pH Responsive Surfaces with Nanoscale Topography

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ABSTRACT: We report the preparation of nanostructured adaptive polymer surfaces by diffusion of an amphihilic block copolymer toward the interface. The surface segregation of a diblock copolymer, polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA), occurred when blended with high molecular weight polystyrene employed as a matrix. On annealing, the polymer surfaces changed both the chemical composition and the hydrophilicity depending on the environment and pH, respectively. By exposure to either water vapor or air, the surface wettability varied between hydrophilic and hydrophobic. In addition, surface enrichment on diblock copolymer by water vapor annealing led to self-assembly occurring at the interface. Hence, nanostructured domains can be observed by AFM in liquid media. Moreover, the PAA segments placed at the interface respond to pH and can switch from an extended hydrophilic state at basic pH values to a collapsed hydrophobic state in acidic media. Accordingly, the surface morphology changed from swelled micelles to nanometer size holes. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 2982–2990, 2010

KEYWORDS: block copolymers; polymer surfaces; self-assembly; stimuli-responsive; surfaces; surface segregation; topography

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INTRODUCTION The ultimate performance of materials depends, for many applications, not only on their bulk properties but also on their interfacial behavior. The fabrication of patterned surfaces with controlled functionality, shape, and structure dimensions has attracted considerable attention as these surfaces can be employed for the development of new materials with improvements in such properties as adhesion, wettability, gas impermeability, stain resistance, or biocompatibility.[1]

Till date, most of the research groups have been involved either in the functionalization or the structuration of polymer surfaces. On the one hand, methodologies to obtain functionalized surfaces are based on physical[2] or chemical modifications,[3] such as plasma or flame treatment, surface grafting,[4] or metal coating.[5] All these modifications are bound up with several major drawbacks including tedious additional steps, relatively low control of the surface composition and structure, which can be additionally altered in terms of mechanical properties and are normally difficult to replicate.[6] An alternative approach, employed throughout this study, concerns the use of spontaneous segregation of one of the components 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.[7] The resulting composition of the surface is markedly different than that of the bulk. The driving force for this reaction is the minimization of the surface energy. Whereas low-surface-energy functions (—F, —Si), which are usually hydrophobic, migrate to the air surface to reduce the surface energy,[8] polar functional groups (high-surface-energy functions) either stay hidden beneath the surface[7,9] of diffuses away from the interface into de bulk.[10] On the contrary, exposure to a polar condensed phase induces surface reconstruction and force the diffusion of the polar organic functional groups from the bulk to the surface until the hydrophilic functions are in contact with the solvent.[3,11] Equally, the molecular parameters such as chain length or chain topology (entropic driving force)[12] suppose an additional driving force for surface segregation. Finally, the

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interactions between the polymer and the contact phase, the exposure of the film to either a hydrophobic or hydrophilic environment can lead to a surface rearrangement where the chemical composition can be modified in response to a change in the polarity of the environment. Hence, 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 behavior offers interesting advantages compared with other surface modification methods including the control of the type and density of functional groups at the interface (determined by the nature of the additive employed) or the stability of the chemical groups at the interface. Moreover, the rest of embedded block copolymer within the homopolymer matrix can provide, in case of surface damage, an additional source of functional groups by simple additional annealing.

On the other hand, many strategies are currently under investigation to prepare structured interfaces with controlled shape, dimensions, and the regularity of the patterns.[13] Surface patterning of polymeric materials has been obtained by different approaches including soft-lithographic techniques, oxygen plasma etching, electron beam lithography, or through electrodynamic instabilities produced by applying an electric field.[14] Although, all these approaches formed well-defined moieties, they often require expensive equipments. Equally, they are often limited by the size of the patterned area and the minimum feature size is usually above 100 nm.[15]

Attempts to obtain surfaces with both controlled structure, with moieties sizes of tens of nanometers (molecule size), and functionality have been recently reported in which “top-down” and “bottom-up” approaches have been combined in the so-called templated self-assembly (TSA) approach.[16] Hence, topographically patterned surfaces[17] [lithographically defined grooved substrates, polydimethylsiloxane (PDMS) stamps or hard imprint molds] and/or chemically patterned substrates[18] are typical templates used to order block copolymer films at larger length scales. Equally, hydrophobic surfaces in which the roughness has been artificially modified have been fabricated with hierarchical structures such as electrodeposition, nanowire arrays, colloidal systems, or photolithography.[19] As an alternative to those complex procedures, Brittain and coworkers described the preparation of tethered PS-*b*-PMMA brushes in which the surface chemical composition could be reversibly modified upon treatment with selective solvents.[20] More interestingly, this group demonstrated the structural variations at the surface after exposure either to a common solvent forming a smooth polymer layer or to cyclohexane in which the PS blocks are swollen. Nevertheless, to the best of our knowledge all the approaches previously reported concerned the preparation of structured polymer films using inorganic supports.

In this manuscript, we prepared functional polymer surfaces with nanostructured domains by surface segregation of a block copolymer, used as additive in a block copolymer/homopolymer blend. Self-assembly of block copolymers leads to long range order at the nanometer scale due to the incompatibility between the blocks.[21] Thus, depending on parameters such as the preparation conditions (solvent cast, spin coating), interactions with the interface (air, water, organic solvent), or the molecular parameters (ratio between the blocks, chain lengths) different structures can be achieved.[22] Hence, based on the advances on polymer synthesis, self-assembly of block copolymers offers unprecedented ways to form nanostructured interfaces.

