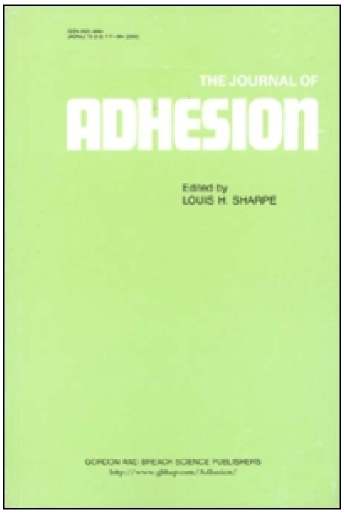

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Control of the Surface Properties in Polymer Blends

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Control of the Surface Properties in Polymer Blends

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We report on the preparation of amphiphilic diblock copolymers containing a hydrophilic segment, poly(acrylic acid)(PAA), and a polystyrene hydrophobic part. We analysed, by means of contact-angle measurements, how the hydrophilic segments usually bury themselves under the hydrophobic when exposed to air to reduce the surface free energy of the system. In contrast, in contact with water, the hydrophilic blocks have a tendency to segregate to the interface. We first describe the parameters that control the surface reconstruction when the environmental conditions are inversed from dry air to water vapour. Then, annealing time, temperature, composition and size of the diblock copolymers, and size of the matrix that influenced the surface migration process are the main parameters also considered. Finally, the density of the carboxylic functions placed at the surface was determined using the methylene blue method.

Keywords: Compatible blends; Diblock copolymers; Surface segregation; Wettability

1. INTRODUCTION

For many applications, the ultimate performance of materials depends not only on their bulk properties but also on their interfacial behavior. Controlling the preparation of functional surfaces is essential for the development of new materials with improvements in such properties

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as adhesion, wettability, gas impermeability, stain resistance or biocompatibility [1].

Until now, the most common procedures used to prepare functionalized surfaces were based on physical or chemical modifications, such as plasma or flame treatment, chemical reaction, surface grafting, or metal coating. All these modifications are bound up with several major drawbacks including tedious additional steps and relatively low control of the surface composition and structure, which can be additionally altered in terms of mechanical properties and are often proved difficult to replicate [2,3].

An alternative in which chemists have rarely been involved concerns the use of spontaneous segregation in compatible binary blends. Surface segregation, which is a phenomenon common to most materials, uses the preferential migration of one blend component to the interface, thereby inducing selective enrichment at the near-surface level. The resulting composition of the surface is very different from that of the bulk and is controlled by surface segregation, which is the result of two main factors: enthalpic and entropic forces. These forces, which can operate independently or jointly, depend very much on the exposure environment (air/solid or water/solid). In the case of air/solid interfaces, a large number of studies have allowed the enthalpic factor to be identified in terms of two types of functions: either low-surface-energy functions (–F, –Si) or high-surface-energy functions (–COOH, $-NH_2$). Whereas low-surface-energy functions, which are usually hydrophobic, migrate to the air surface to reduce the system enthalpy, the hydrophilic functions (high-surface-energy functions) stay hidden beneath the surface. In contrast, exposure to water induces surface reconstruction until the hydrophilic functions are in contact with water [4,5]. When additives exhibit lower entropy than the blend matrix, this supposes an additional driving force for surface segregation. Such additives can be formulated with low molar mass, or their entropy can be restricted by introducing branching points in the structure [6–8]. Surfaces can be enriched on star polymers, for instance, when these are mixed with linear homologues exclusively by entropic factors.

Whereas several groups have already described the preparation of functional surfaces through surface migration [9–11], experimental studies on the parameters behind this process are somewhat scarce. In this contribution, we first report on the preparation of hydrophilic or hydrophobic surfaces using amphiphilic diblock copolymer/linear polystyrene mixtures and then analyze the parameters influencing spontaneous surface segregation. The polymer surfaces were characterized by contact-angle measurement, a technique sensitive to the density of polar groups at the surface, and X-ray photoelectron spectroscopy (XPS) in some selected cases.

2. EXPERIMENTS

2.1. Materials

Styrene (St) (Sigma, Aldrich, France, 99%), *t*-butyl acrylate (tBA) (Sigma-Aldrich, France, 98%) were distilled under reduced pressure over calcium hydride prior to use. Copper(I) bromide (CuBr) (Sigma-Aldrich, France, 98%), 2,2′-bipyridyl (bipy) (Sigma-Aldrich, France, 99+%), *N,N,N′,N″,N″*,-pentamethyldiethylenetriamine (PMDETA) (Sigma-Aldrich, France, 99%), phenylethyl bromide (PhEBr) (Sigma-Aldrich, France, 97%), and other solvents were used as received.

