observe that when the PS block increases in the copolymers series (PHS3), the π - A isotherm is similar to that corresponding to the PS homopolymer. Taking into account the fact that some authors have reported π versus A data for PS onto water, it seems widely accepted that PS does not form true Langmuir monolayers.¹

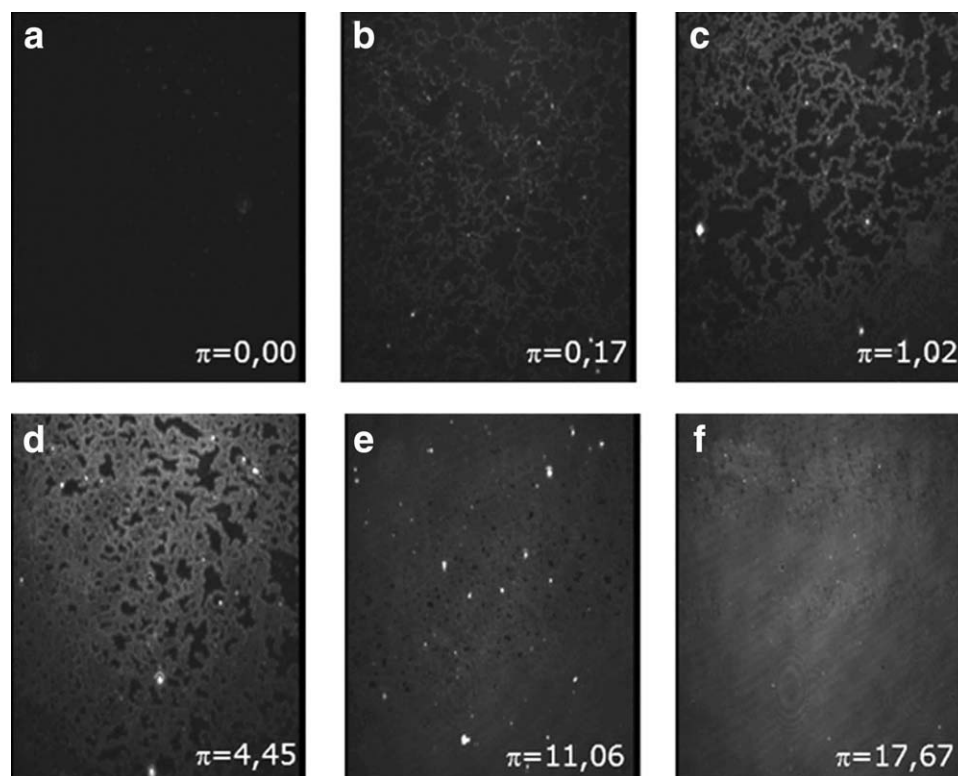


Figure 5 BAM images of PHS1 monolayer at different surface pressures π , using toluene as spreading solvent. (a) 0 mN/m , (b) 0.17 mN/m , (c) 1.02 mN/m , (d) 4.45 mN/m , (e) 11.06 mN/m and (f) 17.67 mN/m .