The block copolymer employed is an amphiphilic block copolymer, polystyrene-*b*-polyacrylic acid (PS-*b*-PAA), having a polar and pH sensitive segment which is expected to decorate the interface upon annealing to polar media.[23] Several major advantages can be obtained from this approach. First, the number of functional groups available at the interface is enhanced compared with single end-functionalized polymers.[24] Second, the use of a polar segment instead of a single functional group stabilizes the functionalized interface in air, retarding the diffusion from the surface to the bulk.[25] Finally, the combination of block copolymers in a homopolymer matrix has been demonstrated to form unprecedented morphologies.[26] Thus, if the block copolymer concentration at the interface might be sufficient to induce simultaneously macro- and microphase separation upon annealing, a structured interface is obtained. As a conclusion, one single preparation step combining surface segregation and block copolymer self-assembly (microphase separation) could substitute in many cases time-consuming and tedious procedures combining separately functionalization and structuration steps.

In addition, the block copolymer was designed to include pH sensitive segments (PAA). Thus, the last part of this manuscript will describe the variations of the surface nanostructures on the polymer surfaces by changing the environmental pH.

EXPERIMENTAL

Materials

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

Sample Preparation

The diblock copolymers have been prepared by ATRP in two steps following previously reported procedures which are briefly described below.

Synthesis of 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; 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, were filtered and washed with CH_2Cl_2 and finally dried under vacuum.

Preparation of the Films

Thin films of diblock/linear PS (M_n: 600,000 g/mol) mixtures were prepared by spin coating from THF concentrated solutions (60 mg/mL) onto clean silicon wafers (piranha solution at 80 °C for 30 min) and were dried under vacuum during several hours at room temperature. Film thicknesses were determined by AFM to be between 200 and 300 nm. Annealing was carried out either by exposure to saturated water vapor or to dry air. Whereas humid treatment temperatures were varied between 90 °C and 130 °C, treatments carried out at dry air were done at 95 °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.

Characterization

^1H NMR spectra of the copolymers were recorded at room temperature on a Bruker Avance 400 MHz spectrometer, 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 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 (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 10. 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 (The Netherlands). The films, supported on silicon wafer, were put under UHV to reach the 10^{-8} Pa range. The Nonmonochromatized Mg X-ray source was used at 100 W, as well as a flood gun 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.

Atomic Force Microscopy

The AFM images recorded in tapping mode and force curves reported were measured using a Digital Instruments NanoScope IIIa Multimode. The solution was held in a standard fluid cell sealed by a silicone O-ring. Both were cleaned by rinsing with ethanol and distilled water and dried using filtered nitrogen. Experiments were performed at room temperature (~22 °C). Millipore water with a conductivity of 18 MΩ cm^{-1} was used for the solution preparation. The pH of the aqueous phase was adjusted by adding small amounts of NaOH (Prolabo, France) or nitric acid (Sigma-Aldrich, France) as necessary. The ionic strength of the aqueous phase was not controlled, as no extra salt was added to it. FESP cantilevers with standard tips (Veeco, CA; nominal spring constant 2 N/m and nominal tip radius 20 nm) were irradiated with ultraviolet light for 30 min before use. All the AFM force curves reported were measured with the same tip to avoid discrepancies due to the variability in the spring constant of the cantilevers and the radius of the tip.

RESULTS AND DISCUSSION

Surface Segregation of Amphiphilic Diblock Copolymers

The spontaneous surface segregation is a particular case of self-assembly where a functional additive in a blend diffuses toward the interface. Surface segregation is driven both by the type of functional groups enclosed on the polymer structure (enthalpic driving force) and the molecular parameters such as chain length or chain topology (entropic driving force).[27]

The block copolymer/homopolymer blends employed throughout this study were prepared mixing an amphiphilic block copolymer polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) (additive) with linear homopolystyrene (host). The amphiphilic block copolymer was designed to have a segment similar in nature to the polymer host, in this case polystyrene, and a second block that will provide the surface functionality upon water annealing. In this case, polyacrylic acid has been chosen for several reasons: first, it can be easily obtained by controlled radical polymerization techniques. Second, carboxylic acid groups placed at interfaces can be employed for further chemical modifications, thus providing access to a variety of surface functionalities. Final, organic acids respond to environmental pH by protonation/deprotonation modifying their charge. Hence, when the PAA is at the interface the surface wettability may exhibit large changes with pH.[28]

Series of PS-*b*-PAA block copolymers were prepared by two consecutive ATRP polymerization reaction steps in which the conditions employed were adapted to obtain block

TABLE 1 Molecular Characteristics of the Diblock Copolymers

		GPC[b]			
Composition[a]	M_n[a]	M_n	M_w	M_w/M_n	Mol % of PAA
PS_{20}-*b*-PAA_{11}	3,500	5,800	6,500	1.12	28.6
PS_{36}-*b*-PAA_{33}	8,000	11,800	13,300	1.23	40
PS_{58}-*b*-PAA_{135}	16,000	34,000	36,000	1.08	63
PS_{86}-*b*-PAA_{38}	12,000	16,500	19,400	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.

copolymers with variable composition (i.e., the percentage of acrylic acid units) and molar masses.[29] The molecular characteristics of the block copolymers prepared are summarized in Table 1.