2.2. Sample Preparation

The diblock copolymers have been prepared by atom-transfer radical polymerization (ATRP) in two steps following previously reported procedures, which are briefly described next.

Synthesis of a Polystyrene (PS) Macroinitiator by ATRP

All polymerizations were performed in Schlenk flasks previously flamed and dried under vacuum. ATRP was carried out using the following stoichiometry [M]/[I]/[CuBr]/[L] = 250:1:1:2, where M = styrene, I = initiator (PhEBr), and L = ligand (bipy). The reactants were added under N_2. The reaction mixtures were then degassed by three freeze–pump–thaw cycles and placed in a thermostated oil bath at 110°C. After the polymerization, the mixtures were cooled to room temperature; the contents were diluted with dichloromethane (CH_2Cl_2) and passed through a neutral alumina column to remove the copper salt. After evaporation, the polymers were precipitated in ethanol, filtered, washed, and dried under vacuum.

Synthesis of PS-b-PtBA by ATRP

The macroinitiator PS-Br and 5 mL of degassed acetone were added to the mixture ([M]/[I]/[CuBr]/[L] = 400:1:1:1). Acetone enhanced the solubility of the CuBr/PMDETA complex. The *t*BA polymerizations were carried out at 65°C.

Hydrolysis of the PtBA Block in the PS-b-PtBA Copolymers

Copolymers were first dissolved in CH_2Cl_2. Trifluoroacetic acid (TFA) was then added (10 equivalents to *t*-butyl ester units), and the mixture was stirred at room temperature for 3 days. The deprotected polymers precipitated in the reaction media and were filtered, washed with CH_2Cl_2, and finally dried under vacuum.

2.3. Preparation of the Films

Thin films of diblock/linear PS mixtures were prepared by spin coating from THF concentrated solutions (120 mg/ml) onto cleaned silicon wafers and were dried under vacuum for several hours. Film thicknesses were determined by atomic force microscopy (AFM) to be between 200 and 300 nm. Annealing was carried out either by exposure to saturated water vapour or to dry air. Whereas humid treatment temperatures varied between 90°C and 130°C, treatments carried out in dry air were done at 90°C. After annealing, the samples were rapidly cooled. Those films treated under humid conditions were additionally dried under vacuum to remove possible adsorbed water at the surface.

2.4. Characterization

^{1}H NMR spectra of the copolymers were recorded at room temperature on a Bruker Avance 400 MHz spectrometer (Bruker AXS, Karlsruhe, Germany) using the residual proton resonance of the deuterated solvent as internal standard. Average molar masses and molar mass distributions of the samples were determined by size exclusion chromatography (SEC), using a Varian 9001 pump (Varian UV, Les Ulis Cedex, France) with both a refractive index (Varian RI-4) and a UV detector (Spectrum Studies UV 150). Calibration was obtained using narrowly distributed polystyrene standards and THF as the mobile phase at a flow rate of 0.5 ml/min^{-1}.

Contact Angle Measurements

Contact angles of water were determined using a Krüss DSA100 (Hamburg, Germany) contact-angle measuring system at room temperature. A water droplet of 2 μl was placed on the specimens at two different pH values: 2 and 6. A charge-coupled-device camera was used to capture the images of the water droplets for the determination of the contact angles.

XPS Experiments

The surface composition of selected blends was obtained by X-ray photoelectron spectroscopy (XPS). XPS spectra were recorded with a 220i-XL Escalab from VG (Netherlands). The films supported on silicon wafer were put under ultra high vacuum (UHV) to reach the 10^{-8} Pa range. The nonmonochromatized Mg X-ray source was used at 100 W, and a flood gun was used to compensate for the nonconductive samples. The spectra were calibrated in relation to the C1s binding energy (284.6 eV), which was applied as an internal standard. Fitting of the high-resolution spectra was provided through the Avantage program from VG.

Load and Release of Methylene Blue (MB)

The films supported on a silicon wafer were submerged in a buffered MB solution at pH 7.0 with a concentration of MB of 10^{-3} M. After 1 h, the films were rinsed in a separate bath at pH 7.0 for 30 min. Note that at neutral pH values poly(acrylic acid) (PAA) is negatively charged and establishes electrostatic interactions with the positively charged MB (load). Release of the MB was carried out by dipping the films into an acidic water solution (pH 3.0). Finally, the quantity of MB released was estimated by ultraviolet (UV) spectroscopy (Lambert–Beer's law).