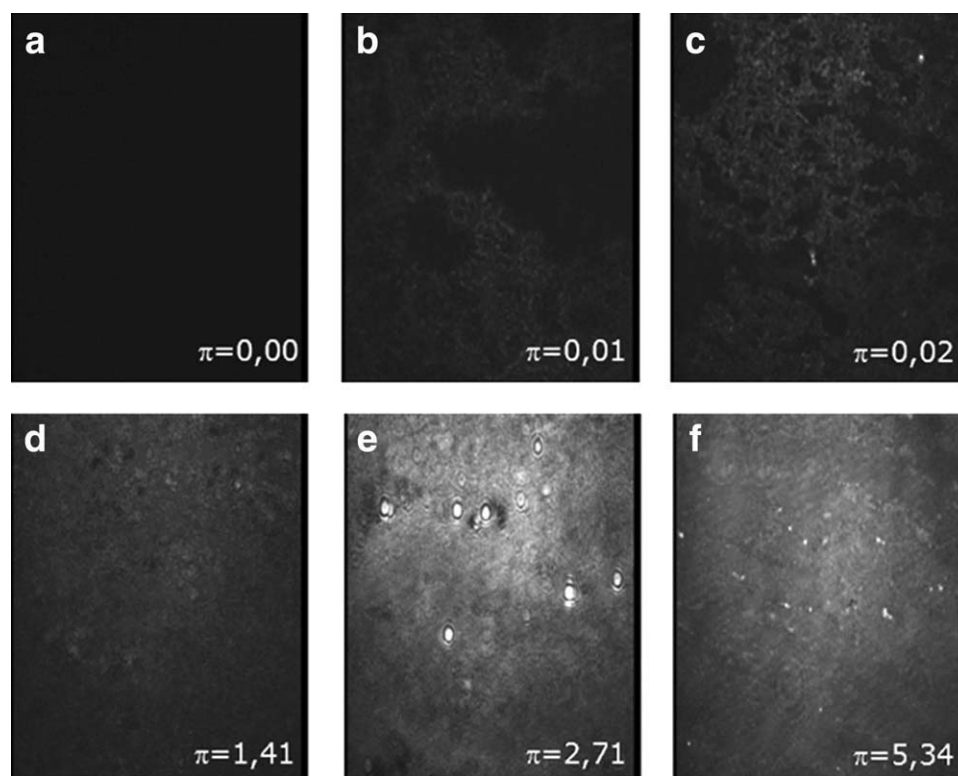


Figure 6 BAM images of PHI monolayer at different surface pressures π , using toluene as spreading solvent. (a) 0 mN/m, (b) 0.01 mN/m, (c) 0.02 mN/m, (d) 1.41 mN/m, (e) 2.71 mN/m and (f) 5.34 mN/m.

In general, three regions can be distinguished upon compression shown by the isotherms, corresponding to the expanded liquid, condensed liquid, and condensed-like states. In the case of PHIC, two pseudoplateau regions can be observed (Fig. 2). At high surface pressures, there is a pseudoplateau appearing between 15 and 20 $\text{\AA}^2 \text{ r.u.}^{-1}$, which could correspond to the transition between the condensed-like state and the condensed liquid state. At low surface pressures, the observed pseudoplateau region is similar to those distinguished for the PHIC-containing diblock copolymers (Fig. 1). For these copolymers, the transition is slightly shifted to lower areas per repeating unit compared with the PHIC homopolymer. The reason for this behavior remains unknown; currently, MDS experiments to clarify if there is a change in the polymer chains conformation when a hydrophobic block is present that could cause this behavior are in development. It is also possible that this shift be due to the calculated area per repeating unit for the block copolymers.

The isotherms corresponding to the copolymers containing PS in their structures (PHS1 and PHS2) are very similar, probably due to the small difference in their composition, since the size of the PS block is the same in both copolymers. In the case of PHS3, the content of PS is higher, leading to an unstable pseudomonolayer, with an isotherm show-

ing no transitions and very similar to that of pure PS. In the case of PHI, the shape of the isotherm is slightly different to those of PHS, showing a less pronounced transition, comparable with that observed for pure PHIC, probably due to the size of the hydrophilic block.

Taking into account of these results, the affinity of these systems for the air–water interface could provide complementary and important information. The interface could have different thermodynamic quality as a solvent for each of the diblock copolymers according to their PHIC content. To quantify this property, the classic eq. (1), by de Gennes was employed; according to this, the $\log \pi$ versus $\log \Gamma$ plot at the semidilute region shows a linear variation with a slope of $2v/2v - 1$. Starting from the slope calculated for these plots, the v exponent values for each block copolymer were obtained, the results are summarized in Table III. For polymer chains in two dimensions in good

TABLE III
Critical Exponent of the Excluded Volume v Values Obtained from the Linear Region of $\log \pi$ Versus $\log \Gamma$ Plots for PHS1 and PHS2 Monolayers

Diblock copolymer	% PHIC	$v \pm 0.02$
PHS1	85	0.58
PHS2	89	0.63

TABLE IV
Static CA, Total SE, Dispersion Force, γ_d and Polar Contribution, γ_p for PHS1, PHS2, PHS3, and PHI Copolymer Surfaces

Diblock copolymer	% PHIC	CA ($^\circ$) ^a	CA ($^\circ$) ^b	SE	γ_d	γ_p
PHS3	8	101.9 \pm 0.3	22.2 \pm 0.7	50	50.3	0.2
PHS2	89	15.1 \pm 0.2	24.2 \pm 0.2	71	29.4	41.8
PHS1	85	36.8 \pm 0.3	26.1 \pm 0.3	68	31.3	30.5
PHI	80	19.6 \pm 0.3	36.8 \pm 0.5	61	25.4	43.3

^a From water.