Films of the blends were prepared by spin coating from concentrated solutions of THF (60 mg mL^{-1}) and subsequently exposed either to air (95 °C) or to water vapor (temperatures ranging from 90 °C to 130 °C) as is schematically shown in Figure 1. Spin coating that leads to homogeneous films with controlled thicknesses was employed to produce films with low roughness. As it has been extensively reported, rough surfaces dramatically modify the contact angle.[30]

The first important insight on the interfacial diffusion of the diblock copolymer and further surface rearrangement as a function of the annealing environment was obtained from contact angle measurements of the annealed films either to humid or dry air at high temperature for three days. The contact angle values obtained as a function of the diblock percentage within the initial blend are represented in Figure 2. As depicted in Figure 2, films annealed to dry air exhibit contact angles of about 90° independently of the quantity of diblock in the mixture. Under these conditions, the driving force is the minimization of the surface energy and the PAA polar functions diffuses away from the surface into the bulk. Hence, the resulting surface is hydrophobic due to the polystyrene contribution provided by either the segment within the block copolymer or the host. On the opposite, in those films exposed to water vapor the contact angle values decreased in comparison with the films annealed to dry air. Moreover, the contact angle decreases linearly with the quantity of diblock within the blend, that is, those samples containing a larger amount of diblock exhibit larger changes in the surface composition. The interactions between the polar functional groups of PAA and the polar environment force the diffusion of the block copolymer from the bulk to the surface.[9]

Contact angle measurements were complemented with XPS measurements to obtain quantitative (surface concentration) and qualitative (type of functional groups) information on the surface chemical composition. XPS analysis evidenced (Fig. 2) that the quantity of oxygen on the surfaces annealed to water vapor is higher than in those heated in dry air. In a particular case depicted in Figure 2, in which the block

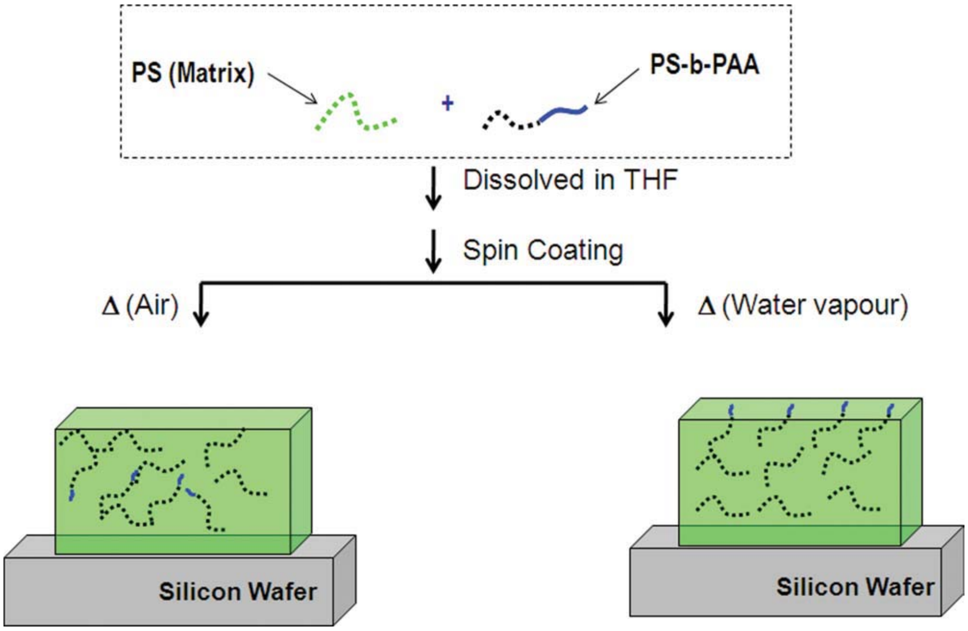

FIGURE 1 Illustration of the film preparation and the diblock copolymer surface rearrangement within the polymer blend when annealed. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

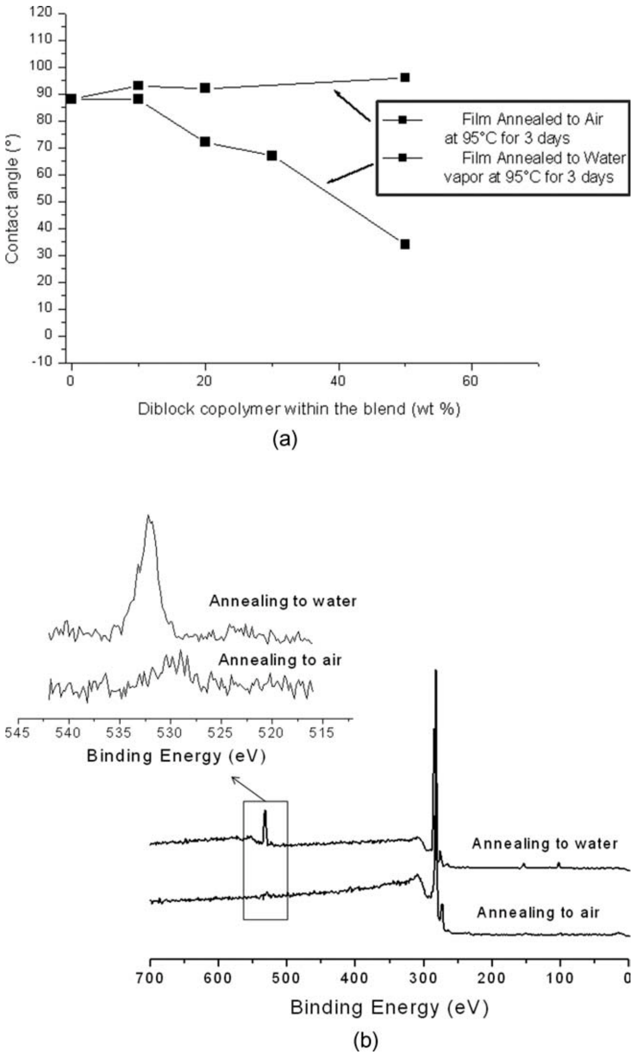

FIGURE 2 (a) Contact angle measurements of a blend containing different percentages of PS_{36}-*b*-PAA_{33} that was either annealed to water or to air at 95 °C during 3 days. (b) XPS spectra of the same blend annealed either to air or to water. The amount of O1S increases upon annealing to water vapor indicating the surface segregation of the PAA block towards the interface.

copolymer PS_{36}-*b*-PAA_{33} was employed, the amount of oxygen detected at the surface upon water vapor annealing was as high as ~6% in mixtures that contains only 10% of diblock copolymer. The quantity of oxygen within the bulk material was calculated from the initial blend composition to be ~1%, which resulted to be in good agreement with the percentage obtained (~1.3%) upon surface sputtering to remove the outmost layer. These values indicate that the surface has been largely enriched in oxygen, and therefore in block copolymer upon exposure to water.