3. RESULTS AND DISCUSSION

3.1. Surface Segregation of Amphiphilic Diblock Copolymers

The spontaneous surface segregation of amphiphilic diblock copolymers to an interface is dominated either by enthalpic (*i.e.*, functionality of the monomer units) or entropic (*i.e.*, chain lengths or chain topology) parameters. The exposure of the block copolymer to either a hydrophobic or hydrophilic milieu leads to a morphological rearrangement of the surface composition in response to a change in the environment. Whereas hydrophilic blocks will migrate to the surface upon exposure to water, they will stay hidden beneath the surface in contact to dry air. The appropriate use of this themodynamical property may offer interesting alternatives to other surface modification methods with relevance in a variety of domains such as surface lubrication, biofouling, and also adhesion.

In this contribution, we study the parameters that govern the surface segregation of hydrophilic–hydrophobic diblock copolymers using polystyrene-b-poly(acrylic acid) (PS-b-PAA) mixed with linear PS to form a compatible polymer blend as model system. For that purpose, we have synthesized a series of PS-b-PAA copolymers varying the composition (*i.e.*, the percentage of acrylic acid units) and the molar mass. The molecular characteristics of the systems prepared are summarised in Table 1.

TABLE 1 Molecular Characteristics of the Diblock Copolymers

Composition[a]	M_n[a]	GPC[b] M_n	M_w	M_w/M_n	Mol % of PAA
PS_{20}–PAA_{11}	3500	5800	6500	1.12	28,6
PS_{36}–PAA_{33}	8000	11800	13300	1.23	40
PS_{58}–PAA_{135}	16000	34000	36000	1.08	63
PS_{86}–PAA_{38}	12000	16500	19400	1.17	24,4

[a] Calculated from the ^{1}H NMR spectra measured in THF for the protected polymers.
[b] Carried out on the PS-b-PtBuA protected polymers in THF as solvent.

Films of the blends were prepared by spin coating from concentrated solutions in THF and annealed either to air or to water as is schematically shown in Figure 1. The first important insight on the surface rearrangement was obtained by contact-angle measurements of the films after 3 days of treatment. The values of contact angle as a function of the diblock percentage in the blend are

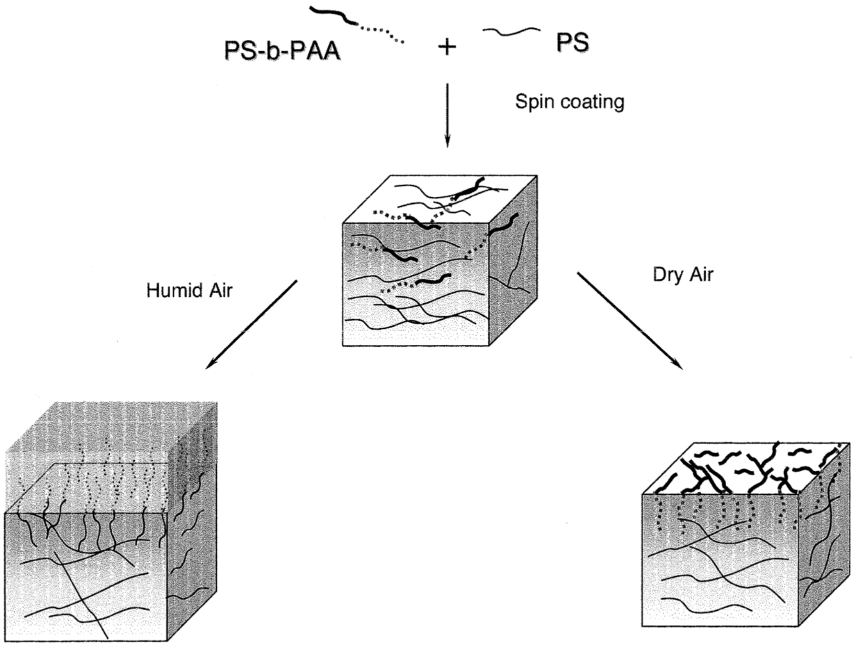

FIGURE 1 Illustration of the film preparation and the diblock copolymer surface rearrangement within the polymer blend when annealed.

represented in Figure 2. Films annealed to air exhibit contact angles of about 90° independent of the quantity of diblock in the mixture. In contrast, those films exposed to water vapour for a short period of time show two main characteristics: the contact-angle values decreased in comparison with the films annealed to air and the decrease is proportional to the quantity of diblock within the blend (*i.e.*, those samples containing a larger amount of diblock have largely changed the surface composition). An additional curve containing the contact-angle values of the untreated films for every composition has been added for clarity.