^b From diiodomethane.

solvents, the theoretical predictions point to a ν value narrowly centered at 0.75. Monte Carlo simulations predict a value of 0.753,³⁴ while by the matrix-transfer method,³⁵ a value of 0.7503 is predicted. In the case of a bad solvent, the situation is not clear, the predictions are less precise. Monte Carlo simulations^{36,37} have suggested $\nu_0 \approx 0.51$ while matrix-transfer data suggest $\nu \sim 0.55$. The ν values for the PHSs summarized in Table III indicate that the copolymers have different affinity for the interface, the air–water interface is lightly better solvent for PHS2, which has a higher content of PHIC. A lower value of ν is observed for PHS1, indicating a less affinity for the interface. These results are reasonable considering the hydrophobicity degree of the respective polymers (Table IV).

Static elasticity ε_0 of diblock copolymer monolayers

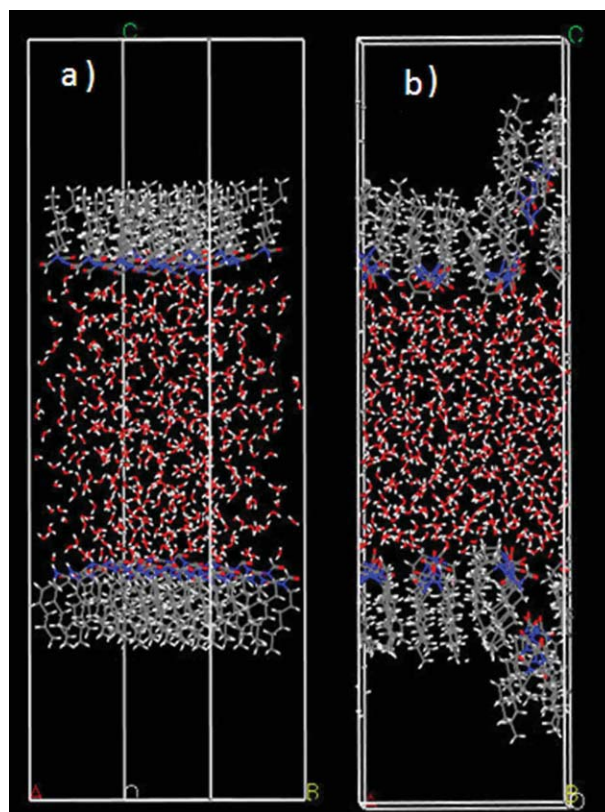
It is known that the behavior and stability of a polymeric monolayer partially depends on the strength of interfacial interactions with substrate molecules and of polymer intersegmental interaction. Therefore, the viscoelastic properties of polymer monolayers could also be dependent on these interactions. From the experimental π -A or π - Γ curves, it was possible to calculate the classical static elasticity modulus ε_0 , according to eq. (2), which only accounts for hydrostatic compression:

$$\varepsilon_0 = -A \left(\frac{\partial \pi}{\partial A} \right)_T = \Gamma \left(\frac{\partial \pi}{\partial \Gamma} \right)_T \quad (2)$$

The plot of the compressibility modulus or static elasticity, ε_0 , calculated from the surface pressure isotherms (π versus the surface concentration Γ) is provided in Figure 4. It can be observed that the greatest increase in elasticity occurs within the semidiluted regime. The presence of a hydrophobic block as PS or PI in the macromolecule shifts the maximum of the elasticity values ε_0 to lower areas.