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 and should be reversible, back and forth, when the external conditions drive or counteract the surface energy minimization.[9] Previous studies evidenced a similar behavior in plasma modified polyethylene with reversible wettability by exposure either to 2-propanol or upon protonation with sulfuric acid.[31] To address the reversibility of the process, we investigated the response in terms of surface chemical composition to environmental changes 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. In Figure 3 are illustrated the contact angles obtained as a function of the exposure time. Water contact angles decreased upon annealing in contact with water as a result of the surface enrichment in polar (polyacrylic acid) functional groups. Upon subsequent heating of the film in air, initial water contact angle values are perfectly recovered (θ, ~90°), as a consequence of the diffusion of the polar groups back into the bulk thus forming a top layer preferentially occupied by polystyrene. The annealing procedures dry air and humid water vapor were repeated several times producing alternatively hydrophilic and hydrophobic surfaces which is an evidence for the reversibility of the surface rearrangement.

Nanostructured and pH Responsive Interfaces

Surfaces annealed to water have the PAA block oriented toward the interface as is schematically shown in Figure 4. As PAA, which is a soft acid, can exist either as a charged anion or as a protonated neutral group depending on the pH of the water droplet, the wettability of the annealed surfaces depends also on pH. For pH values below 4, the carboxylic acid groups are protonated and the surface relatively hydrophobic (contact angle, θa comprised between 65 and 70°). At pH values above 6, the carboxylic groups are as carboxylate anions forming an ionic surface, which is more hydrophilic as evidenced by the decrease of the contact angle to 35–40°. As a consequence, the wettability of the surface increased

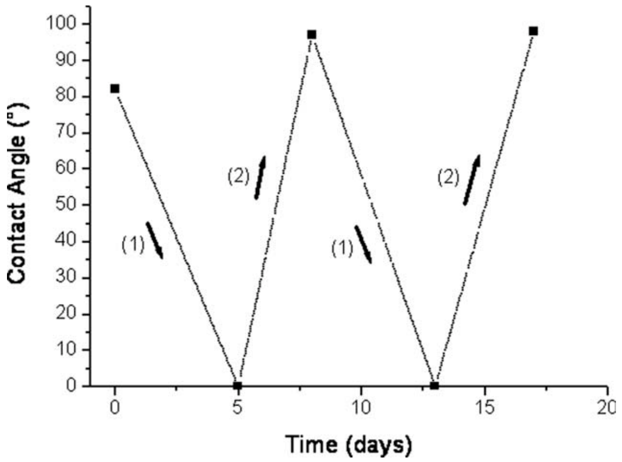

FIGURE 3 Contact angles of a film composed of 20% of block copolymer PS_{20}-*b*-PAA_{11} and 80% of homopolystyrene measured after successive annealing either to air at 95 °C (2) or to water vapor at 95 °C (1). (pH of the water droplet 7)

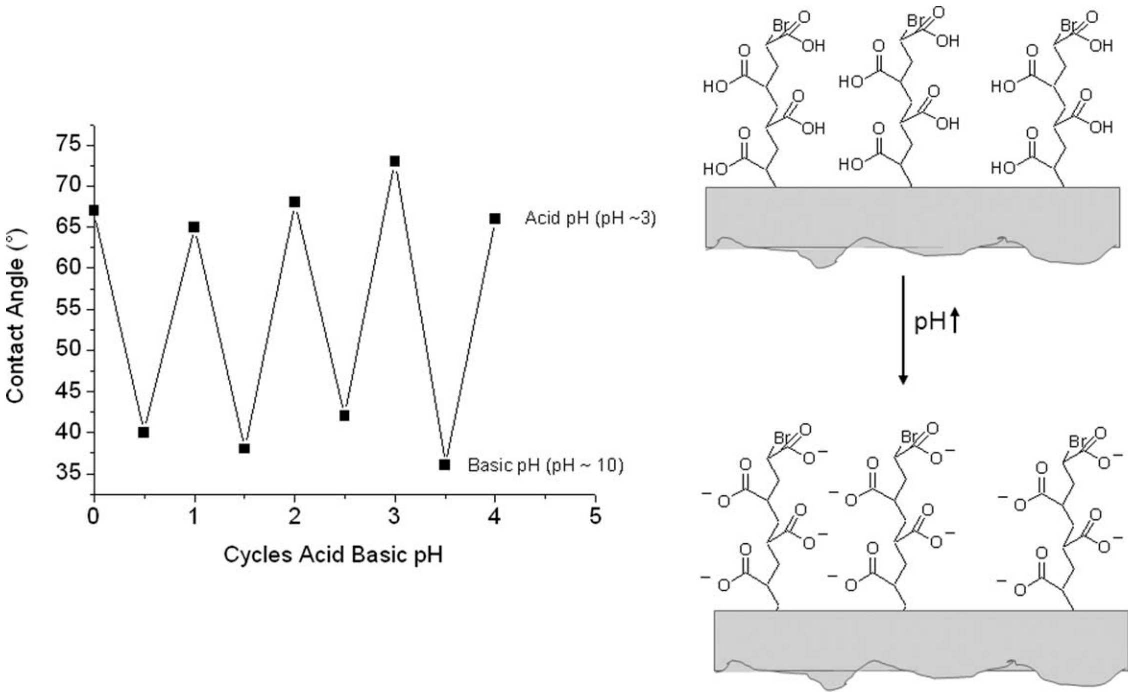

FIGURE 4 Contact angle measurements as a function of pH of the water droplet obtained from polymer blends composed of 20% of block copolymer PS_{20}-*b*-PAA_{11} and 80% of homopolystyrene.

with the pH of the water drop. This result is in agreement with those reported by Whitesides and coworkers, who observed large variations on the wettability of polyethylene surface functionalized with acid groups when exposed to acidic or basic water.[28] More interestingly, the process is reversible so that carboxylic acid groups can be protonated/deprotonated several cycles without decreasing the stability of the interface.