The annealing temperature has a direct influence on the kinetics of the surface segregation process. This effect has been evidenced following the contact angle of different blends treated at two different conditions (see Figure 3). The annealing conditions have been chosen after consideration of a general DSC thermogram of a PS-b-PAA diblock copolymer showing two glass-transition temperatures corresponding to PS (100°C) and PAA (120–125°C). Annealing carried out at temperatures above the T_g of both PS and PAA considerably

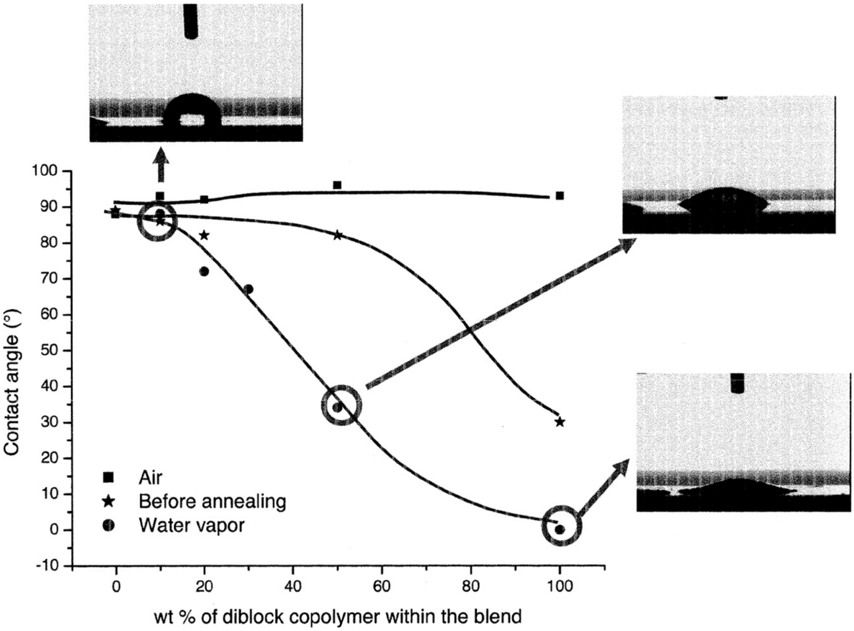

FIGURE 2 Contact angle measurements of a blend containing different percentages of PS_{36}-b-PAA_{33} that was either annealed to water or to air at 95°C during 3 days.

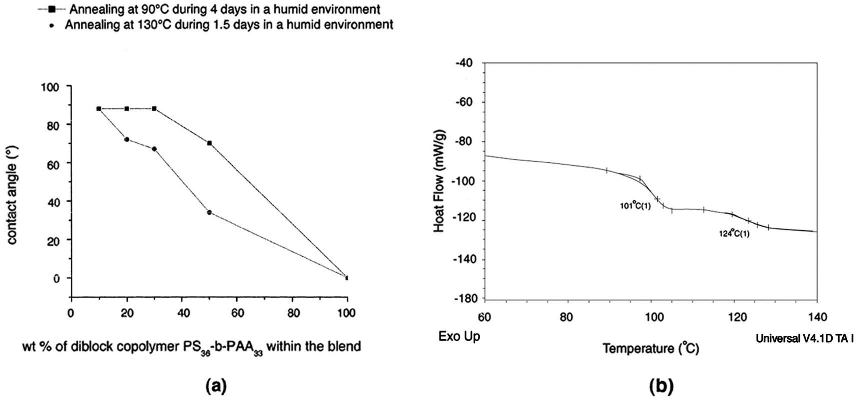

FIGURE 3 (a) Contact angle measurements for different ratio diblock/homopolymer for films that were annealed to water at two different conditions: 95°C for 4 days and 130°C for 1.5 days. (b) DSC traces of a PS_{36}-b-PAA_{33} carried out at 5°C/min (First heating run).

improves the surface rearrangement, a fact that confirms the relevance of the chain mobility in the reorientation process. Whereas blends containing 10–20% of diblock copolymer annealed at 130°C for 36 h. show a decrease of the contact angle from 90° to 70°, blends with similar composition annealed to water at 90°C did not shown any significant variation of the contact angle even after 4 days.