The variation of static elasticity values ε_0 in the semidilute region is the typical behavior for polymer

monolayers. It is known that the maximum ε_0 values, in the case of polymeric systems, are in this region (diluted and semidiluted), since the chains behave independently or are in mutual contact, but responding almost in individual form to the deformation. For PHIC, the plot of compressibility modulus or static elasticity, ε_0 in Figure 4 shows two maxima, located in the semidilute region, where the contact between chains of PHIC is very close, and could respond to the deformation like a sort of polymer lattice. In the case of the diblock copolymers, these can respond to the deformation in almost



Scheme 2 Box under periodic boundary conditions in the initial state 27 Å²/repeating unit (a) and in the final state 15 Å²/repeating unit (b) of the simulation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

individual form. According to the results shown in Figure 4, the static surface elasticity for copolymers shows high values and the surface pressure would be more sensitive to changes at smaller values of area per repeating unit.

Hydrophobicity degree

To obtain information about the hydrophobic degree of diblock copolymers, the total SE, was also estimated by CA measurements of water and diiodomethane on the copolymer surfaces. The dispersion force and polar contributions to SE, γ_d and γ_p , respectively, were calculated by the Owens, Wendt, and Kaible method.^{38,39} The measurement of CAs on a solid surface is one of the most practical ways to obtain surface free energies.

The results obtained are summarized in Table IV. The hydrophobicity degree of the surface indicated by the γ_d values, varies in logic form decreasing when the PHIC amount in the copolymer increases. In the case of PHS3 with only 8% of PHIC, γ_d is significantly higher since this copol-

mer is more hydrophobic than the other diblock copolymers.

Brewster angle microscopy

Direct visualization of changes in the monolayer arrangement was achieved in certain cases by means of BAM.³¹ To obtain additional experimental data for the behavior in the plateau regions, we have examined the morphology of the monolayers of PHS1 and PHI at different surface pressures, Figures 5 and 6, respectively. From these images, it can be seen that at low surface pressures both copolymer monolayers are not completely homogeneous. When the surface area is decreased and the plateau is reached, the monolayers become heterogeneous. At surface pressures higher than the plateau, this heterogeneity increases showing that the collapse may have been reached.

From these results, it is difficult to say if the collapse region is close to the pseudoplateau region or is at higher compression. This aspect is very conflictive; however, the hysteresis experiments confirm