Atomic force microscopy (AFM) was used to complementary study the responsive character of the PS-*b*-PAA enriched surfaces by measuring the interaction force between a silicon nitride AFM tip and the functionalized surfaces.[32] Figure 5 depicts the deflection-distance curves between the Si_3N_4 AFM tip and the water vapor annealed surfaces measured under water at different pH values. A long-range exponential repulsion, typical of the interaction between charged

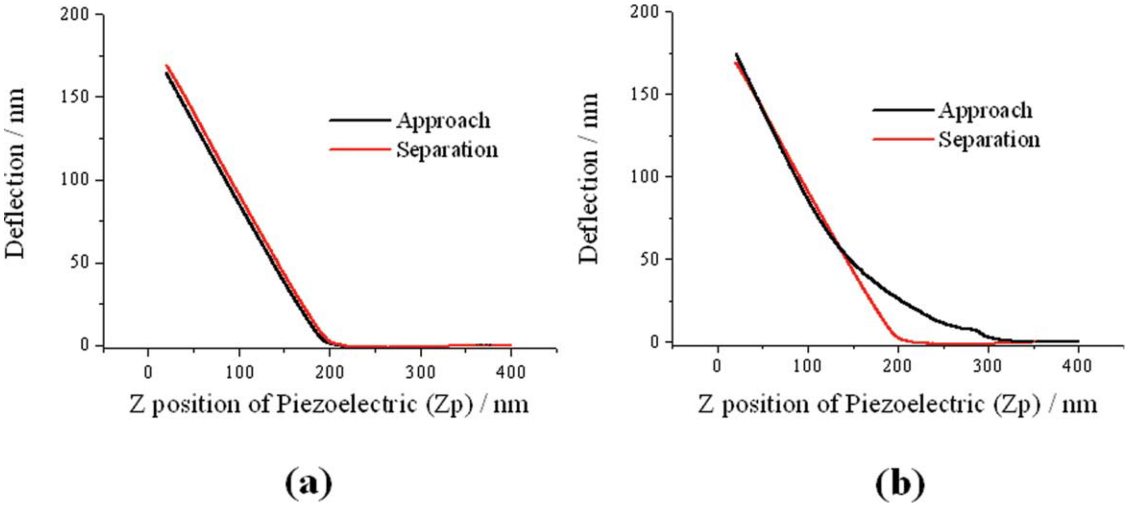

FIGURE 5 AFM deflection-distance curves for silicon nitride tip and polymer surface of a blend composed of 20% of block copolymer PS_{20}-*b*-PAA_{11} and 80% of homopolystyrene annealed to water vapor for 3 days at 95 °C. The curves were obtained at two different pH values: (a) Acidic pH (pH 3.5) below the pKa of the acrylic acid, i.e., 4.8, (b) Basic pH (pH 8.0). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