The molar mass of the amphiphilic diblock copolymer used as additive [12] and the molar ratio hydrophilic to hydrophobic has also a direct influence on the surface segregation. To analyze both parameters, we prepared blends containing amphiphilic diblock copolymers in which either the molar mass or the percentage on the PAA block has been varied. Figure 4 summarises the results obtained for the three types of blends that have all been annealed for 3 days at 95°C. As a result of the comparison between samples with different molar masses and similar PAA percentage (*i.e.*, PS_{86}-b-PAA_{38} and PS_{20}-b-PAA_{11}), we observed that the migration to the surface readily occurs in those samples with lower mass. Although hydrophilic surfaces are obtained with as little as 5–10% of PS_{20}-b-PAA_{11} within the blend, contact angles of the mixtures containing less than 50% of PS_{86}-b-PAA_{38} as additive remain about 90°.

Similarly, the role of the percentage of PAA on the surface migration has been explored by comparing polystyrene blends containing different amounts of either PS_{86}-b-PAA_{38} or PS_{58}-b-PAA_{135} diblock copolymers. In this case, the surface segregation of the block copolymer with the

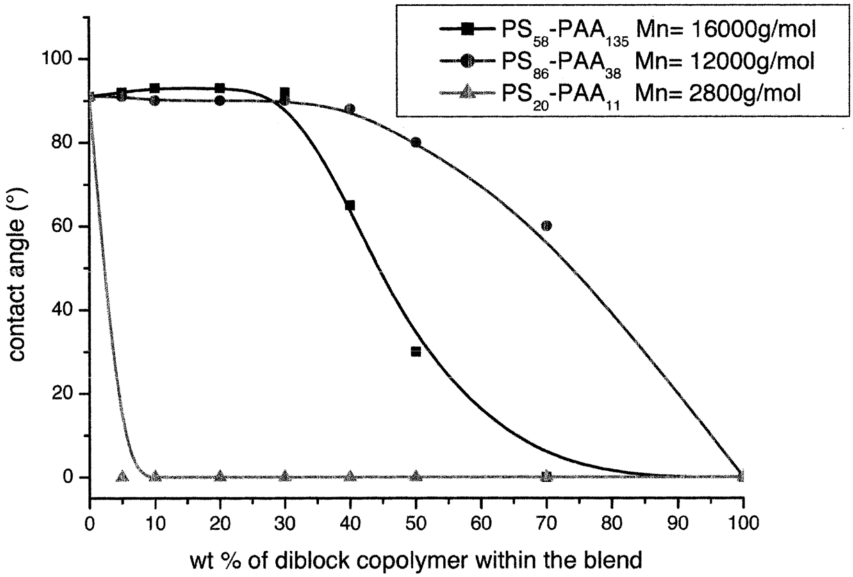

FIGURE 4 Contact angle measurements for different ratio diblock/homopolymer for blends prepared from three different diblocks: PS_{58}-b-PAA_{135}, PS_{86}-b-PAA_{38}, PS_{20}-b-PAA_{11} annealed to water vapour during 3 days at 95°C. The diblock copolymers have been chosen to evidence the contribution of either the molar mass or the ratio hydrophilic/hydrophobic on the kinetics of the surface segregation.

larger PAA block (PS_{58}-b-PAA_{135}) occurs for blends having a lower percentage of diblock (40% vs. 50%) in spite of its larger molar mass.

As described later, the entropy (*i.e.*, either the molar mass or the topology of the additive) can modify the surface segregation in polymer blends. In addition, the size of the polymer used as a matrix within the blend may have an influence. The size of the polymer matrix (linear PS) varied between 6800 g/mol and 74000 g/mol. The results of the experiments obtained using both the longest and the shortest polystyrene chains are illustrated in Figure 5. The linear PS were charged with the desired amount of additive (PS_{58}-b-PAA_{135}) and exposed to humid air at 95°C for 3 days. The difference in the molar mass between additive and polymer matrix creates an entropic driving force that enable those diblock copolymers incorporated in the high molecular matrix (filled circles) to migrate to the interface easier than those incorporated in a low molar mass matrix (stars).