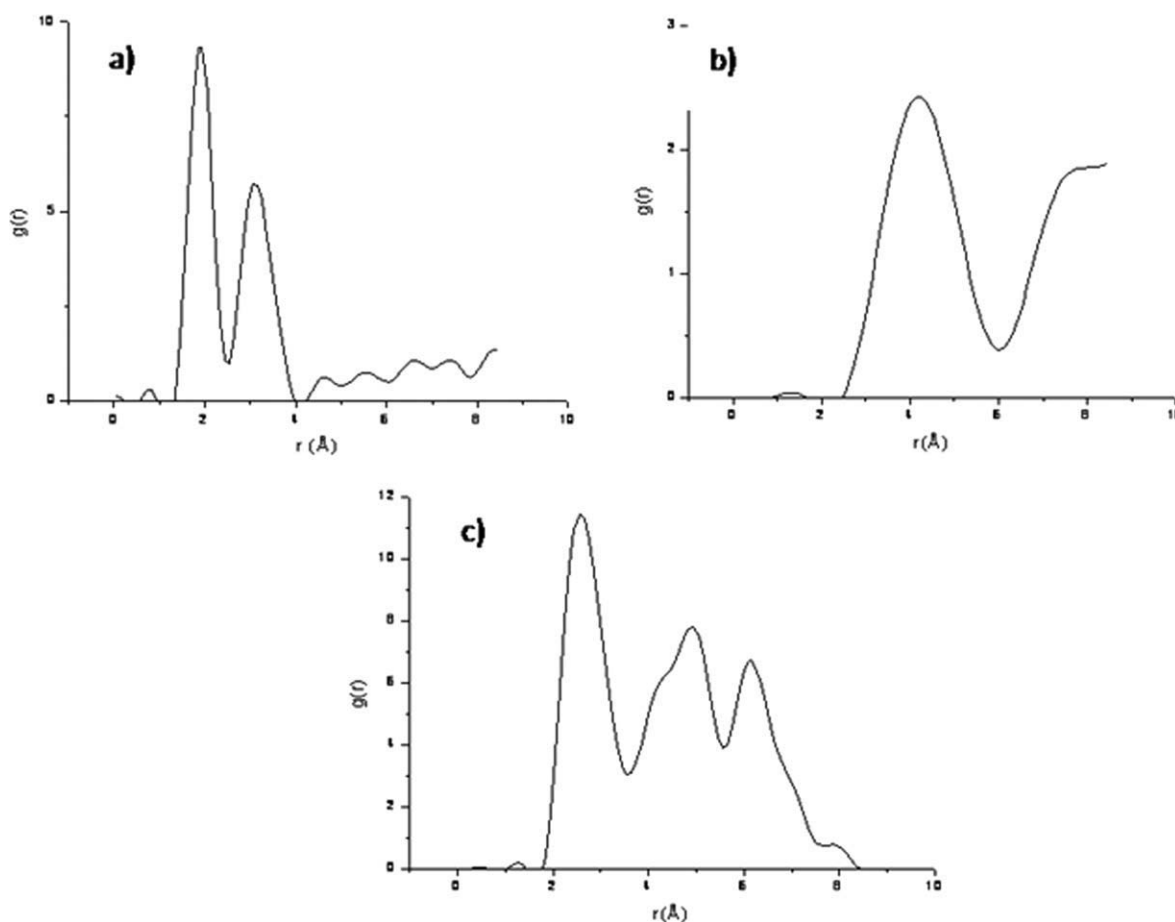


Figure 7 RDF, between oxygen atoms of the isocyanate groups and hydrogen atoms of water molecules (a), between oxygen atoms of water molecules and aliphatic groups (b), and between aliphatic groups (c).

that the monolayers are stable, except for the diblock copolymer with 8% of PHIC.

Molecular dynamic simulation

Taking into account that the overall shape of the isotherm seems to be determined by the behavior of the PHIC segment at the air–water interface, MDS was used to visualize the orientation of the amphiphilic homopolymer. In a first approach for 27 \AA^2 /repeating unit of surface area, the results indicate that the macromolecules could adopt a specific orientation in the monolayer, see Scheme 2(a). The aliphatic chain could be expelled toward the air and the isocyanate groups could be oriented toward the water.

From MDS trajectory, the radial distribution function (RDF) plots obtained for oxygen atoms of isocyanate groups relative to hydrogen atoms of the water are presented in Figure 7(a), 1.9 \AA of distance was obtained. The RDF between hexyl groups and water molecules was also calculated, and the results indicate that the moieties of PHIC are at a larger distance, about 4.2 \AA , relative to water molecules [Fig. 7(b)]. On the other hand, in Figure 7(c), a distance of 2.5 \AA between aliphatic groups was obtained, indicating significant interactions such as was reported by Kawaguchi et al.⁷

The distance found between atoms of the hydrophilic moieties of PHIC and water molecules (1.9 \AA), and between aliphatic chains (2.5 \AA) could correspond to hydrogen bonds and hydrophobic interaction, respectively.

When the monolayer is more compressed, about 15 \AA^2 /repeating unit, the results from RDF are similar to those obtained at 27 \AA^2 /repeating unit. The main feature in this state is that two chains begin to extend toward the air, this situation could probably destabilize the monolayer and finally could cause the collapse of this.

CONCLUSIONS

The spreading experiments showed that all the diblock copolymers with 80–89% of PHIC form stable monolayers. The surface pressure–area isotherms present a pseudoplateau region at low surface pressure, irrespective of the hydrophobic block nature, PS or PI. The limiting area A_0 and approximate values of πc were estimated from π - A isotherms and BAM images. The hydrophilic block of PHIC seems to be responsible of the surface properties of diblock copolymers. The experimental results were satisfactorily described by MDS. For PHIC block, the surface pressure induced by the hydrogen bonding

between the isocyanate groups and water could be compensated by the surface pressure loss due to the cohesive interaction among the hexyl groups. The RDF between oxygen atoms of the isocyanate groups and hydrogen atoms of the water molecules; between oxygen atoms of water and aliphatic groups and finally between aliphatic groups can predict the possible organization of the hydrophilic block PHIC at the air–water interface at two different surface areas.

In conclusion, the results indicate that the surface behavior of the diblock copolymer systems is mainly determined by the hydrophilic segment, while the role of the polyisoprene or polystyrene block is mainly to anchor the copolymer at the interface.

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