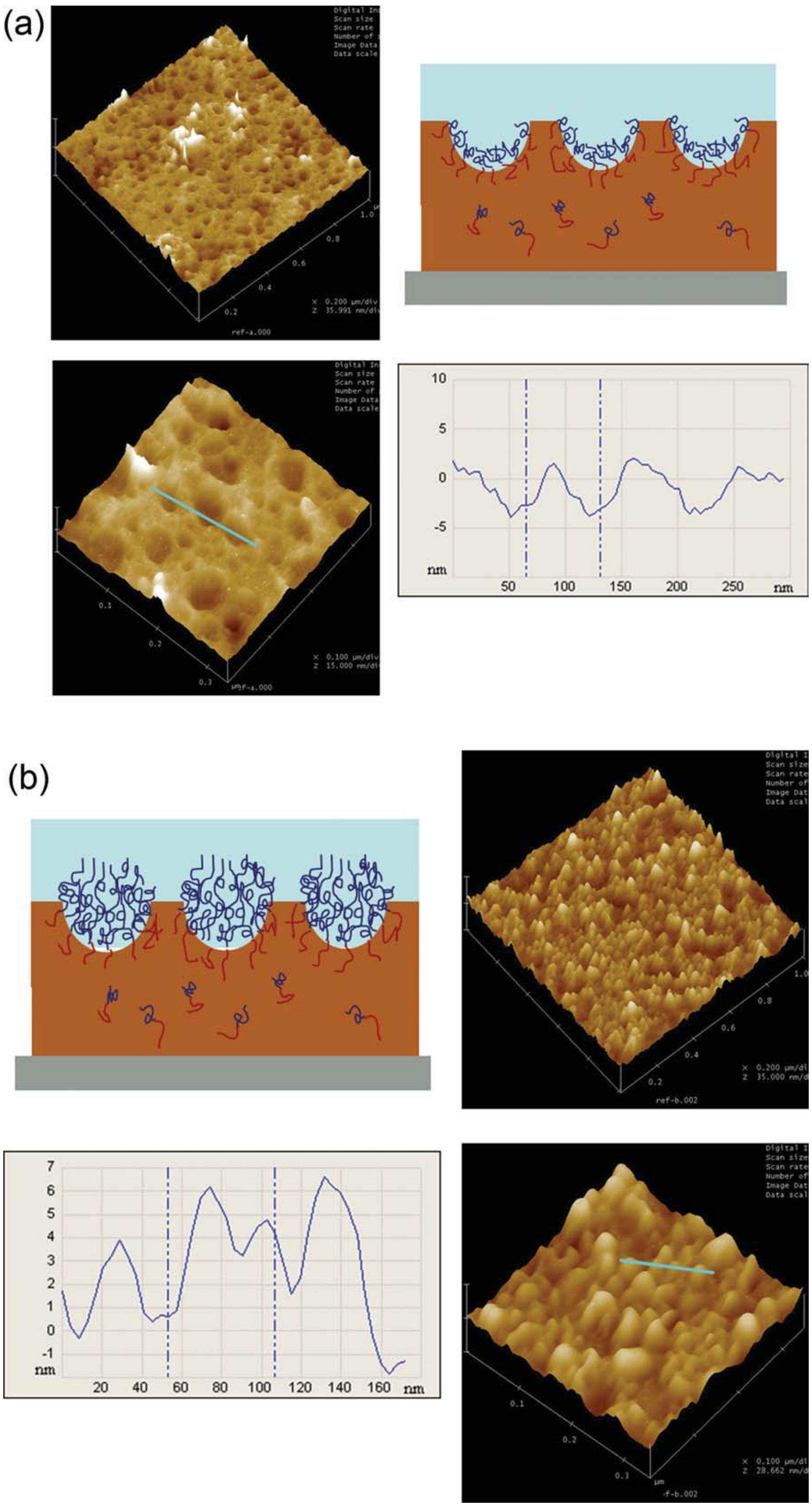

FIGURE 6 AFM height images of PAA-*b*-PS/PS blends upon annealing to water vapor (during 3 days at 95 °C) obtained in aqueous media at two different pH values: (a) pH 3.0 and (b) pH 7.0. Right images above are 1 × 1 μm^2, below images are 0.35 × 0.35 μm^2, and the height scale is 0-10 nm. As depicted in the cartoons, depending on the environmental pH values, the PAA either protonated or dissociated collapse or stretch respectively, resulting in the formation of nanometer sized holes or grains.

surfaces, is observed at pH 8.0. It is not related to the steric interaction between extended chains on the substrate and the tip assuming an extended chain of PAA. The electrostatic repulsion disappears at low pH values below the isoelectric point of Si_3N_4, where the tip is positively charged but the carboxylic acid groups are neutralized, illustrating the responsive character of the surfaces.

Analysis of the surface morphology was carried out by AFM in aqueous media. The images of the water annealed surfaces, obtained by means of AFM at acid and basic pH values, are depicted in Figure 6. As can be seen in Figure 6(b), the images obtained in neutral aqueous media, exhibit the formation of micellar structures with characteristic dimensions of 35–50 nm in lateral direction. Taking into account the asymmetry of the block copolymer employed, PS_{20}-*b*-PAA_{11}, the micelles should be formed by an external PS block in contact with the homopolystyrene host and a central PAA core.

In these mixtures, there is interplay between two phase-transition phenomena, that is, homopolymer domains as a result of macrophase separation coexisting with microstructured domains rich in diblock copolymers.[33] Significant differences in terms of molecular weight between polymer host and additive produce a macrophase and microphase separation to occur. Whereas the addition in solvent-cast mixtures of diblock and low molecular weight homopolymers led to its localized/uniform solubilization,[34] the incorporation of a diblock copolymer in high-molar-mass matrices ($N_{HOMO} \gg N_{diblock}$) induces macrophase separation.[35] The theory behind these processes was elaborated by De Gennes with the introduction of the concept of wet and dry brushes.[36] Thus, careful design of the diblock copolymer (molar mass and composition) and homopolymer (molar mass) may allow the preparation of hierarchically structured surfaces having different levels of order. Such structures with dual periodicities (micro and macro) are known as mesoscopic superlattice structures.[37] Several examples have been reported in which double hydrophobic block copolymers were blended with a high-molecular-weight homopolymer.[38] Similarly, the images depicted in Figure 6(b) clearly indicate the complete segregation between the diblock copolymer and the homopolymer matrix.

The exposure of the functionalized surface to a different pH, in this case acid pH, changes the surface morphology dramatically. Instead of grains related to phase separated domains, the formation of holes of similar dimensions could be observed [Fig. 6(i)]. Above the pKa, the number of dissociated carboxylic acid groups increases, hence a higher degree of dissociation produces a greater repulsion between the acrylic acid monomer units.[39] As a consequence, at pH > 7.0 the chains become fully dissociated which results in the maximum degree of swelling[40] of the core of the micelles. At low pH (pH < 4.0), the surface exhibits holes with a characteristic dimensions of 35–45 nm. This behavior can be attributed to the protonation of the acrylic acid monomer units that favors the contraction of the PAA chains as pH decreases.

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 vapor. 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 been also considered. The control of the hydrophilicity and the surface charge is of highly importance due to 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. Equally, blends of PS and PS-*b*-PAA are interesting responsive materials with PAA domains that exhibit functionality and PS provide mechanical stability.

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REFERENCES AND NOTES

1 Wu, S. Polymer Interface and Adhesion; Marcel Dekker: New York, Basel, 1982.

2 (a) Ozdemir, M.; Yurteri, C. U.; Sadikoglu, H. Chem Rev Food Sci Nutrition 1999, 39, 457–477; (b) Chu, P. K.; Chen, J. Y.; Wang, L. P.; Huang, N. Mater Sci Eng R 2002, 36, 143–206; (c) Chan, C. M.; Ko, T. M.; Hiraoka, H. Surf Sci Rep 1996, 24, 1–54.