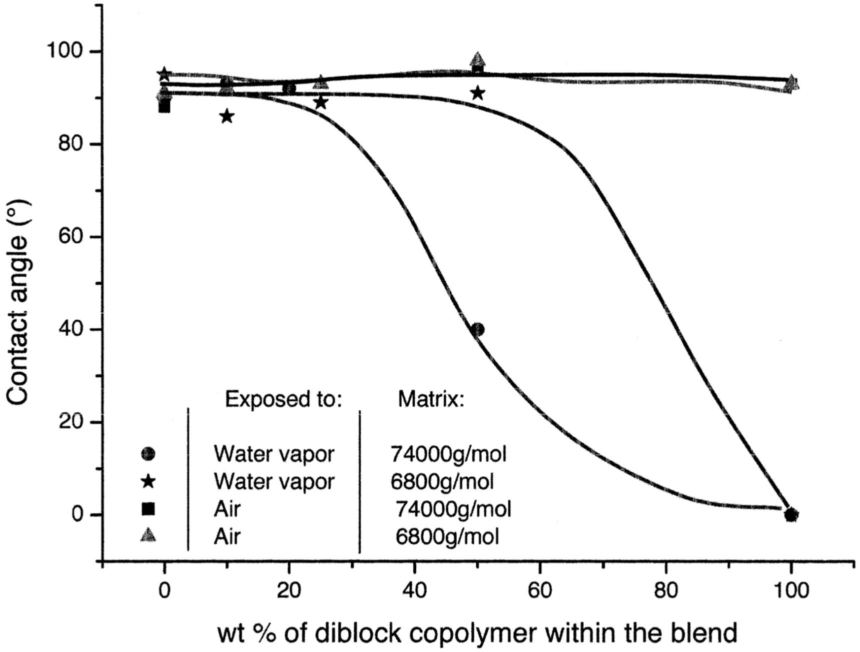

FIGURE 5 Illustration of the matrix contribution on the surface segregation using linear PS of two different sizes: 6800 g/mol and 74000 g/mol. The films of the blends were treated 3 days at 95°C either to water vapour or to air.

Surfaces annealed to water have the PAA block oriented to the interface as is schematically shown in Figure 6. Because PAA, which is a soft acid, can either exist as a charged anion or as a protonated neutral group depending on the pH of water, the wettability of the annealed surfaces depends also on pH. As a result, the wettability of the surface increased with the pH of the water drop. This result is in agreement with those reported by Whitesides and coworkers, who observed large variations in the wettability of a polyethylene surface functionalized with acid groups when exposed to acidic or basic water [13].

Contact-angle measurements constituted a first step in the characterization of the surfaces in terms of wettability. These analyses were complemented with XPS measurements to obtain quantitative (surface concentration) and qualitative (functional groups) information about the surface composition. As result of the XPS analysis, the quantity of oxygen on the surfaces that have been annealed to water is higher than those treated to air, being as high as ~6% in mixtures

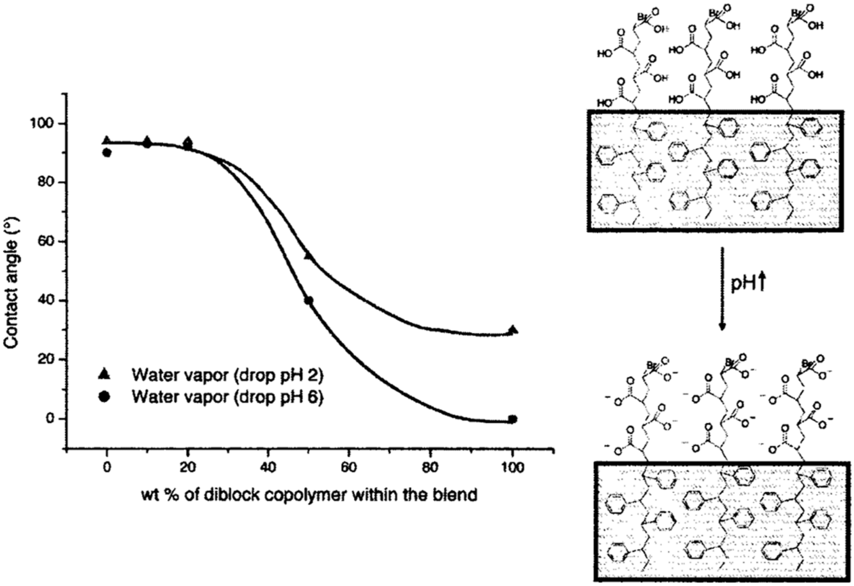

FIGURE 6 Variation of the contact angle as a function of the composition of the polymer blend at two different pH: 2 and 6.

that contain only 10% of diblock (PS-b-PAA). XPS has been also used to obtain a depth profile (see Figure 7), used to determine the chemical composition of the material as a function of depth. For that purpose, the film surface is sputtered by energetic ion bombardment to remove the outmost layer. Using this method, we can estimate the quantity of oxygen within the bulk material (~1.3%), which was in relatively good agreement with the percentage calculated from the molecular composition (~1%).

3.2. Reversible Surface Rearrangement by Changing the Environment

Spontaneous surface rearrangement of either the hydrophilic or the hydrophobic block to the surface depends on the environment of exposure. All the studies carried out clearly show that the hydrophilic part will orient to the interface in contact with water vapour. To address the eventual reversibility, we investigated the response to environmental change by measuring both contact angles and the amount of oxygen at the surface (XPS) during successive annealing treatments either to water or to dry air. Figure 8 shows the contact angles obtained as a function of the exposure time. Whereas water contact angles decrease for material annealed in contact with water,

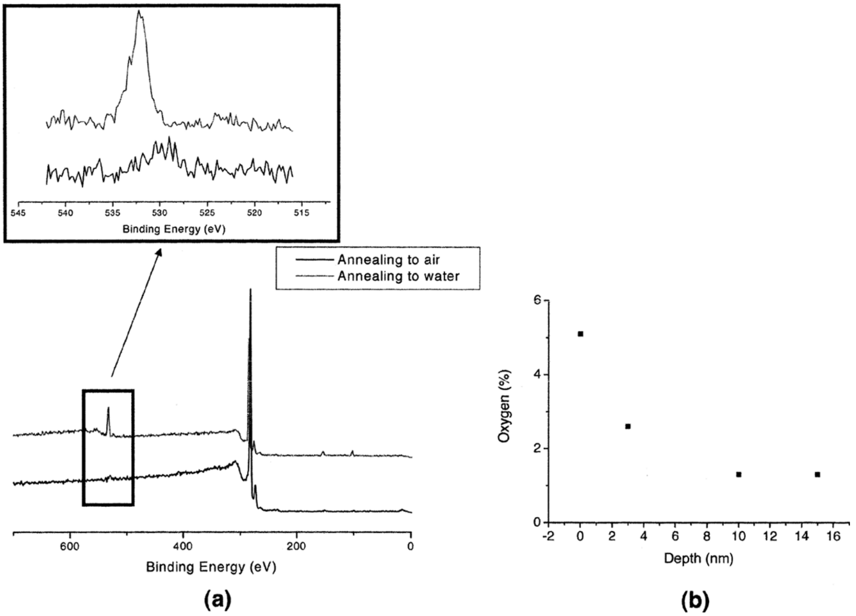

FIGURE 7 XPS spectra of the same blend annealed either to air or to water. Depth profile: Oxygen concentration (O1s) as a function of depth (nm).

they perfectly recover after annealing in air. Consecutive treatments with dry air/humid vapour produced hydrophilic and hydrophobic surfaces and evidenced the reversibility of the surface rearrangement.

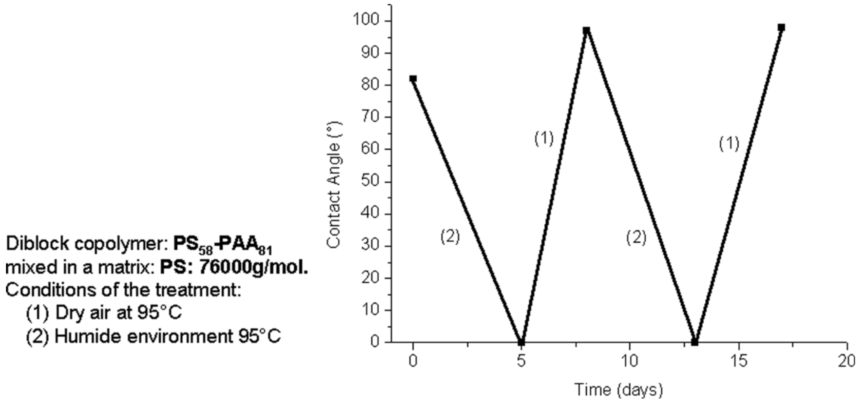

FIGURE 8 Contact angles measured after successive annealing either to air at 95°C (1) or to water at 95°C (2).