3 (a) Chen, W.; McCarthy, T. J. Macromolecules 1998, 31, 3648–3655; (b) Garbassi, F.; Morra, M.; Occhiello, E. In Polymer Surfaces: From Physics to Technology; Wiley, 1997.

4 (a) Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Rühe, J., Eds. In Polymer Brushes; Wiley-VCH: Verlag, Weinheim, 2004; (b) Matyjazewski, K.; Dong, H.; Jakubowski, W.; Pietrasik, J.; Kusumo, A. Langmuir 2007, 23, 4528–4531; (c) Rainer, J., Ed. Suface-Initiated Polymerization; Advanced Polymer Science Vols. 197–198, 2006.

5 Goddard, J. M.; Hotchkiss, J. H. Prog Polym Sci 2007, 32, 698–725.

6 (a) Bergbreiter, D. E.; Franchina, J. G.; Kabza, K. Macromolecules 1999, 32, 4993–4998; (b) Ma, H.; Davis, R. H.; Browman, C. N. Macromolecules 2000, 33, 331–335.

7 (a) O'Rourke-Muisener, P. A. V.; Koberstein, J. T.; Kumar, S. Macromolecules 2003, 36, 771–781; (b) Jones, R. A. L.; Norton, L. J.; Shull, K. R.; Kramer, E. J.; Felcher, G. P.; Karim, A.; Fetters, L. J. Macromolecules 1992, 25, 2359–2368; (c) Mansfield, T. L.; Iyengar, D. R.; Beaucage, G.; McCarthy, T. J.; Stein, R. S.; Composto, R. J. Macromolecules 1995, 28, 492–499; (d) Shull, K. R. Macromolecules 1996, 29, 2659–2666.

8 (a) O'Rourke-Muisener, P. A. V.; Jalbert, C. A.; Yuan, C. G.; Baetzold, J.; Mason, R.; Wong, D.; Kim, Y. J.; Koberstein, J. T. Macromolecules 2003, 36, 2956–2966; (b) Koberstein, J. T. J Polym Sci Part B: Polym Phys 2004, 42, 2942–2956; (c) Hopkinson, I.; Kiff, F. T.; Richards, R. W.; Bucknall, D. G.; Clough, A. S. Polymer 1997, 38, 87–98; (d) Schaub, T. F.; Kellogg, G. J.; Mayes, A. M.; Kulasekere, R.; Ankner, J. F.; Kaiser, H. Macromolecules 1996, 29, 3982–3990; (e) Narrainen, A. P.; Hutchings, L. R.; Ansari, I. A.; Clarke, N.; Thompson, R. L. Soft Matter 2006, 2, 126–128.

9 Gagnon, D. R.; McCarthy, T. J. J Appl Polym Sci 1984, 29, 4335–4340.

10 Rasmusen, J. R.; Bergbreiter D. E.; Whitesides, G. M. J Am Chem Soc 1976, 99, 4746–4756.

11 (a) Luzinov, I.; Minko, S.; Tsukruk V. V. Prog Polym Sci 2004, 29, 635–698; (b) Russell, T. P. Science 2002, 297, 964–967.

12 (a) Yokoyama, H.; Miyamae, T.; Han, S.; Ishizone, T.; Tanaka, K.; Takahara, A.; Torikai N. Macromolecules 2005, 38 5180–5189; (b) Oyane, A.; Ishizone, T.; Uchida, M.; Furukawa, K.; Ushida, T.; Yokoyama, H. Adv Mater 2005, 17, 2329–2332; (c) Hester, J. F.; Banerjee, P.; Mayes, A. M. Macromolecules 1999, 32, 1643–1650; (d) Foster, M. D.; Greenberg, C. C.; Teale, D. M.; Turner, C. M.; Corona-Galvan, S.; Cloutet, E.; Butler, P. D.; Hammouda, B.; Quirk R. P. Macromol Symp 149:263–268.

13 (a) Xia, Y.; Rogers, J. A.; Paul, K. E.; Whitesides G. M. Chem Rev 1999, 99, 1823–1848; (b) Nie, Z.; Kumacheva, E. Nature Mater 2008, 7, 277–290.

14 Tsai, I. Y.; Crosby, A. J.; Russell, T. P. Methods Cell Biol 2007, 83, 67–87.

15 Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. Science 1997, 276, 1401–1404.

16 (a) Gorzolnik, B.; Mela, P.; Moeller, M. Nanotechnology 2006, 17, 5027–5032; (b) Seagalman, R. A.; Yokoyama, H.; Kramer, E. J. Adv Mater 2001, 13, 1152–1155; (c) Cheng, J. Y.; Ross, C. A.; Thomas, E. L.; Smith, H. I.; Vancso, G. J Adv Mater 2003, 15, 1599–1602; (d) Sundrani, D.; Darling, S. B.; Sibener, S. J. Langmuir 2004, 20, 5091–5099.

17 (a) McCord M. A.; Rooks, M. J. Handbook of Microlithography, Micromachining, and Microfabrication, Vol. 1; Choudhury, P. R., Ed.; SPIE: Bellingham, WA, 1997; (b) Xia, Y. N.; Whitesides, G. M. Annu Rev Mater Sci 1998, 28, 153–184; (c) Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. J Vac Sci Technol B 1996, 14, 4129–4133; (d) Resnick, D.; Sreenivasan, S. V.; Wilson, C. G. Mater Today 2005, 8, 34–42.

18 Fasolka, M. J.; Mayes, A. M. Annu Rev Mater Res 2001, 31, 323–355.

19 (a) Chong, M. A. S.; Zheng, B.; Gao, H.; Tan, L. K. Appl Phys Lett 2006, 89, 233104; (b) Shirtcliffe, N. J.; McHale, G.; Newton, M. I.; Chabrol, G.; Perry, C. C. Adv Mater 2004, 16, 1929–1932.