3.3. Density of PAA Functions at the Surface: Methylene Blue Method

The density of the carboxylic functions at the surface has been investigated using the methylene blue (MB) method [14]. This method serves to estimate indirectly the capacity of the PAA surfaces to either react or adsorb low-molecular-Weight molecules. MB is a water-soluble dye positively charged at neutral pH and thus able to establish electrostatic interactions with the PAA polyanion. The annealed films were submerged in a neutral aqueous solution containing the cationic dye. During 1 h, the dye was loaded onto the polymer surface. Then, the films were extensively rinsed at the same pH values to clean the surface of nonadsorbed dye. For that, MB-loaded samples were placed in a 30-ml volume of deionized water stirred gently for 30 min. The release of the dye into the environment proceeds at acidic pH values around 3. At this pH, the carboxylic functions that are protonated liberate the chromophore to the solution that can be, in turn, quantified by UV spectroscopy. The mass amounts of methylene blue were calculated using Lambert–Beer's law. (We determined the extinction coefficient of methylene blue by measuring the

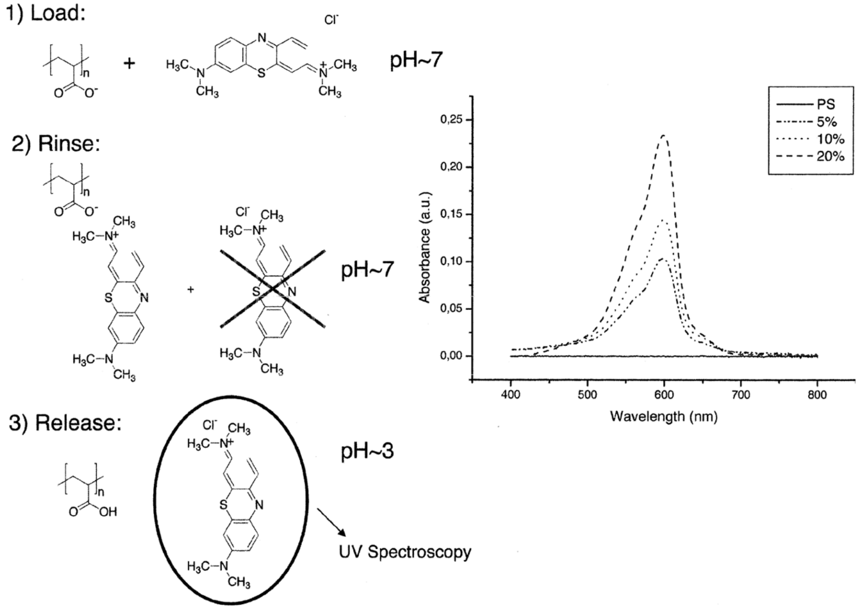

FIGURE 9 UV-vis spectra of the released MB from films having different wt% of diblock in the blend, from 5 to 20%.

absorption of a range of solutions with known concentrations of $\sim 78000\,M^{-1}cm^{-1}$.) The MB method was performed using water-annealed films (2 days at 95°C) containing 5, 10, 20% of diblock copolymer (PS_{20}-b-PAA_{11}) and a PS film used as reference. Figure 9 shows the UV spectra of the released MB for each type of film. The maximum of intensity observed for all films between 570–580 nm increases with the content of diblock in the blend from 5 to 20%. From these spectra and following the Lambert–Beer's expression, we can obtain further insight into the quantity of MB molecules absorbed and, consequently, the quantity of carboxylic functions available at the surface. For that, we just need the molar extinction coefficient of MB ($\sim 78500\,M^{-1}cm^{-1}$) -1) in water and the area of the film surface. As a result, we obtained a relatively accurate value of the surface concentration of the carboxylic functions 3.17 $10^{15}/cm^2$, 4.45 $10^{15}/cm^2$, and 7.15 $10^{15}/cm^2$ for films containing respectively 5, 10, and 20% of the diblock copolymer.

4. CONCLUSIONS

In this contribution, we attempted to identify and analyze the role of a certain number of parameters in the surface segregation process. We first described the surface reconstruction when the environmental conditions are inversed from dry air to water vapour. Annealing time and temperature, composition and size of the diblock copolymer, and size of the matrix in the blend influenced the surface migration process and have also been considered. Finally, both the density and the capacity of the carboxylic functions placed at the surface to absorb small molecules were determined using the MB method.

The control of the hydrophilicity and the surface charge is of high importance because of its role in applications such as polymer adhesion, where polymer surfaces often require activation or even in medical purposes for the development of biocompatible materials able to regulate cell adhesion.

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