20 Zhao, B.; Brittain, W. J.; Zhou, W.; Cheng, S. Z. D. J Am Chem Soc 2000, 122, 2407–2408.

21 Cox, J. K.; Eisenberg, A.; Lennox, R. B. Curr Opin Coll Interf Sci 1999, 4, 52–59.

22 Li, Z.; Qu, S.; Rafailovich, M. H.; Sokolov, J.; Tolan, M.; Turner, M. S.; Wang, J.; Schwarz, S. A.; Lorenz, H.; Kotthaus, J. P. Macromolecules 1997, 30, 8410–8419; (b) Boltau, M.; Walheim, S.; Mlynek, J.; Krausch, G.; Steiner, U. Nature, 1998, 391, 877–879; (c) Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. Science 1997, 275, 1458–1460.

23 Surface migration of polar functional groups has been proved to have a limited durability and high-energy groups tend to migrate inside. To ensure long-term chemical stability several authors prepared functional surfaces by covalent attachment of grafted chains. See for instance: (a) Hu, S.; Brittain, W. J. Macromolecules 2005, 38, 6592–6597; (b) Zhang, M. C.; Kang, E. T.; Neoh, K. G.; Tan, K. L. Langmuir 2000, 16, 9666–9672; (c) Nakayama, Y.; Sudo, M.; Uchida, K.; Matsuda, T. Langmuir 2002, 18, 2601–2606.

24 Hutchings, L. R.; Richards, R. W.; Thompson, R. L.; Bucknell, D. G. Eur Phys J E 2002, 8, 121–128.

25 Hutchings, L. R.; Narrianen, A. P.; Thompson, R. L.; Clarke, N.; Ansari, I. Polym Int 2008, 57, 163–170.

26 (a) Holoubek, J.; Baldrian, J.; Lednicky, F.; Malkova, S.; Lal, J. Macromol Chem Phys 2006, 207, 1834–1841; (b) Winey, K. I.; Thomas, E. L.; Fetters, L. J. Macromolecules 1992, 25, 422–428; (c) Janert, P. J.; Schick, M. Macromolecules 1998, 31, 1109–1113; (d) Matsen, M. W. Macromolecules 1995, 28, 5765–5773.

27 (a) Yokoyama, H.; Miyamae, T.; Han, S.; Ishizone, T.; Tanaka, K.; Takahara, A.; Torikai, N. Macromolecules 2005, 38, 5180–5189; (b) Hester J.F., Banerjee P., Mayes A. M. Macromolecules 1999, 32 1643–1650; (c) Foster M. D., Greenberg C. C., Teale, D. M., Turner, C. M.; Corona-Galvan, S.; Cloutet, E.; Butler, P. D.; Hammouda, B.; Quirk, R. P. Macromol Symp 2000, 149, 263–268.

28 Wilson, M. K.; Whitesides G. M. J Am Chem Soc 1988, 110, 8718–8719.

29 For a detailed description on the procedures followed for the synthesis of the block copolymers the reader is referred to: Bousquet, A.; Ibarboure, E.; Labrugere, C.; Papon, E.; Rodríguez-Hernández, J. Langmuir 2007, 23, 6879–6882.

30 (a) Lee, J. H. J Mater Sci 2009, 44, 4645–4652; (b) Nosonovsky, M.; Bhushan, B. Adv Funct Mater 2008, 18, 843–855.

31 (a) Everhart, D. S.; Reilley, C. N. Surf Interf Anal 1981, 3, 126–133; (b) Everhart, DS; Reilley, C. N. Surf. Interf Anal 1981, 3, 258–268.

32 Kelley, T. W.; Schorr, P. A.; Johnson, K. D.; Tirrell, M.; Frisbie, C. D. Macromolecules 1998, 31, 4297–4300.

33 (a) Ito, A. Phys Rev Lett E 1998, 58, 6158–6165; (b) Hong, K. M.; Noolandi, J. Macromolecules 1983, 16, 1083.

34 Prahsarn, C.; Jamieson, A. M. Polymer 1997, 38, 1273–1283.

35 (a) Quan, X.; Gancarz, I.; Koberstein, J. T.; Wignall, G. D. Macromolecules 1987, 20, 1431–1434; (b) Hashimoto, T.; Tanaka, H.; Hasegawa, H. Macromolecules 1990, 23, 4378–4386.

36 (a) DeGennes, P. G. Macromolecules 1980, 13, 1069–1075; (b) Feast, W. J.; Munro, H. S. Polymer Surfaces and Interfaces; Wiley: New York, 1987.

37 Koizumi, S.; Hasegawa, H.; Hashimoto, T. Macromolecules 1994, 27, 6532–6540.

38 (a) Tanaka, H.; Hashimoto, T. Macromolecules 1991, 24, 5713–5720; (b) Löwenhaupt, B.; Steurer, A.; Hellmann, G. P.; Gallot, Y. Macromolecules 1994, 27, 908–916; (c) Han, C. D.; Baek, D. M.; Kim, J.; Kimishima, K.; Hashimoto, T. Macromolecules 1992, 25, 3052–3067.

39 (a) Ludwigs, S.; Schmidt, K.; Krausch, G. Macromolecules 2005, 38, 2376–2382; (b) Kozlovskaya, V.; Kharlampieva, E.; Mansfield, M. L.; Sukhishvili, S. A. Chem Mater 2006, 18, 328–336.

40 (a) Guo, X.; Ballauff, M. Langmuir 2000, 16, 8719–8726; (b) Xu, C.; Wayland, B. B.; Fryd, M.; Winey, K. I., Composto, R. J. Macromolecules 2006, 39, 6063–6070.